

Central Laser Facility

Annual Report 2003 - 2004





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Central Laser Facility

Annual Report 2003/2004

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The front cover shows a group of young people on an educational visit to the Central Laser Facility with a backdrop of a simulation of the proton distribution resulting from a laser incident on a thin foil (Photograph courtesy of RAL Photographic Section and simulation courtesy of R G Evans of AWE).

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Thanks to all the above for their contribution towards producing this report and of course to all the authors for their submissions.

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Foreword

M H R Hutchinson

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This annual report for the Central Laser Facility (CLF) at the CCLRC Rutherford Appleton Laboratory is an account of the scientific research which has been carried out by users of the Facility and its staff over the financial year 2003-04.

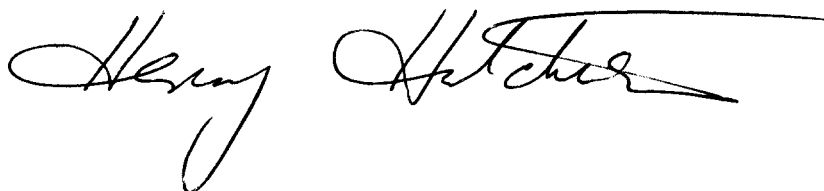
The research covers a wide range of disciplines, including physics, chemistry and biology as well as the development of the facilities themselves and the associated instrumentation. The laser systems are also diverse, from short pulse high repetition rate systems with wide tuning range to ultra-high intensity laser systems for applications in plasma physics.

The high intensity laser programme is carried out with both the Astra and Vulcan laser systems which have complementary characteristics. The Astra laser is a TiS system which provides pulses of 40 fs with energies of typically 0.5 J per pulse (peak power $\sim 10\text{TW}$) and repetition rates of up to 10 Hz, providing focused intensities of up to 10^{19} W/cm^2 , whereas the Vulcan system, operating in the short pulse CPA mode, can deliver up to one Petawatt (10^{15} W) in pulses of $\sim 500\text{J}$, producing intensities of up to 10^{21} W/cm^2 . During the year, approval has been obtained for the upgrading of the Astra laser to a two beam system delivering peak powers of up to one Petawatt and this, in conjunction with the Vulcan system, will further strengthen the capability of the CLF in the field of high intensity laser plasma interactions. The experimental programme has included studies of the generation of energetic electrons, protons and ions, including the first generation of monoenergetic electron beams by laser acceleration, and the study of ultra-fast dissociation of ionic molecules in intense fields.

The PIRATE (Picosecond IR Absorption and Transient Excitation) facility provides both narrow and broadband ultra-fast light sources, enabling the visualisation of short timescale molecular dynamics of scientific relevance across many fields of research. This system forms the core of a facility which has enabled a wide ranging programme within the Lasers for Science Facility which is described in this report. The performance of this system has also been enhanced during the year, both in its tuning range and sensitivity.

The high level of demand for access to the CLF continues greatly to exceed the time available for the scheduling of experiments and a programme has been initiated to increase the amount of time available for users. This is likely to come into effect in 1-2 years time.

The quality of work carried out continues to be of a very high level and the challenge for the CLF and its users is to maintain these very high standards against a background where the complexity of experiments continues to increase. However, the continuing high level of investment in the CLF for upgrading facilities indicates confidence in the Facility and I believe we can look forward to its continuing success and its many users.

A handwritten signature in black ink, which appears to read 'M H R Hutchinson'. The signature is fluid and cursive, with a long horizontal stroke extending to the right.

Overview of the Central Laser Facility

B E Wyborn

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Laser Facilities for Users

The Central Laser Facility (CLF) is a world leading centre for research using lasers. Facilities available to users include the Vulcan Nd: glass laser which delivers a Petawatt beam to one target area and multi- TW beams to two target areas, the Astra ultra- short pulse interaction facility based on titanium sapphire laser technology, a range of state of the art table top laser systems and specialised diagnostic instruments within the Lasers for Science Facility and the Laser Loan Pool.

Vulcan

Vulcan is a highly versatile large scale Nd: glass laser installation which delivers a maximum of 2.5 kJ of energy in its six 10 cm and two 15 cm beamlines to two target areas, each of which is equipped with frequency conversion optics to enable both 1 μ m and 0.5 μ m operation of all beams. A range of pulse durations are available from 100 ps to 20 ns in various geometries. Short pulse (700 fs), high irradiance ($\sim 10^{20}$ - 10^{21} W cm⁻²) chirped pulse amplification (CPA) capability is available, with vacuum propagation to target and reflective beam focusing optics.

The reporting period saw the first full year's operation to the Vulcan Petawatt interaction area. Successful experimental campaigns were carried out by Imperial College into electron acceleration studies; University of Strathclyde into ultra-high intensity solid target interactions and CCLRC into the advanced fast ignitor concept. The University of Dusseldorf were awarded one weeks experiment time to study electron transport through thin foils. In addition to these there were successful experimental campaigns conducted by LLNL and MOD.

Lasers for Science Facility (LSF)

The LSF operates a suite of state of the art table- top laser systems and associated instrumentation giving users access to highly tunable (vuv - ir) and variable pulse width (ns to fs) laser radiation. This includes lasers for ns and ps time-resolved studies and specialises in time-resolved vibrational spectroscopy in the femtosecond and picosecond time domain. The extremely versatile lasers are applied to a wide range of science and engineering applications across chemistry, physics, biology, medical and material sciences. The time resolved resonance Raman (TR³) facility provides unique capabilities to enable highly fluorescent samples to be studied using a 4 ps optical Kerr shutter in combination with a fully tunable kHz femtosecond synchronised pump-probe apparatus based on OPA technology. The same laser source also drives the high brightness PIRATE facility (Picosecond Infrared Absorption and Transient Excitation) giving two independently tunable beams across the mid infra red region of the spectrum for pump / probe experiments. The Laser Microscope Laboratory is also actively developing the use of lasers for imaging and spectroscopic characterisation of biological materials at the cellular level. This technology includes using lasers to provide optical traps (laser tweezers) for investigating pico-Newton forces between particles in solution (including living cells).

Laser Loan Pool

Commercial laser systems are available from the Laser Loan Pool for periods of up to 6 months at the user's home laboratory. Systems available include nanosecond tunable YAG pumped dye lasers (with frequency up-conversion and down-conversion covering the spectral region from 205 nm to

4500 nm), an excimer laser operating down to 157 nm, a CW frequency doubled argon ion laser and an all solid-state femtosecond Titanium Sapphire laser tunable between 680 nm and 1020 nm as well as a 1 kHz ultrafast regenerative amplifier and optical parametric amplifier system. The Loan Pool also makes available a wide range of ancillary and diagnostic equipment to support user experiments.

Astra

The Astra facility is based on titanium sapphire laser technology which gives users access to high intensity laser pulses at 10 Hz repetition rate.

The facility supplies laser pulses to two target areas simultaneously. Target Area I provides pulses of 50fs duration with an energy of 10 mJ, producing irradiance on target in excess of 10^{16} W cm⁻². The Target Area II currently delivers 500 mJ in 40fs with target irradiance in the 10^{19} W cm⁻² regime.

Engineering Services

Mechanical, electrical and computing support is provided for the operation of the laser facilities at the CLF, for the experimental programmes on these facilities and for the CLF's research and development activities. Access to mechanical and electrical CAD tools and workshop facilities enable a rapid response to be provided to users.

Target Preparation

A target fabrication facility is operated within the CLF. It is equipped with a wide range of target production and characterisation equipment, including evaporation and sputter coating plants, interference microscopes and a plasma etch facility. A rapid turnaround service responds quickly to the developing demands for targets, essential for maintaining the scientific productivity of the programme.

Access to Facilities

The mechanism for awarding access to beamtime at all CCLRC facilities is directly to the particular Facility using the formal CCLRC application procedure. Calls are made twice annually at defined dates and applications are peer reviewed by Facility Access Panels. For information please visit the CCLRC Web site at: <http://www.cclrc.ac.uk/Activity/FacilityAccess> or contact Dr Tony Parker (a.w.parker@rl.ac.uk).

During the period covered by this report, beamtime at CLF facilities was awarded to European researchers and their collaborators through the EU Access to Large Scale Infrastructure programme. The CLF will continue this arrangement in the Sixth Framework Programme through LASERLAB. For information on calls for proposals, eligibility criteria, etc. please contact Mr. Colin Danson (c.danson@rl.ac.uk).

Hiring of the facilities and access to CLF expertise is also available on a commercial basis for industrial research and development. Please contact Mrs. Alison Brown for further information (a.j.brown@rl.ac.uk).

CLF Web site

Further information on the CLF, its facilities and the scientific programmes is available on the CLF Web site at <http://www.clf.rl.ac.uk>.

Emittance measurement of energetic proton beams generated with a petawatt laser

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Introduction

In experiments irradiating thin foil targets with ultra high intensity lasers the emission of an intense and very energetic proton beam was observed ^{1,2}. These beams contained 10^{12} protons with energies up to 60 MeV, had an opening angle of around 30° and originated from the non-irradiated rear surface of the target.

The acceleration mechanism for these protons is the *Target Normal Sheet Acceleration* (TNSA) ³. The interaction of the laser with the target produces energetic electrons with a temperature of several MeV moving through the target. As some of the electrons escape, the target is charging up and the other electrons are confined in a cloud on the rear side of the target. This produces strong electrostatic fields (10^{12} V/m), which ionize the atoms on the rear side and accelerates the ions. As the protons, originating from impurities, have the best q/m ratio, they are accelerated faster and consequently shield the electric field for the following heavier ion species. So one always obtains protons independently of the target material.

Earlier experiments have shown that small structures on the rear side of the target lead to intensity variations in the proton beam. The reason for this modulation is a focussing of the protons inside the grooves in the early times of acceleration. This mechanism is called *micro focussing* ⁴. Using targets with a defined structure allows one to get a picture of the acceleration itself at the beginning.

Experimental Setup

The experiments were performed at the Vulcan Petawatt laser target area using the laser at maximum intensity. As targets we used thin (50 μm) tungsten and gold foils with a defined structure on the rear side.

To obtain a two dimensional profile of the proton beam we used radiochromic film (RCF) as detector. RCF is a plastic foil with an active layer inside, which changes colour due to energy deposition by energetic particles. A stack of this RCF was placed several cm behind the target. As the optical density of the RCF is calibrated to the energy deposition and the energy deposition is maximum in the layer, where the proton is stopped, it is possible to assign a certain energy to every layer of the stack.

Results

Figure 1 shows a typical beam profile we obtained with the setup described. To make the structure more visible the intensity gain in the middle of the profile was subtracted. One can clearly see the modulation, which is imprinted by the rear surface structure of the target.

This structure allows the calculation of the beam emittance, a very important parameter of a particle beam, which describes the qualities of the beam such as focusability and spatial resolution for imaging experiments. The emittance is defined as the phase space area of the particles of the beam:

$$\varepsilon = \beta\gamma \iint dx dx'$$

β and γ are the relativistic parameters of the beam.

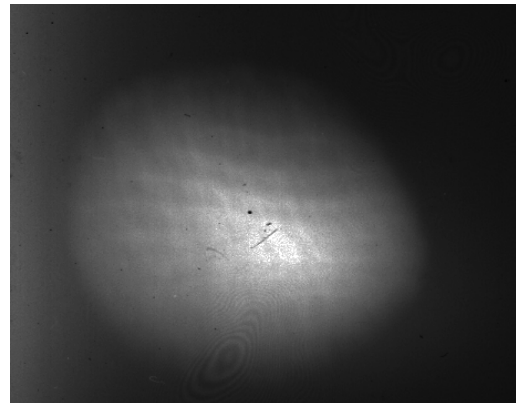


Figure 1. Transverse profile of the proton beam (35 MeV).

As the lines of the structure do not overlap, to every point can be assigned a maximum divergence angle, the size of the source can be calculated directly by counting the number of lines visible in the film. With these measurements we could calculate a maximum emittance of 0.36 mm mrad, which is far better than values reachable with conventional accelerator systems.

It is important to mention, that this value is only an upper limit. As the protons are extracted from a *cold* rear surface a much lower emittance is expected, but limitations in the production process for target structures prevent measurements of such low emittances.

Summary

In these experiments a precise measurement of the emittance of a proton beam generated by a petawatt class laser was done. The emittance is very low compared to conventional systems, which gives these beams unique properties in addition to the high currents and the short emission time.

With a detailed analysis of the intensity modulation of the proton beam, the shape of the proton sheath in the beginning of the acceleration can be investigated. The results of these studies will be published soon.

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A study of residual nuclide production in spallation targets using protons accelerated with the Vulcan petawatt laser

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Introduction

The development of accelerator driven systems (ADS) ¹ as a high yield source of neutrons is based on the physics of spallation reactions in heavy elements such as Pb and Bi ². Proton-induced spallation occurs when a high energy (GeV) proton inelastically interacts with a nucleus to produce multiple secondary particles. The reactions proceed in two stages. Firstly, an incident proton collides with a nucleus, knocking out secondary, high energy protons and neutrons. These secondary particles induce further collisions in an intranuclear cascade. Secondly, the excited nuclei will evaporate low energy particles (or fission). The evaporated MeV particles induce further reactions, producing a range of residual nuclei in the target.

Investigation of residual nuclide production in spallation reactions is important for the development of ADS, to determine the radioactive inventory and damage to materials. This was one of the objectives of the HINDAS project ³. The residual nuclides are mainly produced via the secondary reactions induced by the MeV protons and neutrons produced in the intranuclear cascade and through evaporation⁴. Typical low energy proton production cross sections for 1.8 GeV proton spallation reactions on a high-Z target (Au), as calculated using Monte Carlo codes ⁵, are shown in Figure 1. The integrated proton yield below 40 MeV, resulting from the intranuclear cascade plus evaporation (INC+EVAP), is close to 60% of the total proton yield over the full energy range (up to the incident proton energy of 1.8 GeV), highlighting the importance of having accurate nuclear data for residual nuclide production in this low energy regime.

The typically broad, tens of MeV, energy distributions of protons accelerated in ultraintense laser interactions with foil targets, could be used to experimentally model residual nuclide production in spallation targets. Typical measured proton energy spectra from 400 J laser pulse interactions with a 10 μ m thick Al target are also shown in Figure 1. It should be noted that the energy distribution of protons measured at the rear of the target is in excellent agreement with the shape of the calculated evaporation (EVAP) proton energy spectrum in the important low energy region between 12 and 40 MeV. As the low energy thresholds for the dominant reactions occur at $\sim$ 11 MeV (shown below) and less than 1% of the calculated total evaporated proton yield has energy greater than 40 MeV, the shape of the measured laser-plasma-accelerated proton energy spectrum is ideal for experimentally investigating residual nuclide production due to spallation-evaporation reactions.

In this article we use the protons accelerated from the rear of the laser-irradiated target to quantify residual nuclide production resulting from the important low energy region of the proton spectrum produced in GeV spallation reactions. Measurements of proton induced reactions in Pb, a representative spallation target for many ADS, are compared with results modelled using experimental and theoretical cross sections.

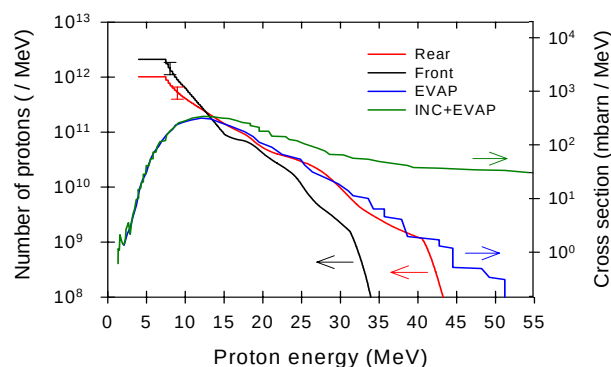


Figure 1. Calculated proton energy spectra produced in 1.8 GeV p+Au spallation-evaporation (EVAP) and spallation-intranuclear cascade plus evaporation (INC+EVAP) reactions and measured proton energy distributions at the front and rear of the laser-irradiated 10 μ m thick Al target. The shape of the measured rear proton spectrum is in remarkable agreement with the calculated EVAP spectrum between 12 and 40 MeV.

Experimental

The petawatt arm of the Vulcan Nd:glass laser was used to deliver 400 J laser pulses, of wavelength $\sim$ 1 μ m and average duration 0.7 ps onto 10 μ m thick, 5 mm x 5 mm, Al foil targets, at an angle of 45°. The 60 cm beam was focused to a 7.0 μ m diameter spot to produce a peak laser intensity of 4×10^{20} Wcm⁻², in a vacuum chamber evacuated to $\sim 10^{-4}$ mbar. The proton energy distributions shown in Figure 1 were measured by nuclear activation of Cu foil stacks. Positron emission from ⁶³Zn, produced from (p,n) reactions on ⁶³Cu, was quantified for each copper foil using NaI-coincidence detectors, and convoluted with the well-known cross sections for the ⁶³Cu(p,n)⁶³Zn reaction and the stopping power of protons in ⁶³Cu, to determine the proton spectra.

A 1-mm thick ^{nat}Pb activation sample (1.4% ²⁰⁴Pb, 24.1% ²⁰⁶Pb, 22.1% ²⁰⁷Pb and 52.4% ²⁰⁸Pb) was positioned along the target

normal direction at the rear of the target, subtending a solid angle of 1 sr. After the laser shot, γ -rays emitted by residual nuclei, produced via proton-induced reactions, were measured using a calibrated germanium detector. Figure 2 shows a measured γ -spectra with a total measurement time of 90 hours.

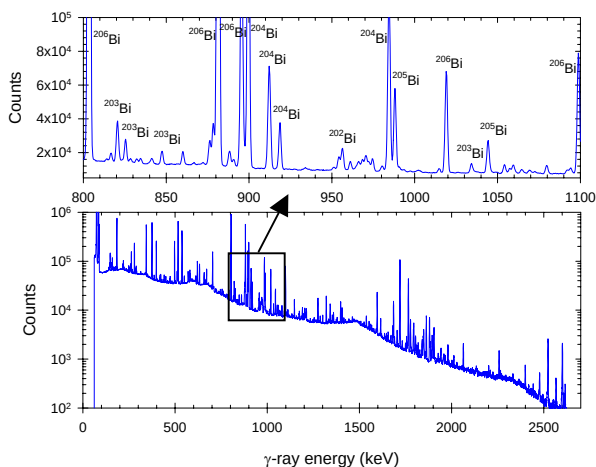


Figure 2. Measured γ -ray spectrum from the Pb sample after a counting time of 90 hours. Part of the spectrum is shown in detail and reactions giving rise to the labelled peaks are listed in Table 1.

Results

The main peaks have been identified as resulting from product nuclides close to the target nuclei; namely ^{206}Bi , ^{205}Bi , ^{204}Bi , ^{203}Bi , ^{202}Bi and ^{201}Bi . Identification was based on the measured γ energies, intensities and half-lives. The net peak areas were used to calculate the numbers of each residual nuclide produced at the time of the laser shot (after correction for detection efficiencies, decay branching ratios, gamma emission probabilities and half-lives), as listed in Table 1, together with the relevant reaction channels and energy thresholds.

Cross sections for individual (p,xn) reactions on ^{206}Pb ($x=1$ to 5), ^{207}Pb ($x=2$ to 5) and ^{208}Pb ($x=3$ to 5) were obtained from the literature⁶⁾ and the relevant cross sections for ^{205}Bi and ^{206}Bi production are shown in Figure 3, scaled to the isotope abundances of the parent nuclei in natural Pb. Scaled theoretical cross sections⁷⁾ for the production of ^{205}Bi via (p,xn) reactions are also shown. The (p,xn) reactions are predominant over other reactions, such as (p,f) and (p, α), in the energy range 10 to 40 MeV, and therefore the sum of the individual (p,xn) reaction cross sections approximates to the integrated experimental cross sections⁴⁾ plotted. Although proton-induced fission of Pb is possible, the (p,f) cross section amounts to only a small percentage of the total cross section at these energies⁸⁾. No signature of proton-induced fission was observed, although it is likely that the small fission cross section is below the detectable limit for this experiment.

The measured (rear) proton energy spectrum, the proton stopping powers in Pb, determined using the SRIM2003⁹⁾ code, and the experimental cross sections for the individual reactions⁶⁾ were convoluted as a function of proton energy to calculate the expected numbers of each residual nuclide produced by (p,xn) reactions. The results are listed in Table 1. There is good agreement between the observed numbers and the yields calculated for the high yield residuals ^{205}Bi and ^{206}Bi . A similar calculation using the theoretical cross sections⁷⁾ for ^{205}Bi resulted in a factor of 2 higher yield, due to the enhanced (p,4n) cross section peaked at ~ 36 MeV. The observed yields for ^{204}Bi and ^{203}Bi are respectively lower and higher by about a factor of 2 than the expected yields. These residuals are produced via (p,4n) and/or (p,5n) reactions with cross sections in the energy range 40 to 50 MeV. At these energies the proton energy spectrum exhibits a sharp cut-off which is sensitive to laser shot-to-shot fluctuations and this may account for the discrepancy. The observed number of ^{202}Bi is much lower than the rest of the residuals, due to the low abundance of ^{204}Pb in natural lead and the high threshold energy of the $^{206}\text{Pb}(p,5n)^{202}\text{Bi}$ reaction (36.3 MeV). It is noted that although ^{201}Bi has a half-life of 1.8 hours and emits γ -rays with energies

Observed Residuals	Half-life	Observed no. of Residual Nuclei	Reactions	E_{Thres} (MeV)	Calculated expected no. of Residual Nuclei		
					Rear p spectrum	EVAP	INC+EVAP
^{202}Bi	1.67h	$(1.2 \pm 0.8) \times 10^6$	$^{204}\text{Pb}(p,3n)^{202}\text{Bi}$	21.4	---	---	---
			$^{206}\text{Pb}(p,5n)^{202}\text{Bi}$	36.3	8.2×10^4	9.6×10^5	5.6×10^7
^{203}Bi	11.76h	$(2.3 \pm 0.3) \times 10^7$	$^{204}\text{Pb}(p,2n)^{203}\text{Bi}$	12.5	---	---	---
			$^{206}\text{Pb}(p,4n)^{203}\text{Bi}$	27.4	8.7×10^6	1.0×10^7	2.4×10^8
			$^{207}\text{Pb}(p,5n)^{203}\text{Bi}$	34.2	8.2×10^4	9.6×10^5	5.6×10^7
					$\Sigma 8.8 \times 10^6$	$\Sigma 1.1 \times 10^7$	$\Sigma 2.9 \times 10^8$
^{204}Bi	11.22h	$(6.4 \pm 0.9) \times 10^7$	$^{204}\text{Pb}(p,n)^{204}\text{Bi}$	5.3	---	---	---
			$^{206}\text{Pb}(p,3n)^{204}\text{Bi}$	20.2	1.1×10^8	1.1×10^8	4.0×10^8
			$^{207}\text{Pb}(p,4n)^{204}\text{Bi}$	26.9	5.5×10^6	8.7×10^6	1.8×10^8
			$^{208}\text{Pb}(p,5n)^{204}\text{Bi}$	34.3	---	---	---
					$\Sigma 1.2 \times 10^8$	$\Sigma 1.2 \times 10^8$	$\Sigma 5.8 \times 10^8$
^{205}Bi	15.31d	$(5.9 \pm 0.9) \times 10^8$	$^{206}\text{Pb}(p,2n)^{205}\text{Bi}$	11.6	3.9×10^8	4.5×10^8	8.4×10^8
			$^{207}\text{Pb}(p,3n)^{205}\text{Bi}$	18.4	9.0×10^7	8.8×10^7	3.1×10^8
			$^{208}\text{Pb}(p,4n)^{205}\text{Bi}$	25.8	1.7×10^7	2.5×10^7	4.5×10^8
					$\Sigma 5.0 \times 10^8$	$\Sigma 5.6 \times 10^8$	$\Sigma 1.6 \times 10^9$
^{206}Bi	6.24d	$(5.8 \pm 0.9) \times 10^8$	$^{206}\text{Pb}(p,n)^{206}\text{Bi}$	4.6	---	---	---
			$^{207}\text{Pb}(p,2n)^{206}\text{Bi}$	11.3	2.9×10^8	3.1×10^8	5.3×10^8
			$^{208}\text{Pb}(p,3n)^{206}\text{Bi}$	18.7	2.5×10^8	2.5×10^8	9.1×10^8
					$\Sigma 5.4 \times 10^8$	$\Sigma 5.7 \times 10^8$	$\Sigma 1.4 \times 10^9$

Table 1. Residual nuclei produced in a ^{nat}Pb activation sample positioned at the rear of the laser-irradiated Al foil target. Proton induced reactions and threshold energies, E_{Thresh} , are listed. The calculated numbers of each nucleus have been determined by convoluting proton energy spectra with the experimental cross sections⁶⁾. Results labelled Σ correspond to a summation over the contributions from the individual reaction channels. The calculation was carried out using the measured proton energy spectrum and the calculated EVAP and INC+EVAP spectra⁵⁾.

in the detectable energy range, it was not observed, again because the abundance of ^{204}Pb for (p,4n) reactions is low and the energy threshold for the other main reaction $^{206}\text{Pb}(p,6n)$ is high (43.7 MeV). The isotope ^{207}Bi has a half-life of 38 years and is of concern for the radioactive inventory of ADS based on Pb spallation targets. Due to its long half-life, it would not have been detected in this experiment, but its production rate from $^{208}\text{Pb}(p,2n)$ reactions will be similar to other Bi isotopes formed by (p,2n) reactions.

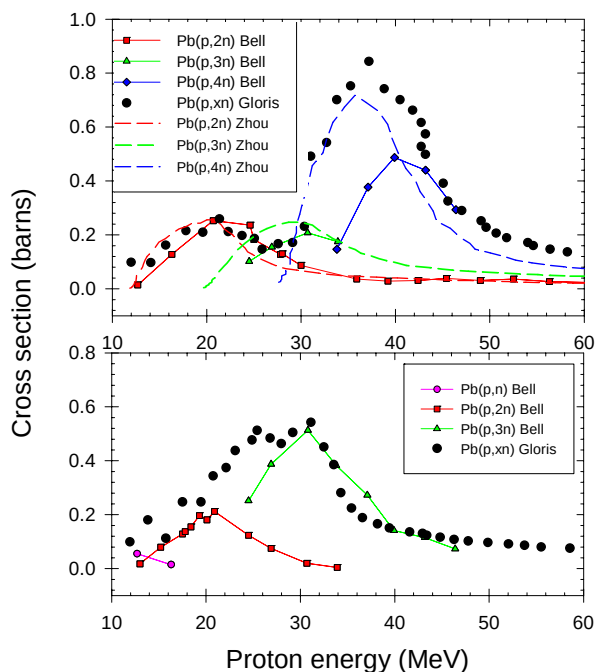


Figure 3. Experimental (Bell⁶⁾) and theoretical (Zhou⁷⁾) cross sections for (p,xn) reactions leading to the production of ^{205}Bi and ^{206}Bi . The cross sections have been scaled to the isotopic abundances of the parent nuclei in $^{\text{nat}}\text{Pb}$. Total experimental cross sections for ^{205}Bi and ^{206}Bi production from $^{\text{nat}}\text{Pb}$ are also shown (Gloris⁴⁾).

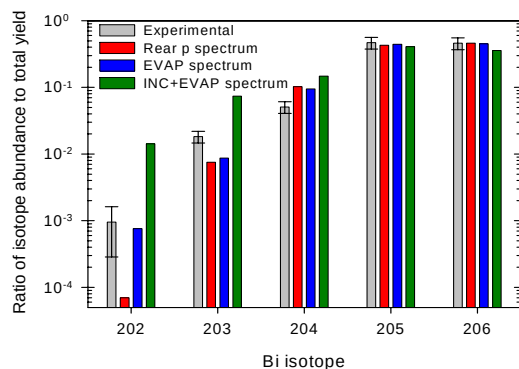


Figure 4. Isotopic distributions of Bi residues in $^{\text{nat}}\text{Pb}$ produced by protons with energies between 12 and 50 MeV. The ratio of the yield of each isotope to the total Bi yield, as measured experimentally (grey) and calculated (coloured) using the experimental cross sections and the experimental and theoretical proton spectra, is plotted.

To determine how closely the measured isotopic abundances of Bi residuals compare with the expected yields, the calculated EVAP and INC+EVAP proton spectra (normalised to the measured spectra), Figure 1, were also convoluted with the experimental cross sections and stopping powers. The calculated yields are listed in Table 1 and the ratio of each isotope yield to the total Bi yield is shown in Figure 4. For the four main isotopes observed (^{203}Bi to ^{206}Bi) there is excellent agreement between the isotopic distributions calculated using

the measured proton spectrum and the calculated spectrum of evaporated protons (EVAP). As discussed above, the experimental measurements of the isotopic distributions are also in good agreement; especially for the high yield isotopes ^{205}Bi and ^{206}Bi . This highlights the potential of this new approach to use the broad energy spectrum of protons from a high intensity laser-plasma interaction to experimentally simulate residual isotope production due to spallation-evaporation protons. When the additional low energy protons resulting from the spallation-intranuclear cascade are factored in (INC+EVAP), the expected Bi isotopic distribution changes slightly in favour of the smaller masses, ^{202}Bi and ^{203}Bi , due to the increased proton flux between 30 and 50 MeV, which enhances contributing (p,4n) and (p,5n) reactions.

Conclusions

In summary, the typically broad energy distribution of protons accelerated in high temperature laser-plasma interactions has been used to investigate residual nuclide production resulting from spallation-evaporation reactions in high-Z targets. The isotopic distribution of heavy residues close to the target element, Pb, has been quantified to produce data to help benchmark nuclear codes in the important low energy regime. The results compare well with the expected isotopic distributions calculated using the proton spectrum produced via spallation-evaporation reactions.

Projected developments in high intensity laser science to deliver focused intensities of the order of 10^{22} to 10^{23} Wcm^{-2} are expected to yield protons with upper energies in the range 250 MeV to 1 GeV. This will facilitate investigation of proton-induced fission and other spallation reactions in the intermediate to high energy regime, where competing spallation processes occur.

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Proton and heavier ion acceleration from petawatt laser interactions with heated target foils

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Introduction

Thomson parabola ion spectrometers and nuclear activation techniques have been successfully employed in a number of experiments to measure the acceleration of fast protons, and, recently, heavy ions, in intense laser-plasma interactions^{1,2,3}. Whereas proton-induced reactions⁴ have been widely used to diagnose proton acceleration, nuclear activation techniques have only recently been developed for measurements of laser-plasma driven 'heavy' ion acceleration^{3,5}. McKenna et al³ have shown that measurements of fusion reactions between fast heavy ions from a laser-produced plasma and stationary atoms in an adjacent 'activation' sample can be used, together with calculated reaction cross-sections, to make quantitative measurements of heavy ion acceleration from a laser-produced plasma.

Experiments employing Thomson parabola ion spectrometers have shown that in addition to the acceleration of constituent heavy ions from a target foil, hydrocarbon and H₂O contaminants on the surfaces of the target are also ionized and accelerated, and result in the production of beams of protons and carbon and oxygen ions^{1,2,3}. These contaminants arise due to the poor vacuum conditions (typically $\sim 10^{-4}$ Torr) under which experiments of this nature are routinely performed. Due to their higher charge-to-mass ratio, parasitic protons are more efficiently accelerated than any other ion species and effectively screen the acceleration potential, reducing the efficiency of heavier ion acceleration. It has also been shown, using Thomson parabola spectrometers and CR-39 plastic track detectors, that sufficient heating of the solid target removes contamination layers increasing the numbers of heavier ions accelerated^{2,6}.

In this work, nuclear activation techniques have been applied to make spatially integrated measurements of both proton and heavy ion acceleration, from the same Vulcan petawatt laser shots, with heated and unheated Fe foil targets. Fe ions with energies greater than 10 MeV per nucleon have been observed, and effects of target heating on the accelerated ion energy spectra and the laser-to-ion energy conversion efficiencies are investigated. The present report is a fuller analysis of preliminary measurements presented previously⁷.

Experimental

The recently developed petawatt arm of the Vulcan Nd:glass laser at the Rutherford Appleton Laboratory, UK, was used in this experiment. P-polarised laser pulses with energy up to

400 J, wavelength $\sim 1 \mu\text{m}$ and average duration 0.7 ps, were focused onto foil targets at an angle of 45° and to a peak intensity of the order of $2 \times 10^{20} \text{ Wcm}^{-2}$. One-hundred micron thick, 5 mm x 5 mm, Fe foil targets were irradiated to generate multi-MeV proton and heavier ion beams. Prior to several of the laser shots the foil target was resistively heated to a temperature of 860°C for approximately 30 minutes.

One-mm thick, 5 cm x 5 cm carbon activation samples were positioned along the target normal direction at both the front and rear of the target, as shown in Figure 1, and used to measure ^{56}Fe acceleration via the production of $^{56}\text{Fe}+^{12}\text{C}$ fusion-evaporation reactions. The carbon activation samples each subtended a solid angle of 1 sr. After each laser shot, two well-shielded germanium detectors were used to measure the characteristic γ -rays emitted by residual nuclei, produced through the evaporation of protons, neutrons and α -particles from the $^{56}\text{Fe}+^{12}\text{C}$ compound nucleus.

Proton acceleration was diagnosed via proton induced reactions in copper. A stack of copper foils (thicknesses from 100 μm to 1 mm) were positioned directly behind each of the carbon samples, as shown in Figure 1. The activity of the positron emitter ^{63}Zn , produced from (p,n) reactions on ^{63}Cu , was measured for each copper foil using a NaI-coincidence detection system.

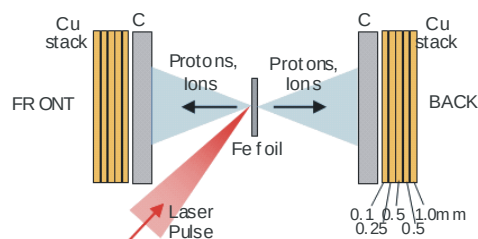


Figure 1. Experimental arrangement. Vulcan petawatt laser pulses are focused onto 100 μm Fe foil targets, which can be resistively heated. Fe ions accelerated from the target are diagnosed via measurements of Fe+C fusion reactions in C activation samples. The accelerated proton energy spectra are measured by proton activation of Cu foils.

To determine both the proton and Fe ion energy spectra, codes were developed to convolute the measured number of reactions induced, the reaction cross sections and the ion stopping powers in the activation targets.

Results

Figure 2 shows regions of interest in the measured γ emission spectra detected from the carbon sample positioned at the front side of the target, which was (a) unheated and irradiated with a 233 J pulse and (b) heated and irradiated with a 274 J pulse. The residual nuclei observed are listed in Table 1, together with the evaporation reactions from the compound $^{56}\text{Fe}+^{12}\text{C}$ nucleus giving rise to these nuclei, the corresponding reaction energy thresholds and the numbers of each observed nucleus produced at the time of the laser shot. For both the hot and cold target shots no ^{56}Fe -induced fusion-evaporation reactions were observed in the C sample positioned at the rear of the heated target foil, indicating that above the detection threshold for this technique no constituent heavy ions were accelerated at the rear of the 100 μm thick Fe foil. This result is in direct contrast with measurements of heavy ion acceleration from heated 50 μm thick Al and W foil targets performed with the 100 TW laser at the Laboratoire pour l'Utilisation des Lasers Intenses (LULI) ²⁾, in which source layers of C and F atoms were ionized and accelerated from the rear of the target.

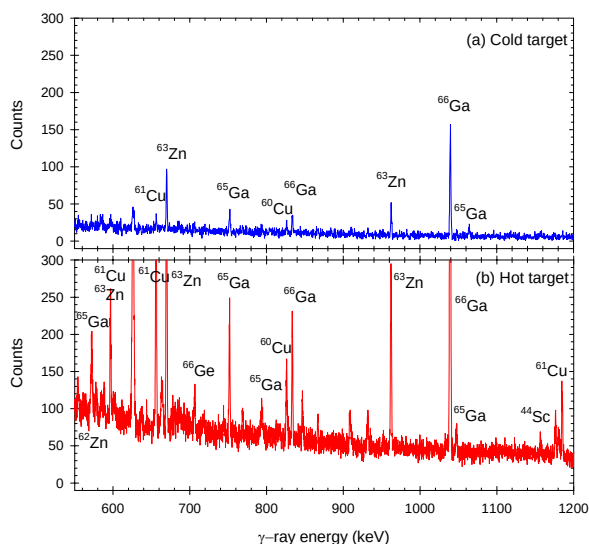


Figure 2. Part of the γ -ray spectrum from C activation samples positioned at the front of the Fe foil target, which was (a) unheated and (b) heated to 860°C. The counting time for each spectrum was ~ 3 hours. Fusion-evaporation reactions giving rise to the observed peaks are listed in Table 1.

In addition to the $^{56}\text{Fe}+^{12}\text{C}$ fusion-evaporation residual nuclei (Table 1), ^{24}Na , resulting from the acceleration of contaminant oxygen ions ($^{16}\text{O}+^{12}\text{C} \rightarrow ^{24}\text{Na}+1n+3p$) was detected in both the front and rear carbon samples for heated and unheated target shots. This indicates that surface contamination atoms heavier than hydrogen can still be ionized and accelerated at the rear of the target.

As discussed in detail elsewhere ³⁾, observed residual nuclides for which the reaction process and mode of decay have been identified can be used to quantify ion acceleration. The technique involves a convolution of the ion stopping ranges in the sample and the reaction cross sections as a function of energy. Cross sections for the observed fusion-evaporation reactions were calculated using the Monte Carlo code PACE-2 ⁸⁾, and are shown in Figure 3. Importantly, the cross sections for the observed reactions extend over a wide range of Fe ion energies, which defines the energy range over which the energy spectrum can be unfolded.

Two techniques (described in detail elsewhere ⁹⁾) were used to convolute the calculated cross sections and stopping powers, with the measured numbers of each reaction, to determine the Fe ion energy spectra. Firstly, a rudimentary calculation was performed in which each reaction process was considered separately, and resulted in the discrete points in the energy distribution shown in Figure 4. The calculations were performed for both the hot and cold target results. Secondly, a code was developed to convolute the various parameters for all of the reactions to unfold the full incident Fe ion energy spectra in small energy steps of 0.5 MeV. The results are plotted as lines in Figure 4 for both the hot and cold target shots. There is excellent agreement in the quantities of ions and the overall shapes of the energy spectra unfolded using both techniques. It should be noted that the effect of the isotopic abundance of the target Fe foil (^{56}Fe (91.8%); ^{54}Fe (5.8%); ^{57}Fe (2.1%); ^{58}Fe (0.3%)) was determined, using ^{56}Fe and ^{54}Fe cross sections weighted to the isotopic abundances. The additional stable isotope had little effect on the final output ion spectra.

As shown in Figure 4, for the unheated target the Fe ion numbers decrease from $\sim 5 \times 10^8$ ions/MeV at low energies (~ 150 MeV) to $\sim 10^7$ ions/MeV at ~ 400 MeV, with a corresponding conversion efficiency from laser energy to Fe ion acceleration (with energy above ~ 150 MeV) of $\sim 0.8\%$. With the Fe target heated to 860°C the numbers of Fe ions accelerated over the observed energy range is up to an order of magnitude higher and corresponds to an energy conversion efficiency of $\sim 4.2\%$. It should be noted that the calculated

Observed nuclei	Evaporation reactions	E_{Thresh} (MeV)	Literature Half-life	Measured Half-life (860°C)	Number of nuclei	
					Unheated	860°C
^{67}Ga	1p	1.2	3.3 d	---	---	3.5×10^5
^{67}Ge	1n	9.8	18.7 m	26.5 m	---	3.9×10^4
^{63}Zn	1a + 1n	10.6	38.9 m	38.5 m	3.8×10^5	2.1×10^6
^{66}Ga	1n + 1p	14.7	9.5 h	9.9 h	6.4×10^5	3.8×10^6
^{66}Ge	2n	18.2	2.3 h	2.2 h	6.2×10^4	4.4×10^5
^{62}Zn	1a + 2n	21.7	9.3 h	9.4 h	---	6.9×10^5
^{65}Ga	2n + 1p	25.7	15.2 m	13.6 m	2.1×10^5	1.6×10^6
^{61}Cu	1a + 2n + 1p	29.4	3.4 h	3.3 h	2.0×10^5	1.3×10^6
^{57}Co	2a + 2n + 1p	35.6	271.4 d	---	---	1.2×10^6
^{60}Cu	1a + 3n + 1p	43.6	24.4 m	23.7 m	7.6×10^4	2.8×10^5
^{56}Mn	2a + 1n + 3p	46.2	2.6 h	---	---	2.3×10^4
^{52}Mn	3a + 3n + 1p	58.5	5.6 d	---	---	3.2×10^5
$^{52\text{m}}\text{Mn}$	3a + 3n + 1p	58.5	21.1 m	---	---	3.1×10^4
^{49}Cr	4a + 3n	59.2	41.9 m	35.0 m	---	4.7×10^4
^{55}Co	2a + 4n + 1p	61.3	17.5 h	---	---	6.8×10^4
^{44}Sc	5a + 3n + 1p	79.9	3.9 h	---	2.3×10^4	1.9×10^4
$^{44\text{m}}\text{Sc}$	5a + 3n + 1p	79.9	2.4 d	---	---	1.2×10^5

Table 1. The residual nuclei observed in the C activation samples at the front of the laser irradiated heated and unheated Fe foil targets. The $^{56}\text{Fe}+^{12}\text{C}$ fusion-evaporation reactions and threshold energies, E_{Thresh} , for each reaction are listed.

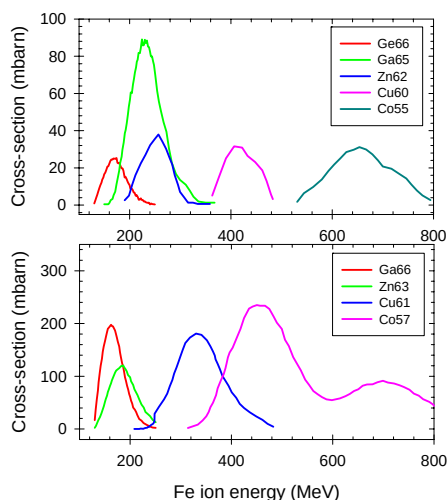


Figure 3. Cross-sections for $^{56}\text{Fe}+^{12}\text{C}$ fusion-evaporation reactions calculated using the PACE-2 Monte Carlo code.

energy conversion efficiency involves ^{56}Fe ions in the energy range of the observed nuclear reactions and contributing to the nuclear reactions. The total energy conversion efficiency to heavy ion acceleration over the full energy range and including the acceleration of any remaining surface contaminant species will be higher. It is clear from these spatially integrated ion flux measurements that heating the primary target has the effect of increasing the efficiency of heavy ion acceleration, in line with previous results using an ion spectrometer to sample a small solid angle ^{2,6}. It is also noted that Fe ions have been accelerated to energies in excess of 10 MeV per nucleon for the heated target shot.

The additional nuclei observed with the hot target (Table 1) are produced due to a higher flux of higher energy ions compared with the cold Fe target. The reactions leading to the production of ^{55}Co and ^{57}Co , for example, both have relatively high cross section values at high incident ion energies (see Figure 3).

Proton acceleration from the front and rear surfaces of the Fe target foils was also diagnosed for the same heated and unheated shots, by measuring (p,n) reactions in ^{63}Cu ⁴. The deduced proton spectra are shown in Figure 5, and have been corrected for the protons passing through the 1 mm thick Carbon sample (Figure 1). The measurement was limited to protons with energy above ~ 13 MeV. Significantly, the numbers of protons accelerated from both the front and rear surfaces of the heated target are reduced by about 2 orders of magnitude compared to the unheated target. The energy conversion efficiency to protons in this energy range is of the order of 2% for the unheated target, falling to $\sim 0.01\%$ for the heated target. The total energy conversion efficiency to protons (over the full proton energy range) from unheated targets under similar experimental conditions was measured to be about 7%.

Conclusions

In summary, heating a 100 μm thick Fe target foil to temperatures in excess of 850°C removes hydrogen-containing contamination layers, reducing the efficiency of proton acceleration by greater than 2 orders of magnitude and significantly increasing the efficiency of heavy ion acceleration.

It should be noted that the removal of target contamination has led to the production of long-lived isotopes such as ^{57}Co (271 day half life) via a laser-plasma driven process. This unique radiation source could potentially be used to produce isotopes in other parts of the table of nuclides, which may be more difficult to produce using conventional techniques on large scale nuclear and accelerator facilities.

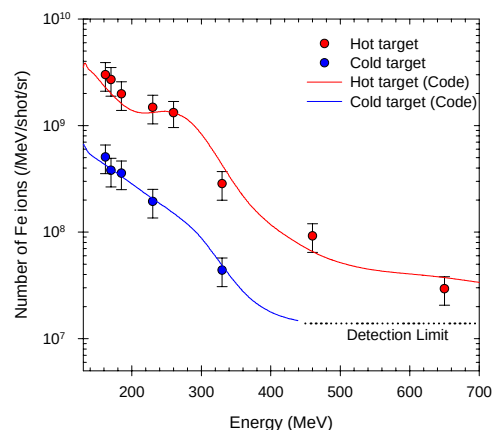


Figure 4. The Fe ion energy distribution, deduced by determining the numbers of ions required to induce the measured activities of the ^{66}Ge , ^{65}Ga , ^{62}Zn , ^{66}Ga , ^{63}Zn , ^{61}Cu and ^{57}Co nuclides. The points result from calculations performed for each observed reaction. The lines are the corresponding results of a full convolution involving all the above reactions ⁹. The detection limit for the technique was determined to be $\sim 10^7$ ions/MeV.

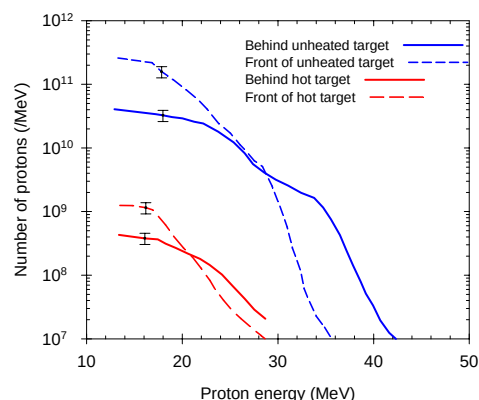


Figure 5. Proton energy spectra determined from measured $^{63}\text{Cu}(p,n)^{63}\text{Zn}$ reactions in Cu foils. The proton flux from the heated target is reduced by about 2 orders of magnitude compared to the unheated target.

Acknowledgements

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Rapid heating of solid density material by the Vulcan petawatt laser

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Introduction

When Petawatt class lasers are focussed to intensities of around 10^{20} Wcm^{-2} on solid targets they generate intense beams of relativistic electrons, much greater than the Alfvén current¹⁾. These intense electron beams find important applications in the 'fast ignition' of IFE fusion pellets²⁾, and as sources of protons and X-rays for medical and materials applications³⁾. There is also the opportunity to create extremely high pressure material by heating solid density material to temperatures of order 1keV and to measure equation of state and opacity under conditions relevant to astrophysics⁴⁾. Understanding the transport and energy deposition from the high current electron beam is challenging because of the interplay of collisional and collective plasma processes and is essential in optimizing any of the above applications. We report the first deep heating results from the Vulcan Petawatt laser, the novel use of implicit PIC methods to model the transport and heating processes and the influence of laser prepulse in reducing the penetration of the heating beam.

If the normalised intensity of the laser is $a_0 = eE/(m_e \omega c)$ then the laser accelerates electrons from a region around the relativistically corrected critical density $n_e = ((1+a_0^2)^{1/2} m_e \omega^2 / (4\pi e^2))^{1/2}$ to energies of about the ponderomotive potential of the focussed laser $\Phi = m_e c^2 ((1+a_0^2)^{1/2} - 1)$. At laser intensities around 10^{20} Wcm^{-2} ($a_0 \sim 8$) these MeV electrons are largely collisionless, having ranges at solid density of more than 100 μm and thermalisation times longer than the laser pulse. However in order to satisfy charge neutrality in the target there must be a return current equal to the current generated by the laser and ohmic dissipation of this return current can be the dominant heating mechanism in the target⁵⁾. The detailed physics is further complicated by the global magnetic field of the plasma currents and the small scale filamentation of the electrons due to the Weibel instability⁶⁾ and also due to the temperature dependence of plasma resistivity, sometimes referred to as an electro-thermal instability. Measurements of the transport and heating effects of the beams of relativistic electrons provide tests for our theoretical understanding of the physics involved and also offer the opportunity to create high temperature, high pressure solid material in a unique way.

Previous experiments have measured the K- α emission induced by the energetic electron beam in passing through relatively cold material and used this to infer the electron beam dynamics. Koch and others⁷⁾ have measured thermal X-ray spectra from buried aluminum tracer layers and deduced temperatures in solid density material of 200eV to 350eV at an irradiance of $3 \times 10^{19} \text{ Wcm}^{-2}$ and a pulse length of 5 psec. Our results extend this technique to an irradiance of more than 10^{20} Wcm^{-2} on the Vulcan Petawatt laser in a sub-psec pulse.

Our targets are a planar sandwich consisting of a front layer of CH of variable thickness, a thin aluminum tracer layer and a rear surface layer of CH 4 μm thick which is sufficient to tamp the hydrodynamic expansion for the duration of the X-ray emission while maintaining good X-ray transmission for the H-like and He-like aluminum X-ray emission. The thickness of the aluminum tracer layer is set to 0.2 μm as a compromise

between excessive opacity in the resonance lines and detectability of the fainter lines.

The layout of the experiment is shown in Figure 1. The Vulcan Petawatt laser was focussed at an incidence of 35 degrees by a 600mm f3 off-axis parabola onto the flat multi-layered targets. The highest irradiance of more than 10^{20} Wcm^{-2} was achieved with 300J of laser energy focussed into a spot size of 10 μm in less than 1ps. The Al H-like and He-like spectral lines were detected by a conical CsAP crystal spectrometer with unity magnification coupled to a Kentech low-magnification streak camera and recorded with a DarkStar 8 bit digital readout. The time resolution of the streaked crystal spectrometer was 14 ps and the spectral resolution was 0.02 Å, limited by the streak camera.

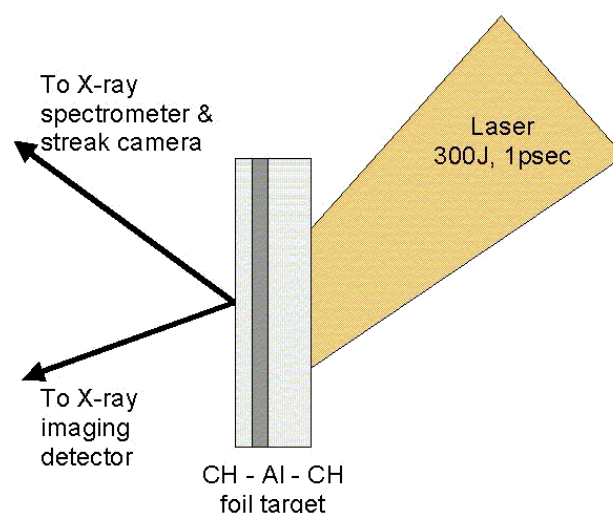


Figure1. Schematic layout of the experiment.

Aluminum spectra were recorded with front CH layer thicknesses from 4 μm to 29 μm . X-ray emission was recorded with a front layer thickness of 54 μm but was too weak to provide quantitative data. Figure 2 shows a sequence of spectra at varying depths of the tracer layer together with identification of the spectral features. The He-like and H-like $n=2$ to $n=1$ transitions each have dielectronic satellite lines which are an aid to diagnosing the density and temperature of the emitting region. The emission labelled K- α corresponds to a K-shell vacancy in five or six times ionised aluminum consistent with a 'background heating' due to the MeV electrons generated by the laser heating a large volume of the target to perhaps 30eV. The K- α emission is not seen at depths of 4 μm and 8 μm which implies that at shallower depths (and thinner targets) the background temperature is higher. There is an emission feature to the high energy side of He- α labeled KK which is clearest at depths of 12 μm and 17 μm which we identify, using Dirac Fock calculations of energy levels, as a 'hollow atom' transition in an aluminum ion with a double K-shell vacancy⁸⁾. Normally

the lifetime of a single K-shell vacancy against fluorescence and Auger emission is so short that the state will decay before a second K-shell ionisation can occur. In these ultra-high intensity, solid density, laser experiments the flux of energetic electrons is so intense (around $3 \times 10^{31} \text{ cm}^{-2} \text{ s}^{-1}$) that a second ionisation can occur before the ion with the single vacancy has relaxed. All the spectra show a temporal oscillation with a period of about 25psec which we believe to be an instrumental artifact due to electromagnetic radiation (EMP) from the target affecting electron paths in the streak camera.

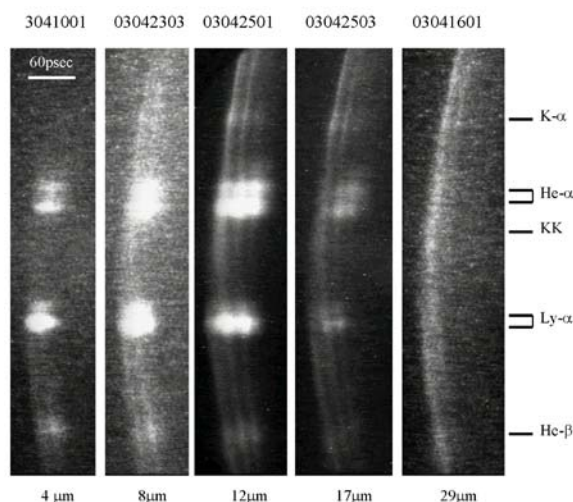


Figure 2. Time resolved X-ray spectra for different buried layer depths.

During the 1 psec laser pulse the electron distribution in the solid material is strongly non-Maxwellian due to the large number of electrons accelerated by the laser. However electrons below 10keV energy (i.e. those responsible for exciting the line radiation) and at solid density have collision times of less than 10^{-13} sec for both electron-ion scattering (isotropisation) and electron-electron scattering (formation of a Maxwellian energy distribution) so that this part of the distribution function will thermalise rapidly once the laser turns off. The observed X-ray emission persists for about 20 - 50psec after the laser pulse depending on the depth of the tracer layer and it is a good approximation to use a thermal distribution to interpret the X-ray spectrum at these times. Moreover the time dependent atomic physics code FLY⁹⁾ shows that at solid density the transient populations due to rapid heating persist for at most 1 - 2 psec so we are able to infer temperatures and densities on the basis of steady state atomic rate equations provided there is evidence that the density remains high. We have corrected the observed spectra for the differential transmission of the rear CH layer and compared with synthetic spectra generated by FLY for a homogeneous finite slab of aluminum including line broadening and radiative transfer. We vary the density and temperature input to FLY to fit various spectral features but always retain the line of sight density of aluminum according to the target fabrication.

The deepest layer from which we obtain good spectral data is at 17 μm . A consistent fit to the satellite lines to Ly- α , the width of He- β , and the line ratio (Ly- α / He- α) requires a temperature of 450 - 550eV and a density of 1 - 3 g cm^{-3} . A second shot at 17 μm depth which is under-exposed gives similar densities and a temperature of 400 - 500eV. This choice of density and temperature predicts too low an intensity in He- β by a factor of about 2 - 3 which is probably due to inhomogeneity in the emitting region and implies that smaller regions may have temperatures around 800 - 1000eV. The density data rules out either decompressed material at 0.1 g cm^{-3} or shock compressed aluminum at around 8 g cm^{-3} and confirms our use of a steady

state calculation. Table 1 summarises the density and temperature measurements.

Depth of Al layer	Density (gcm^{-3})	Temperature (eV)
4.0	< 1	> 600
8.2	1.0 - 3.0	600 - 750
12.1	1.0 - 3.0	450 - 550
17.1	1.0 - 3.0	400 - 550
29	-	< 250

Table 1. Summary of the measured densities and temperatures.

We have used the LSP code¹⁰⁾ to model the heating of the target by the laser generated electron beam. We use LSP in its direct implicit mode with particle beam electrons and fluid target electrons to model the propagation of the relativistic electron beam together with its self-consistent electric and magnetic fields and collisional effects in the beam and return currents. In this mode LSP is broadly comparable to hybrid codes such as Pâris¹¹⁾ but has the advantage that the return currents are formed self-consistently rather than being mandated by current neutrality.

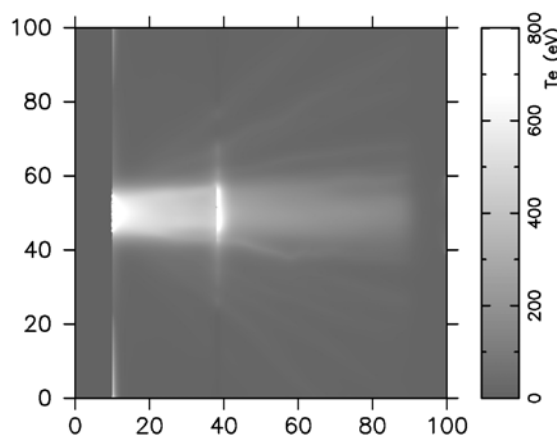


Figure 3. Distribution of electron temperature at 1psec in the LSP simulation.

The LSP calculations use 800 x 800 cells on a grid of 100 μm x 100 μm . An electron beam is injected at the left side of a CH target at solid density containing a buried tracer layer of aluminum. The resistive return current preferentially heats the higher Z layer resulting in the aluminum becoming substantially hotter than the CH substrate as shown in Figure 3. The longitudinal temperature of the injected electrons is 3.0 MeV corresponding to an incident irradiance of 10^{20} Wcm^{-2} , the transverse temperature is 300keV and the current corresponds to an absorbed energy flux of 10^{19} Wcm^{-2} . In the LSP simulations the temperature in the aluminum layer is sensitive to the layer thickness due to strong thermal conduction losses at each surface. The LSP simulations are performed using flux limited thermal conduction for the fluid background electrons but are in a regime where the electron mean free path is not small compared with the temperature scale length and would be calculated more accurately using a 2D Fokker Planck model as recently described by Bell and Kingham¹²⁾. We note that excitation of the 1.5keV - 2.0keV aluminum spectral lines requires electron energies of at least 1.5 - 2.0keV and the mean free path of these electrons in solid aluminum is about half of our tracer layer thickness. With such a large mean free path, the electrons responsible for the X-ray emission will not be in equilibrium with the higher temperature in the aluminum tracer layer but will indicate only the lower temperature in the CH substrate. To a good approximation therefore our X-ray measurements will be indicative of the temperature in the CH and not the higher temperatures in the higher Z aluminum layer.

The temperature in the CH material is not sensitive to the size of the computational mesh.

In Figure 4 we show a comparison of our experimental measurements and the LSP simulations with the depth adjusted for material ablated by the laser pre-pulse. There is good agreement at depths to 15 μm but the baseline LSP simulations show that aluminum layers buried at depths to at least 35 μm should achieve a temperature of 300 eV and generate observable aluminum X-ray emission. Reducing the electron beam energy does not resolve the discrepancy as is shown in Figure 4 with the longitudinal temperature reduced to 2.0 MeV.

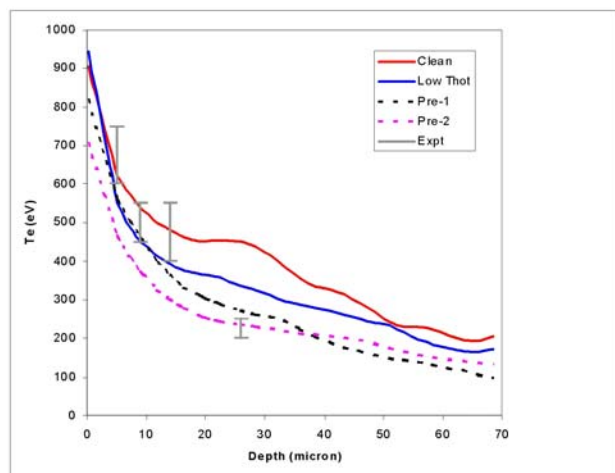


Figure 4. Axial temperature profile from the LSP simulations with different assumptions.

The pre-pulse from the Vulcan Petawatt laser is believed to be at a level of 10^{-7} of the main pulse for up to 2 nsec. With main pulse intensities of 10^{20} Wcm^{-2} the prepulse is of order 10^{13} Wcm^{-2} . 2D fluid simulations show that near the focal spot a steady state is reached where the critical density layer sits about 5 μm from the ablation surface. Although the real blow off plasma is strongly two dimensional due to the small focal spot size we have performed the LSP simulation of pre-pulse effects with a planar blow off layer extending 5 μm from the 'solid' surface and injecting the electron beam where the density is three times the relativistically corrected critical density to reflect some 'hole-boring' by the main laser pulse.

Injecting the electrons a little way from the solid surface strongly affects the electric fields in the target. Since the Spitzer resistivity is largely independent of density, the same electric field is generated as in the solid target but over a larger distance so that the 'potential drop' is larger. Electrons with energies below this 'skin potential' are unable to reach the solid and there is consequently reduced heating in the solid. This is similar to electron preheat inhibition at much lower irradiances described by Bond, Hares and Kilkenny¹³⁾. Figure 4 also shows two LSP calculations including a density tail as might be produced by the laser pre-pulse and showing the reduced heat front penetration in substantially better agreement with the observations.

In conclusion we have significantly extended the experimental measurements of the deep heating of solid targets by Petawatt lasers and through the novel application of the LSP computer model we have demonstrated the reduced penetration of the heat front resulting from the effects of laser pre-pulse. The observation of the double K-shell vacancy 'hollow atom' transition gives rise to the possibility of a new diagnostic technique to measure the fast electron flux inside solid targets in future experiments.

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Neutron generation by fast protons from ultra-intense laser-plasma interactions using the Vulcan Petawatt laser

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Introduction

Laser-solid interactions at intensities $> 10^{19} \text{ W/cm}^2$ leads to the production of fast electrons with maximum energies greater than 300 MeV, multi-MeV γ rays, tens of MeV protons and several hundreds of MeV heavy ions¹. These energetic particles and high energy γ rays have a number of potential applications¹⁻⁴. In particular, the energy spectra of laser-plasma accelerated protons can be measured to study proton generation and acceleration mechanisms. The $^{63}\text{Cu}(p,n)^{63}\text{Zn}$ reactions in copper stacks are used to quantify the proton numbers through measurement of β^+ decay of ^{63}Zn nuclei.

In addition, it is known that (p,n) reactions provide an important method for producing neutron sources and in the present experiment up to $\sim 10^9$ neutrons sr^{-1} have been generated via $^{11}\text{B}(p,n)^{11}\text{C}$ reactions. Neutrons have a variety of existing and potential applications, such as boron neutron capture therapy (BNCT), neutron radiography and transmutation of nuclear waste. There are two types of neutron sources⁵: accelerator- and reactor-based sources. The reactor-based neutron sources can provide steady high flux neutron beams in the range of 10^7 to $10^{15} \text{ ncm}^{-2}\text{s}^{-1}$, but they require very strict radiation shielding, generate nuclear waste and cannot be sited in some areas due to safety reasons, for example in hospitals. Most of the high flux reactors are now operating at around $10^{15} \text{ ncm}^{-2}\text{s}^{-1}$. On the other hand the accelerator-based neutron sources produce neutron beams with fluxes in the range 10^6 to $10^{13} \text{ ncm}^{-2}\text{s}^{-1}$, although the most recent accelerator based pulses systems at ISIS (Rutherford Appleton Laboratory) and the SNS (Oak Ridge) will have higher intensities of the order of 10^{16} to $10^{17} \text{ ncm}^{-2}\text{s}^{-1}$. Accelerators also provide pulsed neutron beams, for example the spallation neutron source (SNS) under construction in USA has a specification to generate pulsed neutron beams with pulse widths in the order of microseconds. In this paper we report on observed proton-induced reactions in zinc and boron using the Vulcan petawatt laser facility. The numbers and energy spectrum of neutrons generated in several different elements have been calculated using the experimentally determined proton spectra and are discussed in the following report.

Experimental

The experiments were carried out on the new petawatt arm of the Vulcan Nd:glass laser at the Rutherford Appleton Laboratory. The 60 cm beam was focused to a $7.0 \mu\text{m}$ diameter spot using a 1.8 m focal length off-axis parabolic mirror, in a vacuum chamber evacuated to $\sim 10^{-4}$ mbar. The pulse durations were ~ 750 fs and the energies on target were 200-300 J. The peak intensities were of the order of 2 to $3 \times 10^{20} \text{ Wcm}^{-2}$. As shown in Figure 1, primary targets of mylar, gold and aluminum foils of various thicknesses were irradiated by the p-polarized laser beam at an angle of 45° to generate multi-MeV proton beams in front of and behind the target foil. Activation samples

such as zinc and boron were positioned on both sides along the target normal direction. The samples were exposed to the proton beams from the target and various isotopes were produced via nuclear reactions in the samples. The $100 \mu\text{m}$ thick zinc samples were analyzed before and after each laser shot using well-shielded germanium detectors. The isotopes and corresponding reactions in the samples were identified based on their emitted γ -ray energies, intensities and half-lives. The detection efficiencies of the two germanium detectors were calibrated using known sources of ^{152}Eu , ^{57}Co , ^{22}Na , ^{137}Cs and ^{60}Co to determine the absolute numbers of laser induced reactions. The activity from $^{11}\text{B}(p,n)^{11}\text{C}$ reactions in each boron sample was measured using a $3'' \times 3''$ NaI coincidence system, to obtain the number of ^{11}C nuclei and hence the neutron numbers.

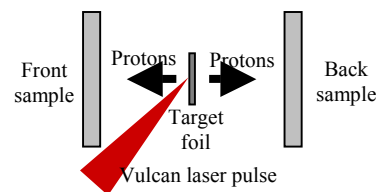


Figure 1. Schematic of experimental set up for proton induced reactions.

Results and Discussion

The zinc samples ($100 \mu\text{m}$ thick $50 \times 50 \text{ mm}$ plates) were positioned in front of and behind the laser-irradiated (230 J) aluminium target ($20 \mu\text{m}$ thick). Regions of the measured γ -ray spectra from the zinc samples are shown in Figure 2.

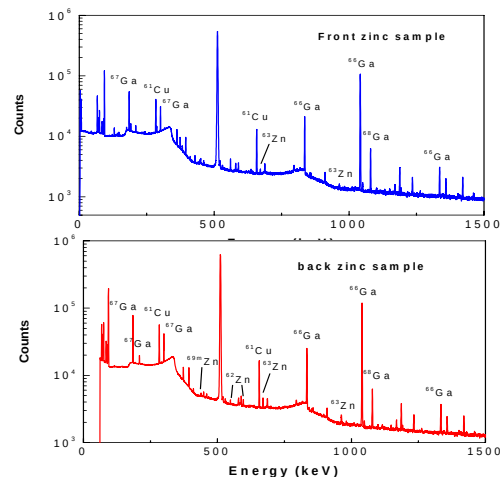


Figure 2. Regions of characteristic γ -ray line spectra for the proton irradiated zinc samples.

Gamma emissions from the nuclei ^{66}Ga , ^{67}Ga , ^{68}Ga , ^{61}Cu , ^{62}Zn , ^{63}Zn and $^{69\text{m}}\text{Zn}$ have been identified. The numbers of these nuclei and the corresponding reactions are listed in Table 1. As shown in Figure 2 and Table 1, the nuclei ^{66}Ga , ^{67}Ga , ^{68}Ga , ^{61}Cu and ^{63}Zn have been observed in both the front and back zinc samples, but the nuclei ^{62}Zn and $^{69\text{m}}\text{Zn}$ have been seen only in the back sample. This is consistent with the following experimentally determined proton spectra: the back proton spectrum has a larger high energy component than the front one. Since natural zinc has five stable isotopes: ^{64}Zn (48.6%); ^{66}Zn (27.9%); ^{67}Zn (4.1%); ^{68}Zn (18.8%) and ^{70}Zn (0.6%); after irradiation by the proton beams from the aluminium target, the ^{66}Ga nuclei generated in the samples can result from the three reactions $^{66}\text{Zn}(p,n)^{66}\text{Ga}$, $^{67}\text{Zn}(p,2n)^{66}\text{Ga}$ and $^{68}\text{Zn}(p,3n)^{66}\text{Ga}$. The ^{67}Ga nuclei could be generated via $^{67}\text{Zn}(p,n)^{67}\text{Ga}$ and $^{68}\text{Zn}(p,2n)^{67}\text{Ga}$ reactions, and the ^{68}Ga , ^{61}Cu , ^{62}Zn , ^{63}Zn and $^{69\text{m}}\text{Zn}$ nuclei were produced via $^{68}\text{Zn}(p,n)^{68}\text{Ga}$, $^{64}\text{Zn}(p,\alpha)^{61}\text{Cu}$, $^{64}\text{Zn}(p,p+2n)^{62}\text{Zn}$, $^{64}\text{Zn}(p,p+n)^{63}\text{Zn}$ and $^{70}\text{Zn}(p,p+n)^{69\text{m}}\text{Zn}$ reactions respectively.

Nuclei	Observed number of nuclei per shot		Reactions	Q-values (MeV)
	Front	Back		
^{66}Ga	$(2.2\pm0.1)\times10^8$	$(2.2\pm0.3)\times10^8$	$^{66}\text{Zn}(p,n)^{66}\text{Ga}$ $^{67}\text{Zn}(p,2n)^{66}\text{Ga}$ $^{68}\text{Zn}(p,3n)^{66}\text{Ga}$	-5.957 -13.01 -23.21
^{67}Ga	$(1.2\pm0.1)\times10^8$	$(1.1\pm0.1)\times10^8$	$^{67}\text{Zn}(p,n)^{67}\text{Ga}$ $^{68}\text{Zn}(p,2n)^{67}\text{Ga}$	-1.782 -11.98
^{68}Ga	$(3.0\pm0.3)\times10^8$	$(2.7\pm0.3)\times10^8$	$^{68}\text{Zn}(p,n)^{68}\text{Ga}$	-3.703
^{61}Cu	$(4.2\pm0.1)\times10^7$	$(4.2\pm0.8)\times10^7$	$^{64}\text{Zn}(p,\alpha)^{61}\text{Cu}$	0.844
^{62}Zn	-----	$(1.2\pm0.4)\times10^6$	$^{64}\text{Zn}(p,p+2n)^{62}\text{Zn}$	-20.974
^{63}Zn	$(2.5\pm0.8)\times10^7$	$(5.6\pm0.5)\times10^7$	$^{64}\text{Zn}(p,p+n)^{63}\text{Zn}$	-11.861
$^{69\text{m}}\text{Zn}$	-----	$(1.6\pm0.3)\times10^5$	$^{70}\text{Zn}(p,p+n)^{69\text{m}}\text{Zn}$	-9.215

Table 1. Residual nuclei observed in zinc activation target and corresponding proton induced reactions.

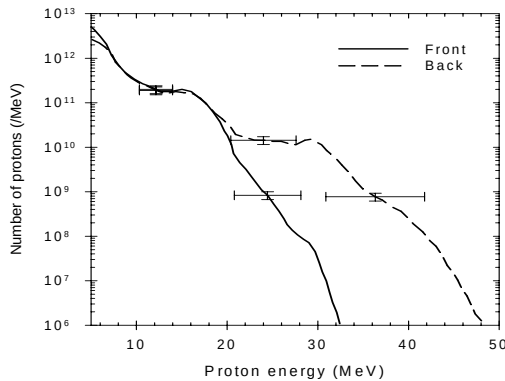


Figure 3. Experimentally determined proton energy spectra.

As shown in Table 1, the proton-induced reactions in zinc have quite different Q-values and cross-section peak energies. A code was developed to unfold the proton spectra using the measured numbers of the observed isotopes in zinc⁶. The first step involved the derivation of a response function. The number of nuclei produced by one proton with energy E_p was calculated for each reaction using the published proton stopping power and cross section data⁷. Then, starting with an arbitrary initial proton spectrum, the number of nuclei for each reaction was calculated by convoluting the spectrum with each response function. The ratio of the measured number of nuclei to calculated value was determined for each nucleus and the proton spectrum was adjusted repeatedly according to the ratio and its corresponding response energy region until the calculated numbers for all observed nuclei were consistent with

the measured ones within a preset error. The deduced proton spectra are shown in Figure 3. Using these spectra, the numbers of the ^{66}Ga nuclei generated from the $^{66}\text{Zn}(p,n)^{66}\text{Ga}$, $^{67}\text{Zn}(p,2n)^{66}\text{Ga}$ and $^{68}\text{Zn}(p,3n)^{66}\text{Ga}$ reactions were calculated. For the front zinc sample, the numbers of ^{66}Ga nuclei from $^{66}\text{Zn}(p,n)^{66}\text{Ga}$, $^{67}\text{Zn}(p,2n)^{66}\text{Ga}$ and $^{68}\text{Zn}(p,3n)^{66}\text{Ga}$ reactions are 2×10^8 , 3×10^6 and 2×10^3 , respectively, and for the back sample, these are 2×10^8 , 5×10^6 and 5×10^5 . Therefore, more than 95% of the ^{66}Ga in the zinc samples came from $^{66}\text{Zn}(p,n)^{66}\text{Ga}$ reactions. Similar analysis has been carried out for the generation of the ^{67}Ga nucleus and the results show that, for the front zinc sample, 74% of ^{67}Ga was produced via $^{67}\text{Zn}(p,n)^{67}\text{Ga}$ reactions and 26% from $^{68}\text{Zn}(p,2n)^{67}\text{Ga}$, but for the back sample, these figures were 60% and 40% respectively due to the larger fraction of the high energy proton component in the proton beam at the back of the target.

The measured numbers of ^{11}C nuclei both in the front and back boron samples (3 mm-thick circular discs, 50 mm diameter) for different laser-irradiated targets are listed in Table 2. It can be seen that except for the low energy shot, the numbers of the proton-induced ^{11}C nuclei in the front boron samples are almost constant for all shots with this range of target thicknesses. The small differences in the numbers are reasonable due to the fluctuation of the proton spectrum possibly caused by nonlinear proton generation process and small changes in the shot-to-shot laser pulse conditions. The number of ^{11}C nuclei in the back boron sample increases with decreasing target thickness for all shots with similar laser energies and tends to be close to the number of ^{11}C in the front sample for the thinnest targets.

Target	Target thickness (μm)	Laser Energy (J)	Observed number of ^{11}C per laser shot	
			Front sample	Back sample
Al	1	138	3.8×10^9	3.7×10^9
Au	5	302	1.3×10^{10}	9.3×10^9
Al	30	214	9.9×10^9	4.5×10^9
CH	75	265	7.3×10^9	2.8×10^9
Al	100	239	9.4×10^9	2.9×10^9
Al	250	243	1.1×10^{10}	3.0×10^9
Al	500	226	9.4×10^9	5.6×10^8

Table 2. Observed number of ^{11}C nuclei produced via nuclear reactions induced by proton beams from the front and back of various laser-irradiated targets.

As each $^{11}\text{B}(p,n)^{11}\text{C}$ reaction generates one neutron and one ^{11}C nucleus, the same number of neutrons are produced as ^{11}C nuclei. Using the proton spectra in Figure 3, the number of neutrons, N_n , generated in the samples at the front and back of the target can be calculated as follows

$$N_n = \int_{E_{\min}}^{E_{\max}} \int_0^{x_0} n_i \sigma(E_p) I_p(E_{p0}) dE_{p0} dx \quad (1)$$

$$E_p(x) = E_{p0} - \int_0^x \left(\frac{dE}{dx} \right) dx_1 \quad (2)$$

where, $x_0 = \min(T_0, T_r)$ is the smaller one of the sample thickness T_0 and the stopping range T_r of the proton of energy E_{p0} , n_i is the number density of the reacting particles in the sample, $I_p(E_{p0})$ is the incident proton spectral intensity, $\sigma(E_p)$ is the cross-section of the (p,n) reaction and dE/dx is the stopping power of the protons in the sample.

The calculated and observed (^{11}C) numbers of neutrons for the different targets but similar laser energies are shown in Figure 4 (a). The ^{11}B isotopic abundance of 80% and density of 2.35 gcm^{-3} were adopted in the calculations. The same sample thicknesses as the experiment were also used. The calculated

number of neutrons generated in the front boron sample with the 20 μm -thick aluminium target is in good agreement with those observed experimentally (for the range of target thicknesses) and the calculations for the back boron sample also agrees well with the observed reduction of the neutron number with the target thickness, confirming that the proton spectra used in the calculations are realistic. Importantly, up to 10^9 neutrons per steradian have been produced by a very short pulse of protons, providing a bright neutron source.

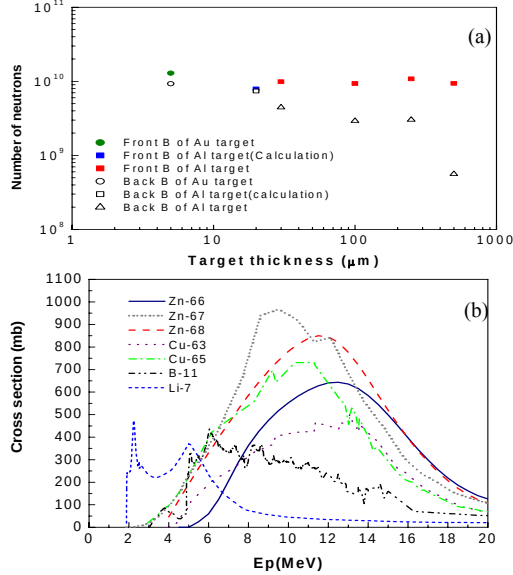


Figure 4. (a) Numbers of neutrons produced by $^{11}\text{B}(\text{p},\text{n})^{11}\text{C}$ reactions in the front and back boron samples as a function of the target thicknesses. (b) Cross sections for the (p,n) reactions in ^7Li , ^{11}B , ^{63}Cu , ^{65}Cu , ^{66}Zn , ^{67}Zn and ^{68}Zn samples⁷.

It is important and necessary to characterise this source, including the neutron intensity, energy spectrum and the angular distribution of the emitted neutrons. Firstly, to calculate the intensity of neutrons produced via (p,n) reactions, lithium (92.5% ^7Li), boron (80% ^{11}B), 100% ^{63}Cu , 100% ^{65}Cu , 100% ^{66}Zn , 100% ^{67}Zn and 100% ^{68}Zn have been selected as activation samples. Using (p,n) cross sections⁷, Figure 4(b), and the measured proton energy spectra, the number of neutrons as a function of thickness for the above samples was calculated using Equations (1) and (2), and are presented in Figure 5.

The number of neutrons produced in the sample increases with thickness for a thin sample and tends to become constant as the thickness of the sample increases. It is apparent from Figure 5 that much thicker low-Z lithium and boron are needed to produce the maximum numbers of neutrons than the medium-Z copper and zinc. This is the result of the much longer proton stopping range in the low-Z samples since the energy loss of a proton in a sample is proportional to the atomic number Z of the sample, in terms of the Bethe formula. Slightly thicker activation samples are required at the back of the target, compared to the front, to maximize neutron production due to the greater number of higher energy protons in the back proton beam (Figure 3). The calculated maximum numbers of neutrons produced by (p, n) reactions are listed in Table 3.

For copper the ^{65}Cu isotope is seen to generate much larger number of neutrons than ^{63}Cu and for zinc samples the largest number of neutrons, as high as $\sim 4 \times 10^8 \text{ sr}^{-1}$, is produced by reactions on ^{67}Zn . This is due to the large cross sections for $^{65}\text{Cu}(\text{p},\text{n})^{65}\text{Zn}$ and $^{67}\text{Zn}(\text{p},\text{n})^{67}\text{Ga}$ (Figure 4(b)). Table 3 also shows that as many as 4×10^9 and 1×10^9 neutrons sr^{-1} could be produced in the front and back lithium samples respectively, which is somewhat higher than is produced in boron samples. $^{11}\text{B}(\text{p},\text{n})^{11}\text{C}$ and $^7\text{Li}(\text{p},\text{n})^7\text{Be}$ reactions have similar peaked reaction cross sections and the cross section for $^{11}\text{B}(\text{p},\text{n})^{11}\text{C}$ has

an even broader energy distribution. However, the main part of the $^7\text{Li}(\text{p},\text{n})^7\text{Be}$ cross section lies in the lower energy region of the proton spectrum and the number of protons decreases almost exponentially with the increasing proton energy (Figure 3). The large number of lower energy protons produce (p,n) reactions in ^7Li nuclei and this could account for the much larger number of neutrons in lithium samples, compared to the ^{11}B sample for which the reaction cross section is peaked at higher energies. In principle the optimum sample to produce the highest intensity neutrons via (p,n) reactions should have a high reaction cross section (neutron-enriched nucleus) and a long proton stopping range (small atomic number nucleus), the main cross section should also lie in the low energy part with low reaction threshold.

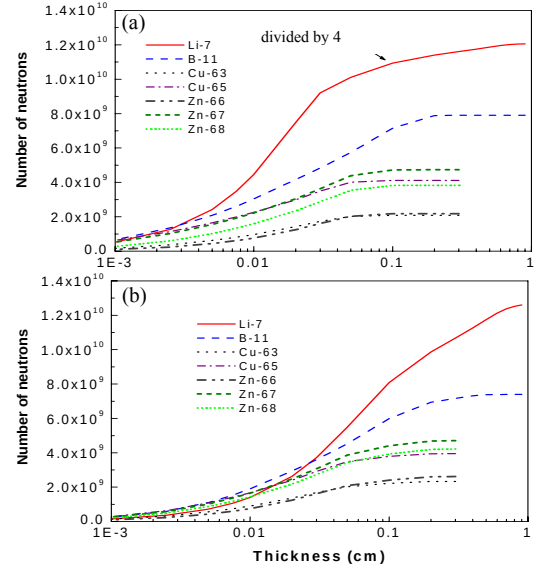


Figure 5. Calculated numbers of neutrons generated by (p,n) reactions in the ^7Li , ^{11}B , ^{63}Cu , ^{65}Cu , ^{66}Zn , ^{67}Zn and ^{68}Zn samples as a function of their thicknesses for (a) front samples and (b) back samples.

Sample	Density of samples (g/cm ³)	Enrichment of nuclei (%)	Calculated maximum numbers of neutrons sr ⁻¹		Reactions	Q-values (MeV)
			Front	Back		
^7Li	0.534	0.925	4×10^9	1×10^9	$^7\text{Li}(\text{p},\text{n})^7\text{Be}$	-1.644
^{11}B	2.35	0.80	6×10^8	6×10^8	$^{11}\text{B}(\text{p},\text{n})^{11}\text{C}$	-2.765
^{63}Cu	8.92	100	2×10^8	2×10^8	$^{63}\text{Cu}(\text{p},\text{n})^{63}\text{Zn}$	-4.149
^{65}Cu	8.92	100	3×10^8	3×10^8	$^{65}\text{Cu}(\text{p},\text{n})^{65}\text{Zn}$	-2.134
^{66}Zn	7.14	100	2×10^8	2×10^8	$^{66}\text{Zn}(\text{p},\text{n})^{66}\text{Ga}$	-5.957
^{67}Zn	7.14	100	3×10^8	4×10^8	$^{67}\text{Zn}(\text{p},\text{n})^{67}\text{Ga}$	-1.782
^{68}Zn	7.14	100	3×10^8	3×10^8	$^{68}\text{Zn}(\text{p},\text{n})^{68}\text{Ga}$	-3.703

Table 3. Calculated maximum numbers of neutrons per steradian produced by (p,n) reactions in activation samples.

An important characteristic of this novel neutron source is the energy spectrum. The neutron energy spectrum produced by (p,n) reactions can be expressed as

$$I_n(E_n) = \int_0^{T_0} n_i \sigma(E_p) \left(\frac{\partial E_{p0}}{\partial E_n} \right) dx \quad (3)$$

$$E_n = \left[\frac{m_1 m_3}{(m_3 + m_4)^2} + \frac{m_2 m_4}{(m_1 + m_2)(m_3 + m_4)} \right] E_p + \frac{m_4}{(m_3 + m_4)} Q^+ \quad (4)$$

$$2 \left[\frac{m_1 m_2 m_3 m_4}{(m_1 + m_2)(m_3 + m_4)^3} \left(E_p^2 + \frac{m_1 + m_2}{m_2} Q E_p \right) \right]^{\frac{1}{2}} \cos \theta$$

where E_n is the neutron energy, $\partial E_{p0}/\partial E_n$ is the derivative of the incident proton energy E_{p0} over energy E_n of the neutron produced at a depth of x in the sample and can be calculated through equations (2) and (4). m_1 , m_2 , m_3 and m_4 are the masses of the incident proton, reacting target particle, produced neutron and reaction residual particle, respectively. Q is the Q -value of the reaction and θ is the angle of the neutron in the centre-of-mass frame.

The energy spectra of neutrons generated in the lithium, boron, ^{65}Cu and ^{67}Zn samples were calculated and are shown in Figure 6. Activation samples of thickness 9.0, 3.0, 2.0 and 2.0 mm were used in the calculation. As we consider the energy spectra of neutrons emitted only in the forward direction (the direction of the incident proton beam), θ was set as zero in the calculation (the angular distribution of neutrons emitted from (p,n) reactions can be estimated to be anisotropic from the differential cross section⁹) and mainly in the forward direction in our case). Other parameters such as Q -values, densities and isotopic enrichments are listed in Table 3. As shown in Figure 6, the neutrons produced in the ^{65}Cu and ^{67}Zn samples have similar energy distributions. The neutron spectra for both front and back ^{65}Cu and ^{67}Zn samples are broad. The neutron intensities remain almost constant in the energy range of 1 to 12 MeV and then decrease with increasing neutron energy (above 12 MeV). In contrast, most of the neutrons produced in lithium samples have lower energies (<4 MeV) due to the energy distribution of the reaction cross section, Figure 4(b). The neutron spectra for boron is similar to the spectra obtained with ^{65}Cu and ^{67}Zn samples in the higher energy range of greater than 7 MeV, but much larger at lower energies.

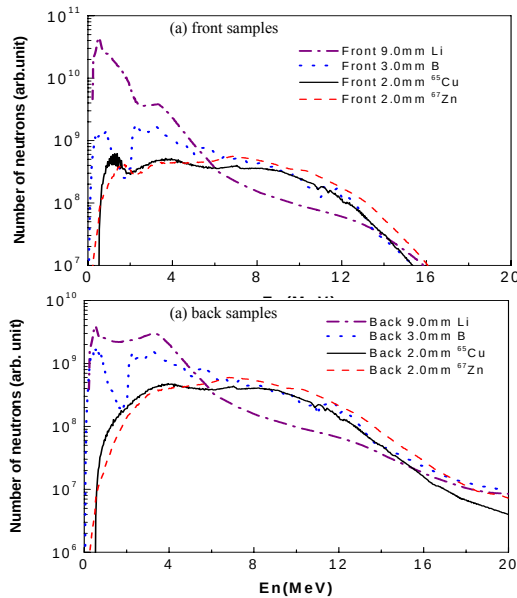


Figure 6. Calculated neutron energy spectra generated in the forward direction of the proton beams by (p,n) reactions in ^7Li , ^{11}B , ^{65}Cu and ^{67}Zn samples.

Summary and conclusions

Using the Vulcan petawatt laser, tens of MeV protons have been generated and used to induce nuclear reactions in zinc and boron samples. ^{66}Ga , ^{67}Ga , ^{68}Ga , ^{61}Cu , ^{62}Zn , ^{63}Zn and $^{69\text{m}}\text{Zn}$ nuclei were produced by proton-induced reactions on zinc. These observed nuclei were quantified and used to deduce the incident proton energy spectra. ^{68}Ga , ^{61}Cu , ^{62}Zn , ^{63}Zn and $^{69\text{m}}\text{Zn}$ were produced via $^{68}\text{Zn}(p,n)^{68}\text{Ga}$, $^{64}\text{Zn}(p, a)^{61}\text{Cu}$, $^{64}\text{Zn}(p,p+2n)^{62}\text{Zn}$, $^{64}\text{Zn}(p,p+n)^{63}\text{Zn}$ and $^{70}\text{Zn}(p,p+n)^{69\text{m}}\text{Zn}$ reactions. More than 95% of the observed ^{66}Ga was produced via $^{66}\text{Zn}(p,n)^{66}\text{Ga}$ reactions. However, analysis on the front zinc sample has shown that 74% of ^{67}Ga was produced via $^{67}\text{Zn}(p,n)^{67}\text{Ga}$ reactions and 26% from $^{68}\text{Zn}(p,2n)^{67}\text{Ga}$ and for the back sample these figures were 60% and 40% respectively.

For boron samples, the numbers of the (p,n) reaction-generated ^{11}C nuclei have been measured for a series of targets. It was shown for the B sample that the number of ^{11}C nuclei produced via (p,n) reactions in the back boron sample decreases uniformly with the increasing target thickness with similar laser energies. For the thinnest targets the same number of ^{11}C nuclei was generated both in the front and back boron samples. If we consider only the front samples, the numbers of the proton-induced reactions are almost the same for all thicknesses of targets for shots with similar laser parameters. The $^{11}\text{B}(p,n)^{11}\text{C}$ reaction is an important reaction for production of the medical isotope ^{11}C . As (p,n) reactions also generate neutrons, it could also be used as neutron source. As many as 10^9 neutrons sr^{-1} were observed in this experiment. Using the deduced proton spectra, neutron generation in lithium, boron, copper and zinc samples via (p,n) reactions has been simulated and analysed. It was demonstrated that up to 4×10^9 neutrons sr^{-1} per shot could possibly be generated by $^7\text{Li}(p,n)^7\text{B}$ reactions driven by protons accelerated by Vulcan petawatt laser interactions with Al foil targets. This is greater than an order of magnitude higher than previously measured using a similar experimental arrangement on the Vulcan 100 TW laser¹⁰. In addition, as the average proton energy increases with increased laser intensity, (p,n) reactions with higher cross sections at higher proton energies could be used to further increase the neutron yield from this novel neutron source.

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Deuteron acceleration from buried layers in petawatt laser matter interactions

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Introduction

The aim of this experimental campaign was to investigate electron transport into the target bulk and the subsequent heating of buried layers. Thick plastic targets were constructed with a buried ‘active’ deuterated layer. By burying the deuterated layer, acceleration mechanisms effective at the front¹⁻³ and rear⁴ of the target will not be responsible for deuteron acceleration in these interactions. The measurement should in theory be a snapshot of possible acceleration / heating mechanisms within the bulk of the target.

Experimental method

The Vulcan Petawatt facility delivered a pulse of ~240J, 1.05µm, 700fs on target with intensities of 10^{20} Wcm⁻². The beam was focused on to target at an angle of 43° to a spot size of 6x7 µm with an F/3 off axis parabola. The targets consisted of solid CD slabs 136 µm thick, and CH-CD-CH layered targets. The thickness of the buried CD layer was 168 µm and the front and back CH thickness was adjusted to keep the total thickness of target constant whilst varying the position of the buried layer. The thickness of the front CH layer ranged from 7 µm to 200 µm, and total target thickness ~400 µm. Plain CH targets, of thickness 136 µm, were also used to give an estimate of the CH background.

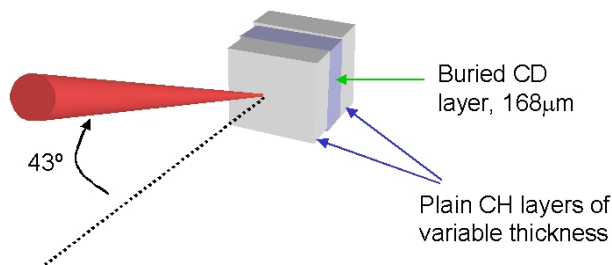


Figure 1. Buried layer target configuration.

Current mode time of flight (TOF) diagnostics consisting of plastic scintillator coupled to photo-multiplier tubes via conical light guides were placed at 137, and 208 degrees with respect to target normal in the forward direction.

Neutron time of flight spectra were recorded using an oscilloscope. The scattering of neutrons from concrete, lead and plastic shielding was modeled using MCNP⁵, a code that relies

on the Monte Carlo method to track particles through user specified geometries.

Results

Figure 2 shows raw time of flight spectra for plain CH slabs, plain CD slabs, and CH-CD-CH layer targets. Neutron scattering and multiple, neutron producing reactions broaden the signal such that there are no resolvable peaks. The basic analysis of the neutron spectra was to integrate under the neutron time of flight signal and normalise by the laser energy. In Figure 3 the signal appears to decrease with increasing depth of buried layer. This indicates that the mechanisms that produce the neutrons depends on the depth of the buried layer. The buried layer at 200 µm is below the signal obtained from plain CH slabs (dotted line) and so cannot be reliably counted as significant.

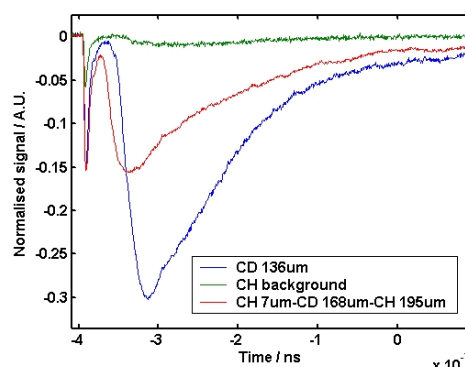


Figure 2. Raw neutron time of flight signals for CD, CH and buried layer targets.

In general the signals obtained from plain CD slabs were larger than obtained from buried layer targets. The signal shape remained broad, with no resolvable peaks regardless of the target type. This suggests that a) there are many neutron producing reactions happening, and b) there is significant neutron scattering in the petawatt target area acting to broaden the signal.

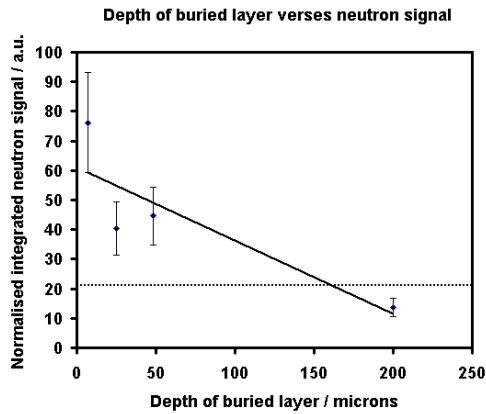


Figure 3. Plot of neutron signal with increasing buried layer depth.

MCNP modeling of neutron scattering in TAP

Scattering in the target area was modeled using MCNP. The petawatt target area was defined in 3D geometry and then mono-energetic neutron sources of 2, 5, 10, and 15 MeV were placed at target chamber centre. The resulting scatter functions were measured at the detector sites. These scatter functions revealed a large pile up of neutrons at very low energies (less than 0.5 MeV).

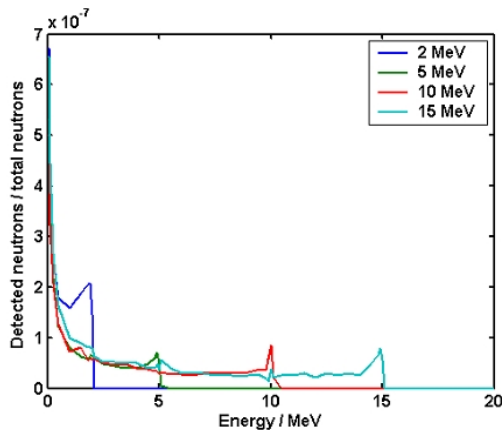


Figure 4. Scatter functions generated in MCNP for monoenergetic neutron sources of 2,5,10, and 15 MeV.

Transforming the experimental spectra from time of flight to energy and unfolding the scattering using the functions generated in MCNP revealed no peaks in the spectra that could help to identify the dominant reaction responsible for the signal.

Discussion of possible nuclear reactions

There are many possible reactions that could be happening to build the total neutron signal. Reactions include $d(d,n)He$, $C(d,n)N$, $d(d,pn)d$, $d(p,np)p$, photo and electro-disintegration of deuterium and $X(p,n)Y$ and $X(\gamma,n)Y$ reactions in surrounding material. The signal from plain CH targets would be a reasonable estimate of any $X(p,n)Y$ and $X(\gamma,n)Y$ reactions in plastic and the surrounding materials. We believe the $d(p,np)p$ and $d(d,n)He$ reactions to be most significant in the buried layer targets for the following reasons.

The $d(d,n)He$, $C(d,n)N$, $d(d,pn)d$ reactions would indicate that energy has been deposited into the buried layer since they involve accelerated deuterons. The contribution from (p,n) and (γ,n) reactions in CH and surrounding material can be eliminated using the CH background measurements obtained from the plain CH slabs. Energies from the $d(\gamma,n)p$ reaction are lower than 1 MeV and therefore these neutrons will be in the

very low energy end of the spectrum, especially after scattering. The contribution of neutrons from electro-disintegration of deuterium is two orders of magnitude lower than the $d-d$ reaction (in plain CD) according to Toupin *et al.* ⁶⁾.

The $d(p,np)p$ reaction is not as significant in CD as it may be in the buried layer targets as the cross sections are equal, but less protons are accelerated from the front as they are boiled off by the prepulse. However in buried layer targets there are many protons accelerated from the front CH layer and the significance of the $d(p,np)p$ reaction will increase compared to the ‘trace’ mechanisms accelerating deuterons in the buried layer. This is only the case provided the protons from the front surface are above the 2.22 MeV threshold for this reaction.

PIC simulations and discussion

To try and gain a greater understanding of the possible ion acceleration mechanisms simulations were run using the 2D particle in cell framework, OSIRIS. A realistic density profile was used to describe a fully ionised deuterium plasma slab of thickness $8.3 \mu m$ and maximum density $100n_c$. The simulation box was a 640×512 grid with 8×8 particles per cell. The laser was incident from the left, with wavelength $1 \mu m$, with a $7 \mu m$ spot size and an $a_0 = 20$.

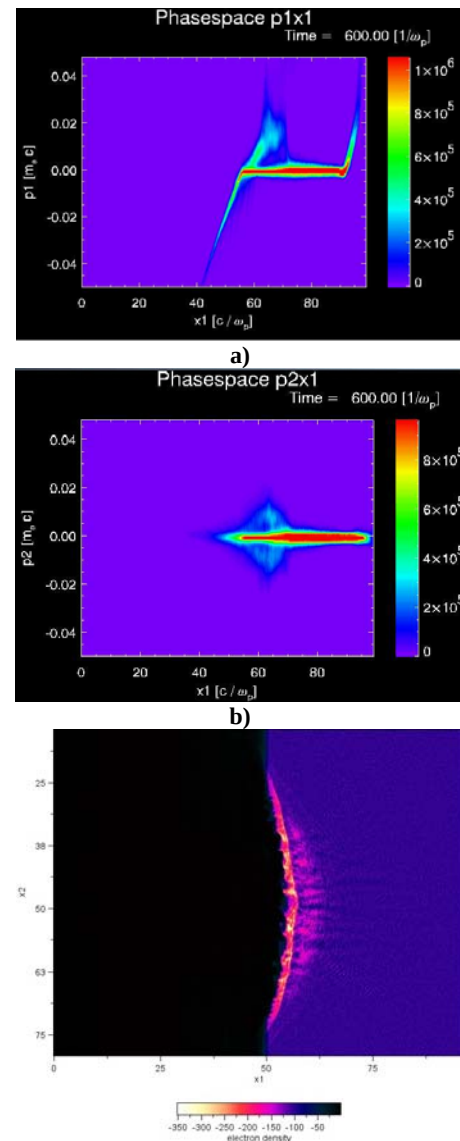


Figure 5. OSIRIS output, a) Ion phase space b) Transverse ion phase space c) Electron charge density.

At 318 fs there is a shock forming in the ion distribution. This can be seen in Figure 5a, a plot of ion momentum in the forward and backward (negative) directions against the position along the laser axis (x). At this time the shock has propagated approximately 1.75 μm into the target. Maximum ion momentum here is $0.04M_d c$, which corresponds to an ion energy of 1.5 MeV.

Figure 5b shows a plot of ion momentum in the transverse plane against x. This shows some lateral ion transport in the region of the shock, the maximum ion momentum here is $\sim 0.01 M_d c$ which corresponds to an ion energy of 94 KeV. These ion energies are above the Q value for d-d fusion but this may not be an appropriate mechanism for deuteron acceleration in the buried layer.

We can calculate the shock speed from the ion speed obtained in these simulations using $v_{ion} = 2v_{shock}$, Silva *et al.*⁷⁾ and this indicates for the shock to penetrate even 7 μm (the thinnest CH front layer thickness) the laser must drive for a duration greater than 1 ps. This will be an efficient mechanism for the plain CD slabs but will probably not be responsible for deuteron acceleration in the buried layer targets.

Another possibility is that filamentary structures observed in the early stages of the OSIRIS simulation, Figure 5c, in the electron beam are penetrating the buried layer and transferring a significant amount of energy to the ions here. A possible mechanism has been described by Honda *et al.*⁸⁾ using a 2D PIC code by which current filaments are observed to coalesce and produce radial ion expulsion.

Honda *et al.* predict that the ions reach energies in excess of 100KeV (for 20KA current, and sub micron spatial scale). In experiments using petawatt lasers we have ~ 40 MA currents and so one may expect ion energies to be higher than 100 KeV. The targets used were thick but the electron filaments should penetrate into the buried layer. Gremillet *et al.*⁹⁾ have observed electron filaments penetrating to a depth up to $\sim 100 \mu\text{m}$ using the PARIS hybrid code. This method may therefore be reasonable for plastic layers on the front of less than $\sim 100 \mu\text{m}$.

Further work

The mechanism described by Honda or similar processes are required to explain the neutron numbers as opposed to background plasma heating to a few KeV via the return current. More simulations are required to understand this mechanism and the LSP code will be used for this. However, it is difficult to separate out the $d(d,n)\text{He}$ (and other reactions relying on accelerated deuterons) from the $d(p,np)p$ reaction at present. It is possible that the $d(p,np)p$ reaction is dominant for the buried layer targets provided protons from the front surface reach energies above the 2.22 MeV threshold.

Further PIC simulations are underway to help confirm that the energy of protons accelerated at the front surface are above the 2.22 MeV threshold for the $d(p,np)p$ reaction. This will help us to quantify the significance of the $d(p,np)p$ reaction.

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Thermal neutron generation in Petawatt laser experiments at the Rutherford Appleton Laboratory

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Introduction

Electron and ion energy transport in dense plasmas is an extremely important topic for the fast ignitor research for inertial fusion energy¹. Recent experiments indicate that the hot electrons generated at the plasma surface carry about 50% of the laser energy into the over-dense plasma. However, the fast electron current propagation involves very complex processes that arise from the strong electric and magnetic fields that are induced and that significantly affect its propagation. Particle-in-cell (PIC) simulations show that electron filaments (that are generated from the Weibel instability) coalesce with each other and result in a significant energy loss in the plasma². The merged single filament induces anomalous stopping due to the electromagnetic turbulence that arises from the interaction of the strong fields with the cold electron return current³.

Recent experiments have shown electron heating of the bulk material to 200-350eV by resonance line emission from buried Al signature layers inside a solid plastic target⁴. The heating there may have been affected by resistivity mismatching between plastic and metal layers⁵. We report here observations of thermal neutron production using a single PW-class laser beam.

Experiment

The experiment was conducted using the new PW laser facility at Rutherford Appleton Laboratory. The PW laser irradiated sandwich targets that consisted of a variable thickness front plastic (CH) layer, a fixed thickness deuterated plastic (CD) layer, followed by a rear plastic layer (CH). The targets were designed to remove any boundary layer heating processes due to density and Z mismatches and were sufficiently thick to reduce heating due to refluxing electrons from the rear surface. The laser pulse was incident at an angle of 45° from the target normal, the focused intensity was 5×10^{20} W/cm² and had a good intensity contrast ratio (10^{-8}). The neutron signals were observed using the multi-channel neutron detector system, LaNSA⁶ that has been reconstituted in the Vulcan PW target area for this purpose.

The observed neutron signal shows the 2.45MeV peak produced by thermal fusion processes of the $d(d,n)^3\text{He}$ reaction as well as higher energy signals by beam fusion reactions. The energy width of the thermonuclear neutron signal decreases with increasing front CH thickness, corresponding to a reduction in temperature inside the target. Figures 1-3 show typical neutron spectra. Figure 1 is when a bare CD target was irradiated with 286J on target. The signature at 2.45MeV is clearly visible and

is much larger than the background level. Figures 2 and 3 show spectra produced with a 3µm-thick and 10-µm thick CH overlay thicknesses, respectively. For these thin CH overlay targets, the ion temperature was estimated from the width of the thermonuclear neutron signal. The thermonuclear signal on thicker CH overlay thicknesses (>50 µm) merged into the beam-fusion neutron background. Consequently, the deconvolution of the temperature from these more deeply buried data points is much more uncertain.

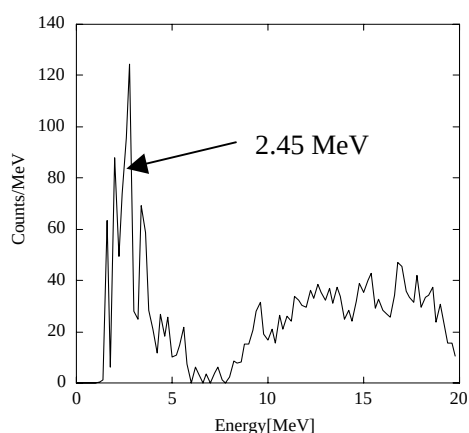


Figure 1. Neutron signal from the LANS instrument with a 140 µm-thick CD target irradiated with 286J on target.

Figure 4 shows the ion temperature dependence as a function of the front CH overlay thickness. The temperature appears to be surprisingly high: for example, we measured 40keV for bare CD targets and 7keV for 3µm CH overcoat thickness.

Discussion

The deduced temperatures are consistent with those calculated from the observed neutron counts assuming a thermonuclear origin with a fixed heating volume. The electron-ion equilibration frequency is given by:-

$$\nu = 3.2 \times 10^{-9} Z^2 \ln \Lambda / (\mu T^{3/2}) \text{ cm}^3 \text{ s}^{-1}$$

where $\ln \Lambda$ is the Coulomb logarithm, T is the temperature in eV and μ is the ion/proton mass ratio. This would suggest that all ion temperatures below ~1keV can be ascribed to resistive heating by the return current.

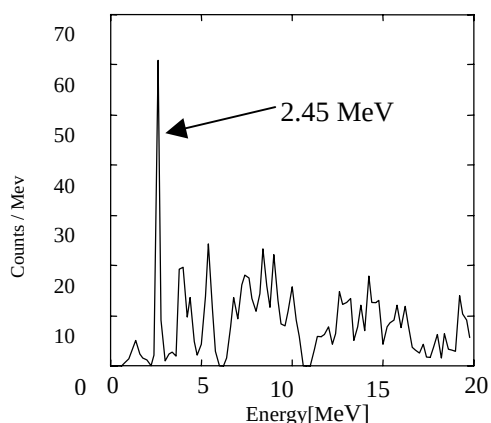


Figure 2. Neutron signal from a $3\mu\text{mCH} / 168\mu\text{m CD} / 195\mu\text{m CH}$ sandwich target irradiated by 428J on target.

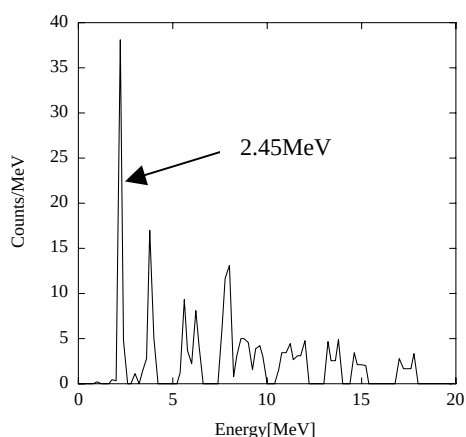


Figure 3. Neutron signal from a $10\mu\text{mCH} / 168\mu\text{m CD} / 195\mu\text{m CH}$ sandwich target irradiated by 400J on target.

We performed 2-dimensional MHD calculations using the POLLUX⁷⁾ code to try to quantify the “bottled up” effect on the fast electron transport in the surface layers when there is a relatively large scale length pre-plasma formed by the pedestal, as reported elsewhere in this Annual Report by R.G. Evans et al. Figure 5 shows the temporal evolution of ion temperature as a function of position in the target. The ion temperature at the critical density surface reaches 100keV, but at $10\mu\text{m}$ inside the target the temperature rises only to 1keV. These heat conduction calculations therefore explain the observed ion temperatures for the thick CH targets as shown in Figure 4.

There are several possible explanations for the high surface temperature seen in Figure 1. Coalescence of filaments of the electron beam can occur during electron transport in dense plasmas²⁾. However this effect is more likely to generate beam fusion reactions which might be the origin of the high energy component in the neutron spectra. Anomalous stopping is also a possible explanation – but here simultaneous measurements of electron and ion temperatures are needed. These experiments are being planned for the near future.

In summary, neutron spectra were observed in the Petawatt Facility at Rutherford Appleton Laboratory using the LaNSA system. The obtained spectra had two components: a high energy component generated by beam-fusion reactions and a component around 2.45MeV most likely to be thermonuclear in origin. The ion temperatures calculated from the neutron signal width clearly demonstrate a dependence on the front CH thickness of the layered target, although further shots are needed to reduce the statistical uncertainties in the data. 2D MHD calculations were performed in order to quantify the ion heating due to the heat conduction into the target, assuming the energy is bottled up between critical and solid density. They

explain the measured temperatures for thin CH overcoat layers, but the details of the physics that causes the high surface temperatures requires further investigation.

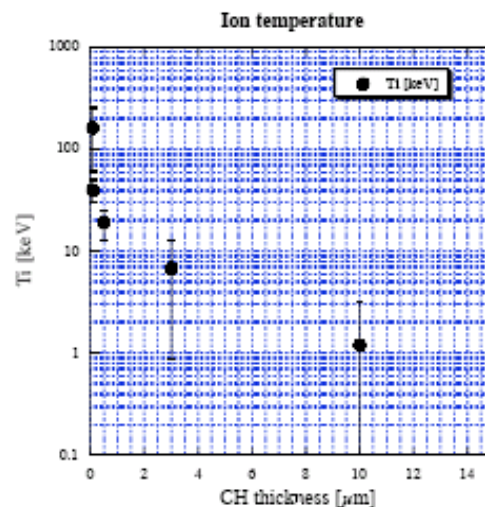


Figure 4. Dependence of the ion temperature on the front CH overlay thickness. There is a very rapid fall-off in temperature into the target.

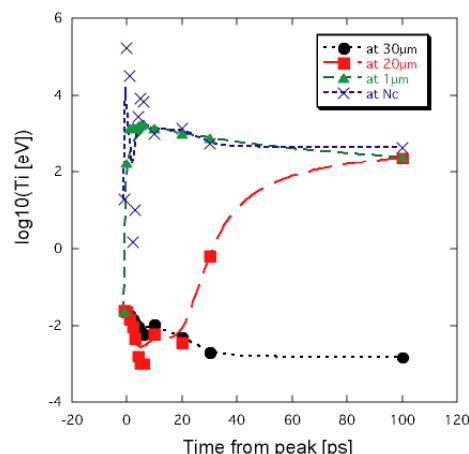


Figure 5. Temporal evolution of the ion temperature at various depths in the target.

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Plasma jets driven by high power laser pulses

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Introduction

Plasma jet formation is a subject of great interest, both in astrophysical and laser-plasma contexts. Experiments carried out in the past on Vulcan employing intense, short pulses ($I \sim 5 \times 10^{18}$ W/cm²) revealed, via interferometric measurements, magnetohydrodynamic (MHD) 'jet'-like formation in the flow of plasma ablated from the front surface of solid targets¹. Magnetic fields surrounding the jet were measured via polarimetry and MHD simulations highlighted the role of these fields in collimating the jets.

In this report we are presenting the evidence of efficient creation of collimated plasma along the laser axis, at the rear of thin solid targets following picosecond laser irradiation at intensities in the range 10^{19} - 10^{20} W/cm². The jets were detected by transverse interferometric measurements of the rear side of the solid target with high spatial resolution. The development of the plasma jets was observed by probing at different times after the interaction. A preliminary interpretation of the phenomenon will be discussed.

Experimental Setup

The experiments were carried out employing the Vulcan Nd-Glass laser operating in the chirped pulse amplification (CPA) mode at a wavelength of 1.054 μ m. In Target Area West (TAW) the laser delivered 60 J of energy on a 12 μ m FWHM spot, focussed by an f/4.5 off-axis parabola, in 0.7 - 1.0 ps duration, giving an intensity of a few times 10^{19} W/cm². The prepulse, about 500 ps long, had intensity approximately 10^{-6} of the peak intensity of the CPA pulse. In the Target Area Petawatt (TAP), the laser delivered 260 J of energy in a 5 μ m FWHM spot, focussed by a f/3 off-axis parabola, in 0.5 - 0.7 ps duration giving a peak intensity of 2.0×10^{20} W/cm². In both experiments an interferometric technique was employed to probe the plasma at the rear side of the interaction target using a 0.527 μ m ps probe beam, created by frequency doubling a small part of the main interaction beam. By varying the optical path length of the probe beam we were able to probe the plasma at different times after the interaction. Reconstruction of the plasma density from the interferograms is performed by obtaining the phase map, using 1D fast fourier transform, followed by Abel inversion of the phase map assuming cylindrical symmetry.

Results

Well collimated jet-like plasma and its expansion with time from the rear side of Al foil of thickness 3 μ m were observed in TAW. A large collimated jet observed at 250 ps after the interaction of CPA pulse is shown in Figure 1. Jets were also observed for Al target of thickness 1.5 μ m. In TAP, we observed the same type of plasma expansion from the back of

5 μ m Cu targets. Such collimated flow was not observed from thicker targets.

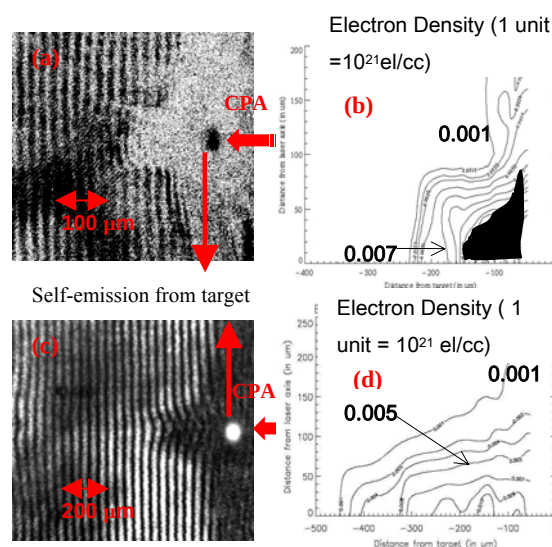


Figure 1. (a) and (b) are the interferogram image and the electron density contour plot obtained from the TAW experiment with 3 μ m Al target at 250 ps after the main pulse. (c) and (d) are the interferogram image and the electron density contour plot obtained from the TAP experiment with 5 μ m Cu target, taken at 400 ps after the main pulse.

The temporal development of the plasma jet coming from the rear side of a 3 μ m Al target in the TAW experiment is shown in Figure 2. The on-axis distance from the target surface of several iso-density lines is shown for three different times. From the graph the expansion velocity of the plasma can be estimated to be of the order of $c/300$, where c is the velocity of light in free space.

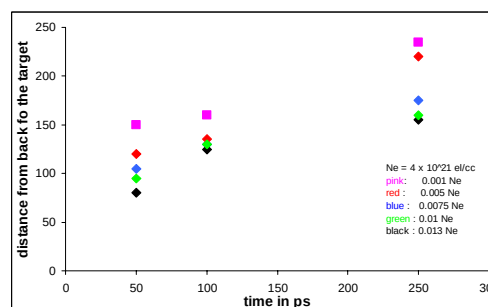


Figure 2. The graph of displacement along the laser axis vs. time for different plasma layers at the back of 3 μ m Al foil.

Discussion

Although a detailed modelling of the jet formation process is still in progress, some general considerations can be made. During the interaction between laser pulses at such high intensities and over-dense/solid density plasma, an efficient directional energy and momentum transfer takes place between the laser pulse and the particles of the target. At the beginning electrons, being lighter than ions, are accelerated in the forward direction by the combined effect of the electric and magnetic field (via the JXB mechanism) of the pulse. The directional flow of electrons into the target and ‘fountain’ like circulation at the back surface, can lead to efficient ion acceleration via the space-charge fields and generation of large toroidal magnetic field at rear surface of the target²⁾. An effect of great relevance to the jet formation is due to the laser pulse acting as a ‘piston’ on the bulk of the plasma. In this regime of laser plasma interaction, the laser pressure can easily be larger than the plasma pressure, even for extremely dense plasma. The light pressure scales approximately as $330 \cdot 10^{-18} \text{ I Mbar}^3$, reaching value of a few tens of Gigabars in our case. This pressure is applied at the light plasma interface which is the plasma layer having density equal to the relativistically corrected critical density. The ions at this surface are driven inward with a velocity which can be estimated by balancing the momentum flux of the mass flow with the light pressure, and is given by:-

$$\frac{v_f}{c} \approx \sqrt{\frac{n_{cr}}{n} \frac{Z m_e}{A m_p} \frac{I}{3 \cdot 10^{18}}}$$

where A and Z are the mass number and atomic number of the target element, m_p and m_e are the mass of protons and electrons. At the interface, ions are accelerated from zero velocity to $2v_f$ and the mass flow or the plasma expansion occurs in a hydrodynamic time scale. For an Al plasma, assuming $n_{cr}/n = 150$ and $I \sim 2 \times 10^{19} \text{ W/cm}^2$ one obtains $v_f \sim c / 280$, which is of the same order of the expansion velocity as the plasma observed in the experiment.

This velocity is high enough for significant motion of the critical density layer to take place during the main laser pulse duration (a few μm in time $\sim 0.5 - 1 \text{ ps}$). In the case of thin foils this can be a significant fraction of the foil thickness. 3D Particle-In-Cell simulations have demonstrated the ‘piston’ effect of the laser pulse, in the extreme case of $I \sim 10^{23} \text{ W/cm}^2$ laser irradiated on a foil of $\sim 1 \mu\text{m}$, creating a ‘cocoon’ like deformation of the foil and accelerating the ions in forward direction in a collimated plasma jet⁴⁾. Although in our intensity regime, the effects will be less dramatic, we can expect that the forward momentum transfer to the plasma will still result in collimated plasma ejection from the back of the target. In this case rather than being a purely ballistic ejection, a MHD expansion may take place following the laser pulse energy and momentum deposition.

A significant role in maintaining the jet’s collimation may be played by the toroidal magnetic field surrounding it and acting as a pinch to the plasma flow⁵⁾. Magnetic field generation at the rear of laser irradiated foils has indeed been predicted by several PIC simulations, due to ‘fountain’ effect of hot electrons exiting the target^{2,6)}.

Some comments should be made regarding the role played by the prepulse. In the TAW experiment, energetic proton beams (up to 15-20 MeV) from the back of the Al target of $3 \mu\text{m}$ were observed. This suggests that the prepulse was not capable of eroding the total target thickness. By using the two dimensional hydro code ‘POLLUX’⁷⁾, we have simulated the hydrodynamic expansion of plasma slab of different thickness but same solid density as Aluminium upon irradiation of a 500 ps long Nd-Glass laser pulse of temporary flat-top and spatially Gaussian intensity profile with peak intensity $1.5 \times 10^{13} \text{ W/cm}^2$, focused on an area of $12 \mu\text{m}$. The simulations indicated that,

while plasma blow off was observed at the rear of $1 \mu\text{m}$ thick plasma slabs, such effect was not observed for thicker plasma slabs. This suggests that in the situations in which the collimated plasma jets were observed, the main CPA beam interacted with a freely expanding solid density plasma backed by undamaged solid target.

Conclusion

Highly collimated plasma expansion from the rear side of thin targets irradiated with high power lasers has been observed in different experimental conditions. The expansion velocity of the ions in the collimated plasma region has been found approximately equal to the velocity of ions driven inward by the radiation pressure of the incident laser beam at the vacuum-solid interface. The thickness of the target is seen to play a vital role, depending on the pre-laser pulse intensity and duration, for the jet formation from the rear side. The process of jet formation is likely to arise from the pushing effect of the longitudinal ponderomotive force of the laser pulse at the bulk of the preformed plasma created by the prepulse, followed by a MHD expansion of the plasma.

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Modelling of proton radiography of cold matter

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Introduction

Theoretical and experimental studies of the properties of highly compressed matter are of fundamental interest to several branches of physics, including inertial confinement fusion (ICF), astrophysics and geophysics. High resolution probing of these matter states is of great importance in order to understand their characteristics and the relevant physical processes. The idea of using proton beams for radiography purposes has been circulated for several years^{1, 2)}. The properties of high-power laser-accelerated multi-MeV protons³⁾ - such as high brilliance in a very short duration, high directionality and highly laminar flow⁴⁾ - are favorable to achieving high spatial resolution when back illuminating an object with the proton beam. The proton radiography technique can be developed as a diagnostic with great potential for the study of the density profile of a compressed DT pellet in the NIF - ICF experiments and the shock characteristics inside shocked samples.

In this report we will discuss two dimensional modeling of proton radiography of cold matter having transverse density variations. The simulations are done for the case of the multi-energy, divergent beam of protons we obtain from the interaction of high power laser with thin foils. A comparison of modeling results with the experimental results will be presented. As an implementation of the modeling, the density profile of a compressed plastic microballoon, during ICF-like compression experiment, is estimated by comparing the proton radiographs obtained from the experiment and the simulation. The feasibility of probing compressed NIF cores by a proton radiography technique will be discussed with the help of results obtained from the simulations.

Fundamentals

Each molecule in matter is a scattering centre for incident charged particles due to the coulomb potential barrier around the molecule. The final velocity of a particle crossing matter depends on the total number of scattering centers with which the particle has interacted along its path. Therefore, for layers of matter of different density but the same thickness, the final velocities of the incident particles will be different.

Protons have the unique property of having a sharp and narrow Bragg's peak in the dose deposition curve, close to their stopping range. Protons, after passing through matter having different density along the direction normal to the proton beam, will have different energy and direction of motion. Therefore, they will stop at different positions of different RCF layers in the detector stack. Due to the complexity of the multiple scattering process, it is very difficult to establish a functional relation between the density of the target and the Optical Density (O.D.) of the RCF. However, a statistical simulation of the total process is very helpful. Modeling of proton radiography in the case where the energy loss of protons by passing through the sample is negligible was described in a previous report⁵⁾. In that case the perturbation of the proton beam density profile was purely caused by scattering effects.

Simulation design

The simulation of proton radiographs of cold matter is carried out in several steps. We considered a point source of protons emitting protons as a diverging beam of finite energy spectrum. We divided the whole beam into small bunches of protons having same energy and direction of propagation. The number of protons in the bunches is set according to the energy spectrum. The bunches, having different direction of propagation, are propagated through a three dimensional object having a variable density profile in its bulk. The average density $\langle \rho \rangle$ along a trajectory is then evaluated numerically as the line integral of the object density along the proton trajectory divided by the length L of the trajectory inside the object.

We then simulate the propagation of each bunch of protons through a layer having a density equal to $\langle \rho \rangle$ and thickness equal to L , in order to evaluate the effect of collisions and stopping. This part of the simulation is done using the Monte-Carlo package, TRIM⁶⁾. TRIM calculates accurately the final spatial and energy distribution of ions passing through the target, taking into account ionization energy loss by the ion into the target, energy transferred to recoil atoms and other processes. The code uses a Kinchin-Pease formalism based on binary collision approximation⁷⁾. The ZBL electronic stopping and interatomic potential used in TRIM has been obtained by fitting a universal screening function to theoretically obtained potentials calculated for a large variety of atom pairs⁶⁾. TRIM allows multilayer target configuration of different materials from its atom and compound directory, which can also be modified as necessary.

The detector we simulate is a multilayer assembly of RCF, which is routinely used in proton probing experiment^{4,8)}. For each bunch of protons emitted from the source, using TRIM we record the energy and position of each proton at different RCF layers after propagation through the respective equivalent object layer, as discussed above. The program calculates the dose deposited in an RCF layer by adding up the contributions from each incident proton. The contribution for each particle is obtained from the response curve of the active layer i.e. from the relation between the incident energy of the proton and the amount of energy deposited in that particular layer. This is also calculated using TRIM.

The procedure described above provides the radiographic projection of a transverse 2-D slice of the target. If the object has a spherically symmetrical density profile (as in the case described in the next section), the full projection radiograph of the three-dimensional object can be obtained by superimposing a large number of the profiles above, rotated in steps of small angles about the center.

Results

The first proton radiography experiment of dense laser-compressed material was carried out at the Rutherford Appleton Laboratory, UK⁸⁾. Six beams of the Vulcan Nd-Glass laser system (each 1.054 μm wavelength, 100-150 Joule energy and 1 ns duration) were focused onto a hollow microballoon of 500 μm outer diameter and 7 μm wall thickness. The

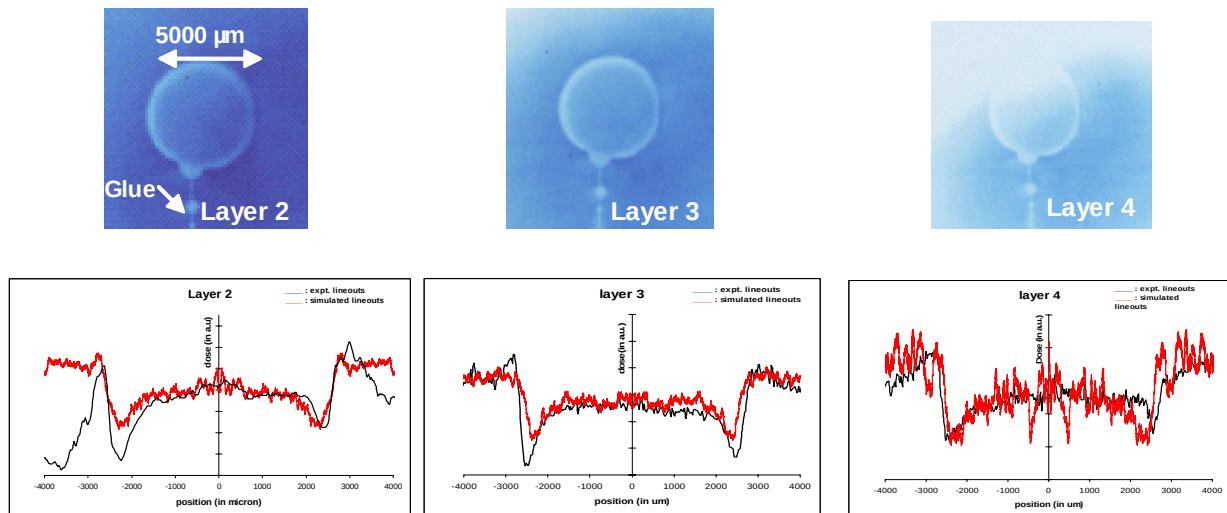


Figure 1. Upper row: proton radiographs of cold microballoon in different layers of RCF. Bottom row: The comparison between the experimental (black) and simulated (red) lineouts of dose deposited for the corresponding layers.

microballoon was made of PAMS (alpha-methylstyrene) of density 1 gm/cc. The heater beams were arranged such that they illuminated the target tangentially from six orthogonal directions at the same time, giving the best symmetry for the implosion. The implosion was diagnosed using the proton beams coming from the back of a 25 μm Tungsten foil irradiated by a chirped pulse amplified beam at an irradiance of $5 \times 10^{19} \text{ W/cm}^2$. The proton beam had an exponential spectrum of mean temperature 2 MeV and a high energy cut-off around 15 MeV. The detector consisted of a 25 μm Al foil followed by multiple layers of RCF.

The comparison between the experimental and simulated O.D. profiles observed in three different layers of RCF for a cold (undriven) microballoon is shown in Figure 1. It can be seen that the main features of the data are successfully reproduced by the simulation. The simulation was done for protons having a Maxwell-Boltzmann energy spectrum for temperature 2 MeV.

The proton radiograph of a microballoon imploded by the heater beams is shown in Figure 2. In order to estimate the density profile of the compressed target, a simulation was done to produce the proton radiographs of a spherically symmetrical PAMS object with a Gaussian density profile along the diameter. The Full Width at Half Maximum (FWHM) and the Peak Density (PD) were varied, as shown in Figure 3. The best fit to the experimental lineout is found for a PD of 3 gm/cc with a FWHM of about 80 μm .

The geometrical magnification of the target in the experiment was approximately 10, while the FWHM inferred from the experimental lineout is about 1100 μm . The blurring of the image is due to the stopping and large scattering undergone by the protons of energy $\sim 5 \text{ MV}$ (contributing mostly to the 2nd layer of RCF) propagating through such a dense core. The simulation shows a drastic reduction in blurring of the image in the RCF layers after the 8th layer in the film pack, as shown in Figure 3.

The above analysis suggests that probing the NIF-like compressed core ($\sim 200\text{-}300 \text{ g/cc}$) should be feasible employing the proton beams with energy up to 50-100 MeV, that can be achieved by PW laser interaction with thin foil⁷⁾. Simulations of proton radiography under these conditions are in progress in order to evaluate the best proton energy range for these studies.

The simulation technique described above has also been employed to design experiments aiming to detect the density profile of shock waves propagating in laser-irradiated samples⁹⁾.

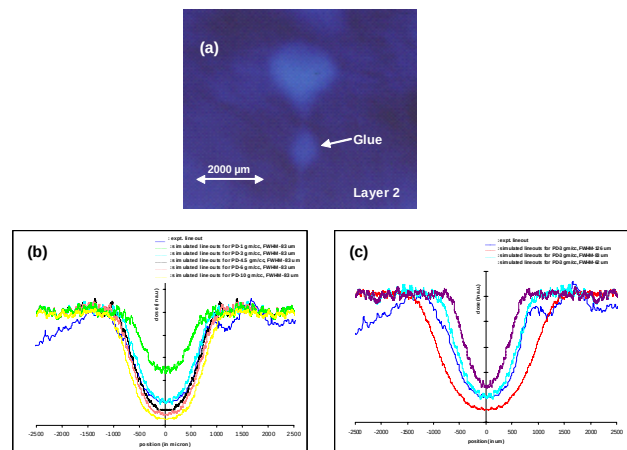


Figure 2. The proton radiograph of a compressed microballoon on 2nd layer of RCF, obtained 2 ns after the arrival of heater beam is shown in (a). The simulated lineouts obtained for different Peak Density (PD) with FWHM of 83 μm are shown in (b) (blue- expt. lineout, yellow- 10 gm/cc, red- 6 gm/cc, black- 4.5 gm/cc, turquoise- 3 gm/cc, green-1 gm/cc). The simulated lineouts obtained for PD of 3 gm/cc and different FWHM are shown in (c) (blue- expt. lineout, red- 126 μm , turquoise- 83 μm , violet- 62 μm).

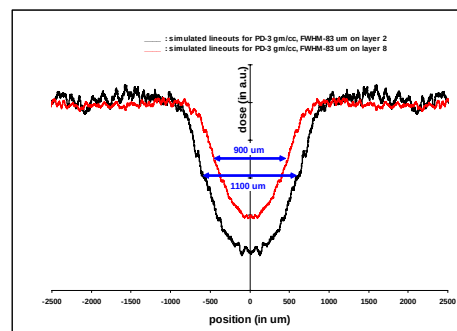


Figure 3. The comparison between the simulated lineout of the proton radiographs of compressed microballoon of 3 gm/cc PD and 83 μm FWHM observed on layer 2 (black) and layer 8 (red) of the RCF film pack having the same configuration as the one used in the experiment.

Conclusions

A proton traveling through cold, electrically neutral dense matter suffers small angle multiple scattering with some loss of its energy during elastic collisions. The total loss of energy depends on the number of scattering centers inside the target. Therefore the number density distribution and the energy of a homogeneous proton beam are distorted after passing through the object. Such distortions depend on the density and composition of the sample that the protons cross. By using simulation tools based on Monte-Carlo collisional calculations it is possible to obtain information on the density distribution helpful for its reconstruction. While these instruments appear fully adequate for modeling proton radiographs of cold matter, modifications of the stopping coefficients due to finite temperature effect may have to be taken into account when modeling proton radiographs of dense, warm plasmas.

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Electromagnetic pulse characterisation within a petawatt laser target chamber

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Introduction

A significant electromagnetic pulse (EMP) can be generated within a target chamber when a laser pulse is focused at high intensity onto a target. The characteristics of the associated EMP pulse are not properly quantified, although its effect on equipment and diagnostics is clearly evident. Signals from target diagnostics are degraded by EMP interference and some items of electrical equipment can be damaged. The purpose of the work reported here is to characterise and potentially predict the EMP, which will be produced by the Petawatt laser interactions.

One can suggest a number of mechanisms which could generate an EMP within a laser target chamber. The mechanism considered here, to produce a significant EMP, is due to electrons ejected from the target mainly in one direction as a beam, which strikes the target chamber wall. The chamber rings at its natural frequency when a side is charged by an impulse of electrons.

Measurements

Measurements of the EMP generated by the Vulcan Petawatt laser were first made in early 2003. Standard EMC (electromagnetic compatibility) test equipment was used to measure the EMP in the target hall external to the target chamber during a laser shot. The set-up used was similar to that for EMC acceptance testing of a large item of electrical equipment. The horizontal and vertical polarised radiation was measured using calibrated antennas from 1kHz to 1GHz. Conducted emission in target chamber cabling was measured using current clamps up to 600MHz. The transient signals were recorded using fast digital oscilloscopes. The EMP was seen as a transient at about 70MHz, with radiated field up to 600V/m and conducted currents up to 46A.

The Vulcan Petawatt target chamber¹⁾ has only one beam port and small diagnostic windows. Hence, the high level of EMP emission must be due to pick-up by wiring inside the chamber rather than radiation through holes in the chamber wall. To mitigate such effects staff have modified the wiring including installing screened twisted pair wiring, filtering, and better earthing. This has improved the reliability of target area equipment but it did not eliminate all the EMP problems.

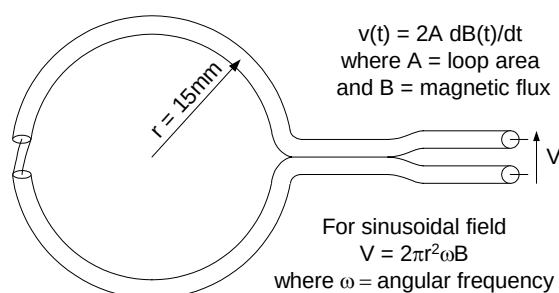


Figure 1. Moebius loop antenna fitted inside the chamber.

To characterise the EMP properly one needs to measure the source inside the target chamber using small vacuum compatible sensors. Moebius loop antennas²⁾ made from solid coaxial copper cable were used for a second series of measurements in late 2003. These, as shown in Figure 1, have a twist in the loop, which doubles the effective loop area and makes them insensitive to charged particles and ionising radiation²⁾. The two outputs are added using a matching unit to give a signal proportional to the rate of change of magnetic field.

The antennas were fitted inside the Vulcan Petawatt target chamber to measure the vertical and transverse (east-west) fields. They were located under a diagnostic table at a point 0.15m above the floor, 0.5m from the side wall and 1.5m from the end wall. Only two antennae could be fitted at this point which was chosen to avoid interfering with an ongoing experiment. A typical waveform taken with 300MHz analogue bandwidth oscilloscopes sampling at 2.5GHz, is shown in Figure 2. This shows harmonics and high frequency noise, which are reduced when the signals are integrated to give the magnetic field. These results are typical of those obtained for aluminium and copper foil targets with beam energy varying from 330J to 450J.

The waveform shown in Figure 2 displays the behaviour of a system with two weakly coupled modes of slightly different frequency. The beam impulse initiates an east-west mode and then energy is transferred slowly to a vertical mode. The latter has a smaller amplitude, which varies at the beat frequency. The waveforms were integrated to give a voltage proportional to the magnetic field and then fast Fourier transformed (FFT) to find the frequency of the modes. The 512 time samples from each time waveform were integrated and transformed into 257 frequency samples as shown in Figure 3. The frequency of the east-west mode was found to be 63MHz and the vertical mode 59MHz. The peak magnetic field measured at the antenna location was 4.3A/m in an east-west direction and 0.46A/m in a vertical direction.

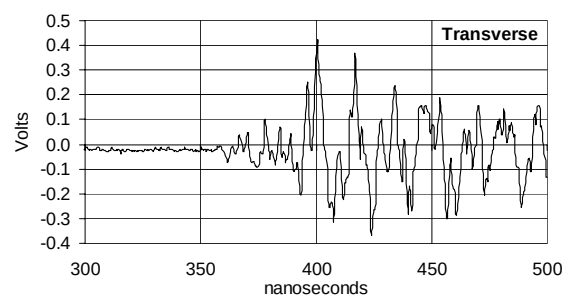


Figure 2. Antenna waveform measured on oscilloscope.

Model

The magnitude and frequency of the EMP generated within an ideal rectangular or spherical target chamber can be calculated. The behaviour of a real target chamber is different due to the effect of equipment inside the chamber such as the target

positioner. These will cause scattering and a shift in the resonant frequency and encourage resonance at harmonics.

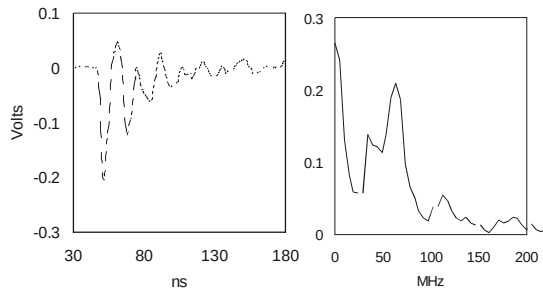


Figure 3. Integrated waveform and FFT from a laser shot.

The magnitude of the EMP depends on the number of electrons ejected from the target, which strike the chamber wall. This is determined by many factors including the laser beam energy and type of target. For a Petawatt laser the number of electrons ejected as a beam from the target has been estimated³⁾ from measurements to be about 10^{12} .

Consider first the Vulcan Petawatt target chamber, which is rectangular of height 2.2m, width 2m and length 4.6m. Assume it resonates in a TE (transverse electric) mode with an east-west E field. The cartesian co-ordinate system is as shown in Figure 4 with $a = 2.2\text{m}$, $b = 2\text{m}$ and $d = 4.6\text{m}$.

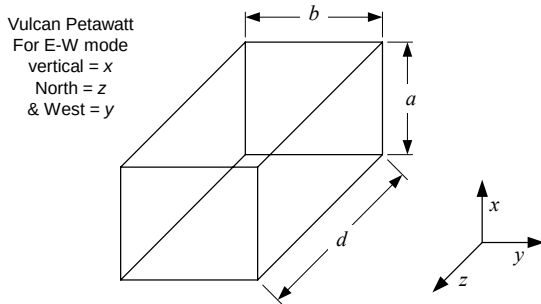


Figure 4. Co-ordinates used for calculating oscillation modes.

The following field equation are given by Reference 4:

$$\text{Wavelength } \lambda_0 = \frac{2ad}{\sqrt{a^2 + d^2}} = 3.97\text{m, frequency } f_0 = 76\text{MHz}$$

$$E_y = E_0 \sin \frac{\pi x}{a} \sin \frac{\pi z}{d}$$

$$H_x = -j H_{x0} \sin \frac{\pi x}{a} \cos \frac{\pi z}{d} = -j \frac{E_0 \lambda_0}{\eta 2d} \sin \frac{\pi x}{a} \cos \frac{\pi z}{d}$$

$$H_z = j H_{z0} \cos \frac{\pi x}{a} \sin \frac{\pi z}{d} = j \frac{E_0 \lambda_0}{\eta 2a} \cos \frac{\pi x}{a} \sin \frac{\pi z}{d}$$

where the wave impedance of free space $\eta = \sqrt{\mu_0 / \epsilon_0}$

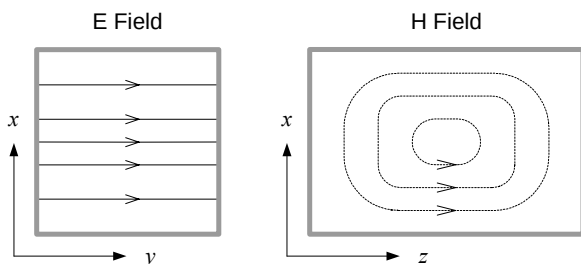


Figure 5. Fields within an ideal rectangular chamber.

Figure 5 shows the field distributions above.

The peak energy in the electric field $= \epsilon_0 a b d E_0^2 / 8$

For a lumped LC circuit energy $= \frac{1}{2} C V^2$ where $V = E_0 b$

Hence the equivalent capacitance $C = \epsilon_0 a d / (4b) = 11.2\text{pF}$

This is charged by 10^{12} electrons so $Q = 1.6 \times 10^{-19} \times 10^{12}$

Hence initial voltage $V = Q/C = 14.3\text{kV}$ & $E_0 = 7.2\text{kV/m}$

The cavity may also resonate in a TE mode with the E field vertical or north-south. The values calculated for all three fundamental modes are given in Table 1.

Mode	a	b	d	λ_0	f_0	C	V	E_0	H_{x0}	H_{z0}
E field	m	m	m	m	MHz	pF	kV	kV/m	A/m	A/m
E-W	2.2	2	4.6	3.97	76	11.2	14.3	7.2	8.2	17.1
Vert.	2	2.2	4.6	3.67	82	9.2	17.3	7.9	8.3	19.2
N-S	2.2	4.6	2	2.96	101	2.1	75.7	16.5	32	29.4

Table 1. Values calculated for fundamental modes.

Comparison with measurements

The experiments generate a beam of electrons, along the line of the laser, which strike the target chamber south end wall. This excites a dominant north-south E field mode, calculated to be at 101MHz, generating an H field in a vertical east-west plane. At the measurement point this H field is largely horizontal so it is seen by the east-west antenna. Hence the 63MHz signal must be the north-south mode shifted down in frequency by the equipment inside the chamber. At the measurement point the H field generated by 10^{12} electrons is calculated to be 11.6A/m. The measured field of 4.3A/m may be due to less electrons being generated or some beam neutralisation due to the presence of ions in the beam. The vertical antenna was not positioned correctly to measure the east-west or vertical modes. However, it measured a small 59MHz signal, which must be one of these modes.

Discussion

The simple model discussed here has provided an estimate of the magnitude and frequency of the EMP measured in the rectangular target chamber of the Vulcan Petawatt laser. Further measurements with better positioned antennas and electron and ion measurement diagnostics are planned to further validate and extend this approach.

Acknowledgements

We would like to thank the experimenters from Imperial College and LLNL for their help in making this set of measurements possible.

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Study of electron beam propagation through dense plasmas using the Vulcan Petawatt Laser

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Introduction

Since Tabak proposed the concept of using high-power lasers to reach gain in fusion of Deuterium and Tritium to Helium in 1994¹⁾, the question how ultra-relativistic currents will propagate through dense plasmas attracts more and more attention. In that concept the compression and ignition of the fuel are separated and laser-accelerated, ultra-relativistic electron currents in the order of 100-1000 MA should start the fusion by depositing their energy in the pre-compressed core. These currents exceed the fundamental limitation by the Alfvén current $I_A = 17.1 \beta \gamma$ kA. This is only possible when return currents in the “cold” background plasma contribute to neutralization. Nevertheless instabilities play a crucial role in the success of the concept since the system of “hot” electrons and counter propagating “cold” plasma electrons is highly unstable. 2D and 3D PIC simulations have predicted that due to Weibel and electrothermal instabilities the beam will break up into filaments that are surrounded by magnetic fields up to 100 MG²⁾. To get more insight into the physics of the propagation of ultra-relativistic electron beams through dense plasmas, we performed experiments using aluminium and pre-ionized CH-foam targets with various thicknesses and densities.

Experiment

The experimental measurements were carried out using the Vulcan Petawatt Upgrade at the Rutherford Appleton Laboratory. The laser energy of 350 J in 750 fs duration was focused by an f/3.2 parabola onto various targets, giving an intensity of approximately $5 \cdot 10^{20}$ W/cm².

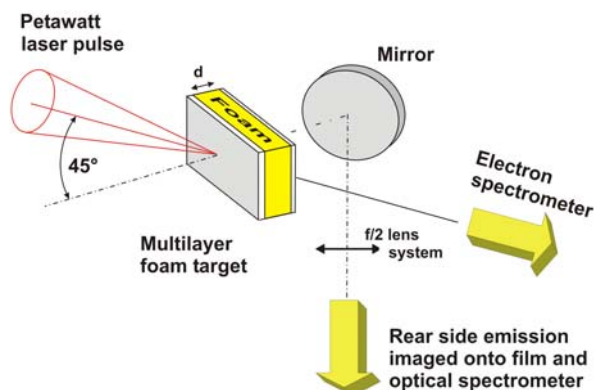


Figure 1. Set-up of the experiment.

The targets were placed at 45 degrees to the laser axis and the focus contained about 75% of the laser energy within 6 μ m. A moveable target holder with multiple targets and a rotating mirror were used to avoid opening the target chamber after each shot. The rear of the targets was imaged with a corrected f/2 lens system simultaneously onto two cameras carrying Ilford HP5 film as well as two optical spectrometers using non-polarizing beamsplitters. The spectral sensitivity of the imaging

system was limited to wavelengths between 400 and 750 nm. One of the cameras was equipped with a 527 nm bandpass filter with a spectral window of $\Delta\lambda = 10$ nm, so that emission at the second harmonic of the laser frequency was recorded. Additionally the energy of the electrons emitted in forward direction was measured with an electron spectrometer located 3.7 m behind the target. Both multilayered foam targets with a cell size of 1 μ m and aluminium foil targets were used. The latter had a thickness of 20 μ m. The density of the foams was chosen to be 100 and 200 g/cm³ respectively ($\sim 10^{22}$ cm⁻³). The thickness was 250, 500 and 750 μ m. The front side was either bare or overcoated with a layer of 75 nm gold to provide a high energy radiation wave to pre-ionize the CH-foam. The rear side was overcoated with 200 nm of aluminium. The electrons crossing the aluminium-vacuum interface at the rear side of the target produce intense radiation in the visible, basically optical transition radiation (OTR) and synchrotron radiation (SR). Imaging this radiation provides a powerful method to study the filamentation process of the electron beam with high spatial resolution³⁾.

Results and Discussion

A typical image of the rear side of the target obtained using foams is shown in Figure 2 (a). Here a density of 100 mg/cm³ and a thickness of 250 μ m has been used. It shows that strong filamentation of the electron current has occurred.

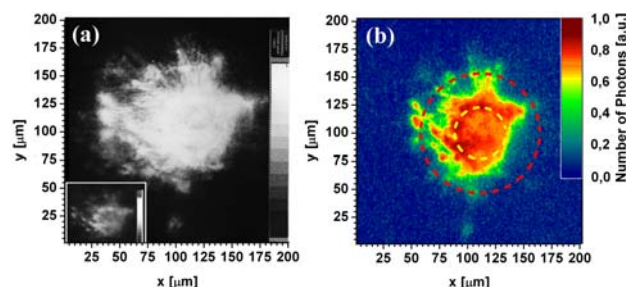


Figure 2. (a) Image of optical emission using 250 μ m foam target. The inset shows the same image but at a different grayscale. Here the substructure is clearly revealed. (b) Postprocessed data. Here the width has been rescaled due to the supposed direction of the electrons (see text).

Near the centre large filaments are found that form a half of a ring. This is clearly revealed in the inset left in Figure 2 (a), that presents the same shot but using a different grayscale. In the outer region small filaments are observed that also can be aligned on a ring. The asymmetry of the cloud in Figure 2 (a) could be explained by the oblique incidence of the laser pulse. This has been corrected by rescaling the width of the image, shown in Figure 2 (b). Figure 3 shows a detailed analysis of inner and outer filaments. The large filaments have a diameter of ~ 10 μ m (FWHM), the smallest structures that could be resolved down to ~ 2.3 μ m. This approximately represents the

resolution limit of the imaging optics. The full opening angle of the filaments is about 17° .

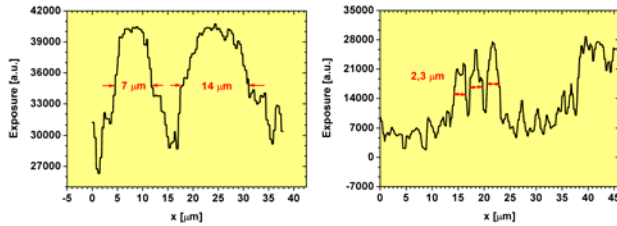


Figure 3. Linescans of inner (left) and outer (right) filaments. While the inner filaments have got a diameter of about $10\ \mu\text{m}$, small structures can be found in the cloud of filaments in the outer region.

For the aluminium targets, the analysis of the optical spectra as well as the comparison of the images with and without the bandpass filter at $527\ \text{nm}$ reveals that the light is basically emitted at the second harmonic of the laser frequency. A typical optical spectrum obtained on a $20\ \mu\text{m}$ aluminium foil target is shown in Figure 4. The spectra can be explained assuming that the electron emission at the target rear side is bunched. A typical candidate for this would be $j \times B$ acceleration. In this case, two electron bunches during each laser cycle are generated at the target front side and injected into the plasma. However, also other mechanisms are possible. Provided that the electrons remain bunched as they propagate through the plasma, the generation of coherent transition radiation (CTR) or synchrotron radiation (CR) leads to the observed peak as a consequence of the temporal characteristics of the electron bunches. The CTR intensity is typically proportional to N^2 , whereas it is proportional to N in the incoherent case, where N is the total number of electrons emitted from the target. This has also been observed on former experiments carried out by Santos *et al.*³⁾ and Baton *et al.*⁴⁾

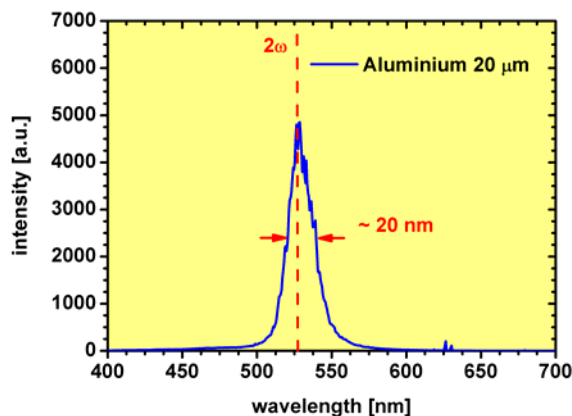


Figure 4. The spectra of light emitted by electrons crossing the aluminium-vacuum interface show a significant peak at a wavelength around the second harmonic of the laser pulse. It is supposed to be coherent transition radiation or coherent synchrotron radiation.

In the case of the foam targets, emission at 2ω is also observed. The highest peak intensity is obtained for the $250\ \mu\text{m}$ target, whereas it rapidly decreases for the thicker targets (500 and $750\ \mu\text{m}$, respectively). This effect can be explained taking into account the velocity dispersion of the electron bunches generated at the target front side. Therefore we have used a simple analytic ballistic model to calculate the effect of dephasing of the electron bunches on the CTR intensity emitted from the target rear^{3,4)}. Electron packets with a 1-dimensional Maxwellian velocity distribution (corresponding to a Boltzmann energy distribution) are injected into the plasma twice a laser cycle. According to the velocity distribution, the electron packets broaden as they propagate through the plasma. This

results in a loss of coherence and consequently in a decrease of the emitted light intensity.

Typical electron spectra obtained on aluminium foils are presented in Figure 5. The energy spectrum of the electrons shows a typical two-temperatures Boltzmann distribution with temperatures in the range of $\sim 3\ \text{MeV}$ and $\sim 10\ \text{MeV}$ respectively. The CH-foam spectra approximately show the same characteristics in temperatures as well as in numbers (not drawn here).

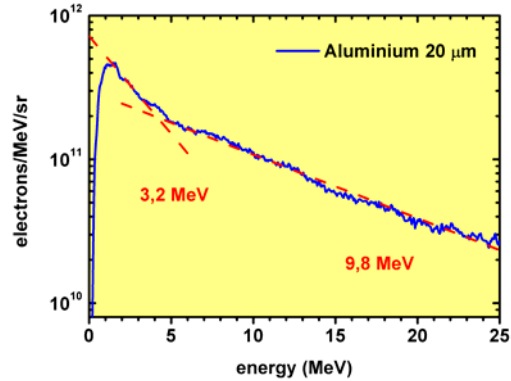


Figure 5. Typical electron spectra obtained using aluminium targets. A two-temperature characteristic is observed.

Various processes are known that contribute to the acceleration of electrons in plasmas such as resonance absorption, $j \times B$ heating or betatron acceleration. As we discussed above, the spectra of the light emitted from the target rear side can be explained assuming $j \times B$ heating. This is also in agreement with the geometry of the filamentary structure observed. Because the $j \times B$ acceleration mechanism will basically drive the current in laser propagation direction, we corrected the widths of the images by a factor that takes into account the oblique incidence of the laser pulse. The result is presented in Figure 2(b). Here the postprocessed image of the raw data is shown and additionally the nonlinearities of the HP5 film are numerically corrected. The filaments follow the geometry of two concentric rings. This gives strong evidence that the laser pulse pushes the electrons in the forward direction.

It is worth mentioning that a population of the electrons might originate from a Brunel-type acceleration mechanism, e.g. resonance absorption that is known to produce electrons directed perpendicular to the target surface. In the images of the rear side of aluminium targets, a small spot was observed that approximately indicates the direction of the target normal. This is schematically discussed in Figure 6. Also in former experiments perpendicular and oblique electron populations with different effective temperatures have been observed⁵⁾.

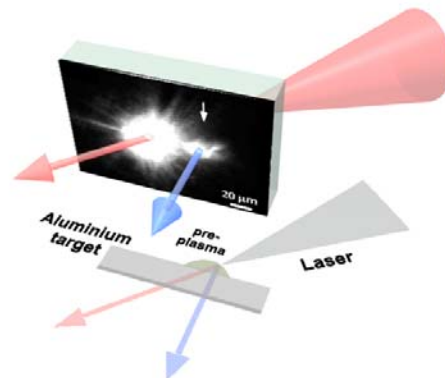


Figure 6. Using aluminium foils, two emission regions are observed. The bright spot is ascribed to $j \times B$ acceleration. Possibly the small one (white arrow) originates from a different acceleration mechanism.

Summary

Using the Vulcan Petawatt Upgrade, the break-up of laser induced electron beams in dense (10^{22} electrons/cm³) plasmas has been studied. The visible light emitted from the target rear side was used for detection of the electron beam. We found that the electron beam produced by the Petawatt laser undergoes filamentation. The filaments form a ring like structure of larger filaments surrounded by a cloud of smaller filaments. As discussed in detail in^{3,4}, the light emitted is either CTR or SR. The peak at 2ω demonstrates that the electrons are emitted in bunches from the target rear side. This can be explained assuming that the electrons are accelerated by $\mathbf{j} \times \mathbf{B}$ heating. The decrease of the peak intensity can be explained using a simple ballistic model of electron transport that results in a loss of coherence of the electron packets for thicker targets. The experiment is of great interest in the context of the fast ignitor concept in laser fusion research.

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Overview of the LLNL experimental campaign on the Vulcan Petawatt laser

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Introduction

High energy short-pulse laser interactions have been found to be a rich source of energetic particles such as x-rays, γ -rays, protons, and relativistic electrons. Some of the unique characteristics exhibited by these particles, including ultrashort temporal durations, small spatial sources, and high energy flux, have suggested their use in creating and probing extreme plasma states. Amongst the most important applications are time-resolved x-ray radiography of dense matter, fast ignition for inertial confinement fusion, and ultrafast heating of matter to high energy density plasma states for material studies.

An exciting prospect is the use of such short-pulse techniques on a future deployment of a Petawatt-class, pulse-compressed arm—or multiple arms—of the 192-beam National Ignition Facility (NIF) laser at the Lawrence Livermore National Laboratory. The anticipation of multi-beam, kJ-level, 1-10 ps laser operation on NIF dictates the need for a high level of preparedness, both in the development of new short-pulse diagnostic techniques and in our specific understanding of the underlying physics of laser-matter interactions in this relativistic regime.

Our campaign, in November 2003, on the new Rutherford Appleton Laboratory Petawatt laser provided an ideal opportunity for carrying out experimental studies at true NIF-like laser conditions. Specifically, in this campaign, our primary goals were to investigate: (i) the characterisation and optimisation of high energy (22 keV) Ag K α x-rays, (ii) 1-D Ag K α radiography, (iii) relativistic electron transport in buried layers and cone targets for fast ignitor studies, (iv) MeV proton generation, radiography, heating, and focusing, and (v) the generation of high temperature thermal radiation fields.

Experiment

The experiment was performed on the Vulcan Nd:glass Petawatt laser. The laser delivered up to 350 J on target in a 700 fs pulse. For some shots the pulse duration was increased to 10 or 70 ps. The 60 cm diameter beam was focused with an f/3 off-axis parabolic mirror. A small part of the beam was split off inside the target chamber and frequency-doubled to provide a sub-picosecond probe for interferometry. A variety of targets were shot during the course of the experiment including flat Al,

Cu, Ag, and Au foils, buried layers, Au cones, Cu cans, and Al hemispheres.

The multiplicity of sub-campaigns and experimental goals necessitated a total of 19 individual diagnostics to be fielded (see Figure 1). The front-side diagnostics measured Cu L-shell x-ray spectra, time-resolved soft x-ray spectra, specular optical spectra, single-hit K α emission, and neutron yields. The rear-side diagnostics measured time-resolved and spatially-imaged XUV emission, time-resolved and spatially-imaged optical emission, MeV electron spectra, spatially-imaged Cu K α and Ag K α x-rays, single-hit K α emission, and proton spectra. Rather than fielding only the principal diagnostics in turn for each sub-campaign we chose a strategy of attempting to field all 19 diagnostics simultaneously for all shots. Although increasing the complexity of the experimental setup this strategy would yield a more comprehensive set of data for each shot, thereby adding to our understanding of the laser-interaction conditions.

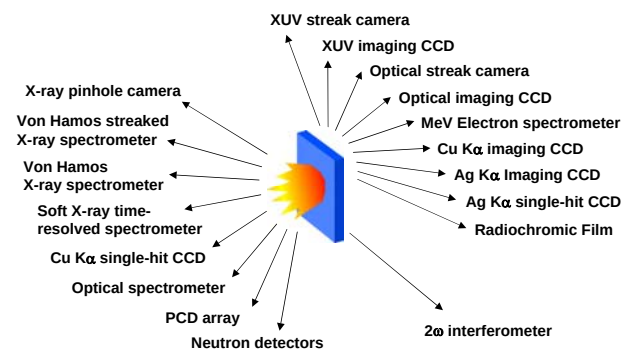


Figure 1. List of diagnostics viewing target from front and rear-side directions.

To assist in the design of the experimental setup a 3-D CAD model of the target chamber and diagnostic instruments was constructed. The CAD model proved to be essential for positioning all of the diagnostics in the PW target chamber without interference with each other. A schematic of part of the interior chamber diagnostics is shown in Figure 2. A total of 48 full energy shots were obtained during the experiment. Almost all of the diagnostics operated successfully on the majority of

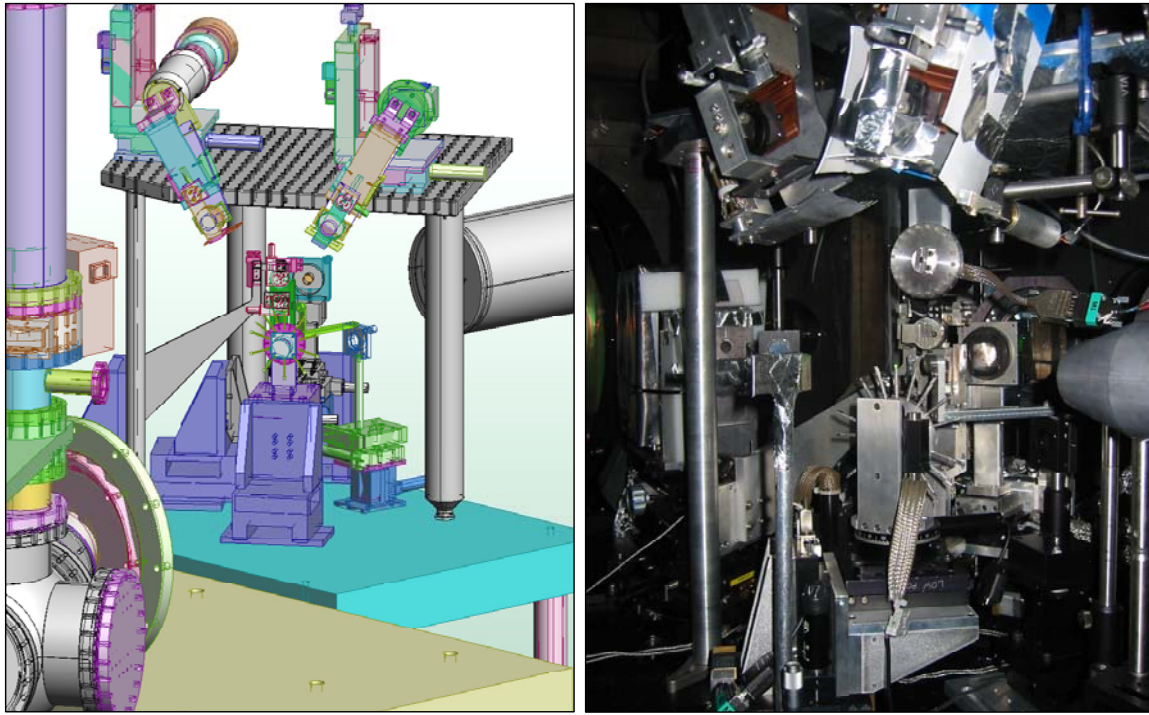


Figure 2. CAD model of experimental setup (left), and actual view of interior diagnostics (right).

shots, producing a large total data set. A selection of results are presented in the remainder of the report.

Focal spot and pre-plasma characterisation

Two of the most important factors which influence the laser-plasma interaction process are the focal spot pattern (which determines the peak focal intensity and spatial distribution), and the laser contrast (which determines the extent of pre-plasma, and thus strongly affects the absorption process). We measured the vacuum focal spot as a function of distance along the laser axis using a $\times 40$ microscope objective and CCD (both 8-bit and 16-bit cameras were used in different series). Figure 3 shows a focal spot image of the 1053nm CW alignment laser (to which the pulsed beam is matched by the adaptive optic).

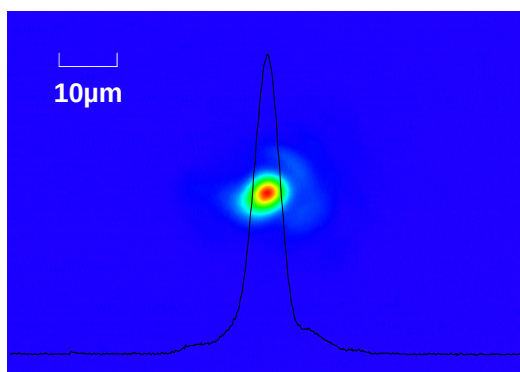


Figure 3. Vacuum focal spot measurement of CW beam with microscope objective and 8-bit CCD camera.

Analysis of the image shows a best focus of $5.2 \mu\text{m}$ FWHM, with 32% of the total energy contained within the FWHM spot (this compares very favourably with the diffraction-limited maximum of 48%). With 350 J on target this gives a peak focal intensity of $8 \times 10^{20} \text{ W/cm}^2$. In reality, the actual peak intensity will be lower since the focal spot measurement does not include the non-linear effects of B-integral present in full system shots.

A Wollaston prism interferometer was set up to provide measurements of the pre-plasma at the target surface. The target plane was image-relayed to the interferometer outside the

chamber, and a 16-bit CCD was used to capture the data. The 2ω probe beam was timed relative to the main pulse with a fast diode to an accuracy of better than 50 ps.

The interferogram shown in Figure 4 is taken from a 300 J shot, at 1 ps and tight focus, on a $20 \mu\text{m}$ thick Cu foil. The probe arrived approximately 100 ps prior to the main pulse. A relatively small pre-plasma is observed on the front of the target, extending up to $200 \mu\text{m}$ in the lateral direction at the surface. An accurate measurement of the extent of the plasma in the target normal direction is complicated by the uncertainty in the precise location of the foil surface, however, an upper limit for the distance to the critical surface of at most $40 \mu\text{m}$ can be established. In addition to the pre-plasma measurement we measured the laser contrast directly on full energy shots using a 20 GHz fast diode coupled to a 6 GHz LeCroy oscilloscope. A series of shots with differing calibrated absorption filters demonstrated no observable signal from pre-pulses or ASE down to an intensity level of 10^{-5} in the 10 ns to 50 ps window before the main pulse. Since the duration of the ASE arising from the OPCPA pump is substantially longer than the main pulse we can derive an upper limit of at most 10^{-7} for the intensity contrast of the ASE with respect to the main pulse.

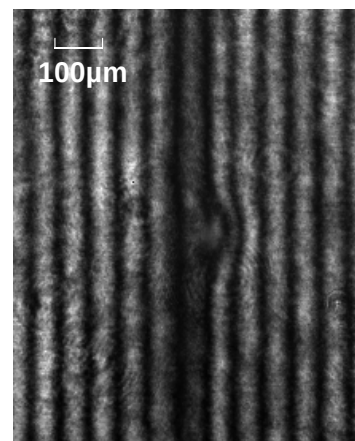


Figure 4. Interferogram of a $20 \mu\text{m}$ thick Cu foil taken 100 ps before the main pulse. The PW beam is incident from the right.

MeV Electron production

Since the coupling of laser energy to hot electrons is one of the dominant absorption mechanism at high intensities measurements of the hot electron distribution can provide great insight into the laser-interaction conditions. We fielded a magnetic spectrometer¹⁾ inside the chamber to measure MeV electrons emitted from the target in the forward direction (i.e., along the laser propagation direction).

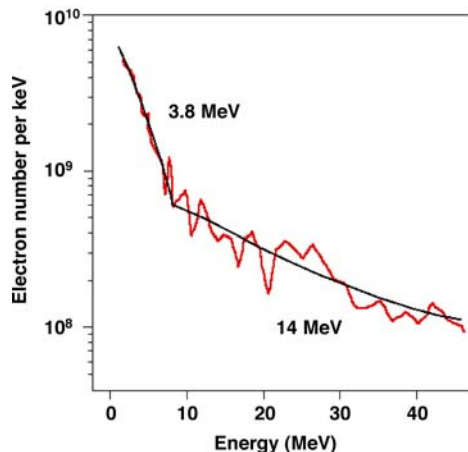


Figure 5. Electron spectrum measured in forward direction from a 5 μm thick Cu foil. Experimental data (red), and exponential fits to the data (black).

The electrons are detected after deflection by an array of over 100 scintillating fibers optically coupled to a 16-bit CCD camera. Figure 5 shows a plot of the electron spectrum from a 289 J shot tight-focused onto a 5 μm thick Cu foil. Two electron temperature components are observed in the spectrum. The first, at 3.8 MeV, agrees well with the traditional $j \times B$ ponderomotive scaling²⁾ of T_{hot} with $I \lambda^2$. The second, higher temperature component, contains electrons with energies extending up to 50 MeV. Similar high energy electrons have been observed on the Vulcan 100 TW and Nova PW lasers.³⁾

High energy X-ray production and radiography

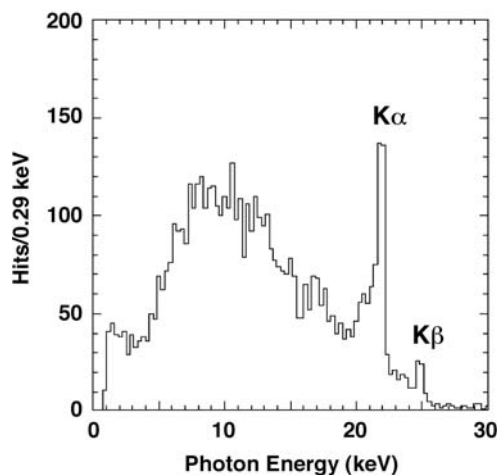


Figure 6. Single-hit CCD histogram showing 22 keV Kα and 24 keV Kβ x-rays from a Ag foil.

A principal goal of the experiment was to demonstrate the feasibility of using a PW laser Kα source for high temporal and spatial resolution x-ray radiography. Ag foil targets, producing Kα radiation at 22 keV, were shot at a variety of pulselengths, and focusing conditions.⁴⁾ A typical spectrum from the single-hit CCD camera is shown in Figure 6. In this shot the pulselength was increased to 70 ps and the spot slightly defocused in order to reduce the laser intensity, and thus,

increase the signal-to-noise between the Kα and the bremsstrahlung background.

The absolute conversion efficiency from laser energy to 22 keV Kα x-rays was measured at 1×10^{-4} . The source size of the Kα emission (plus some component of high energy bremsstrahlung) was evaluated by pinhole imaging using a 30 μm diameter Ta pinhole array and CsI coated CCD camera. This system gave a minimum source size of approximately 60 μm FWHM—a figure substantially larger than the laser spot size due to spreading of the hot electrons within the target.

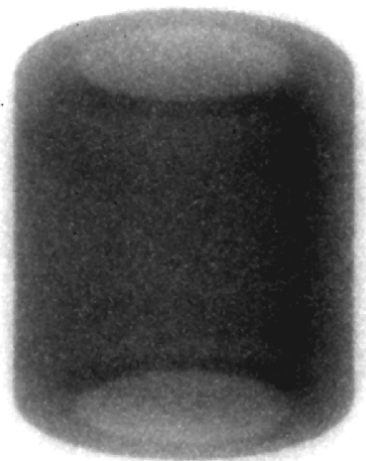


Figure 7. Radiograph of a 3 mm diameter Au hohlraum imaged with broadband bremsstrahlung x-rays between 30 and 70 keV.

An actual radiography test was carried out with a 3 mm diameter, 25 μm thick Au hohlraum. In this case, broadband bremsstrahlung x-rays generated from a Cu target were used. The combined filter response and CsI CCD sensitivity preferentially selected x-rays in the region of 30-70 keV. As can be seen in Figure 7 a high contrast image was successfully obtained, with a spatial resolution of approximately 60 μm, indicating a source-size limitation to the resolution.

Isochoric electron heating

Two monochromatic XUV imaging diagnostics were fielded to study both electron and proton isochoric heating. These diagnostics used multi-layer spherical mirrors to image monochromatic 68 eV XUV emission from the target rear surface onto, in one case a back-thinned 16-bit CCD camera providing a 2-D spatially-resolved image, and in the other a Kentech x-ray streak camera providing time-resolved 1-D spatial images.

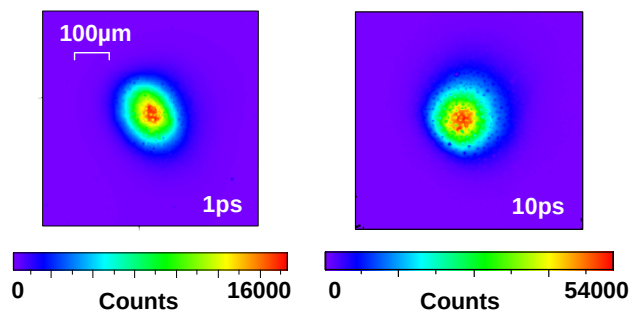


Figure 8. XUV emission from rear surface of 20 μm thick Cu foils from two shots at different pulselengths.

Figure 8 shows data from the 2-D XUV imaging channel for shots on a 20 μm thick Cu foil taken at two different pulselengths: 1ps and 10 ps.

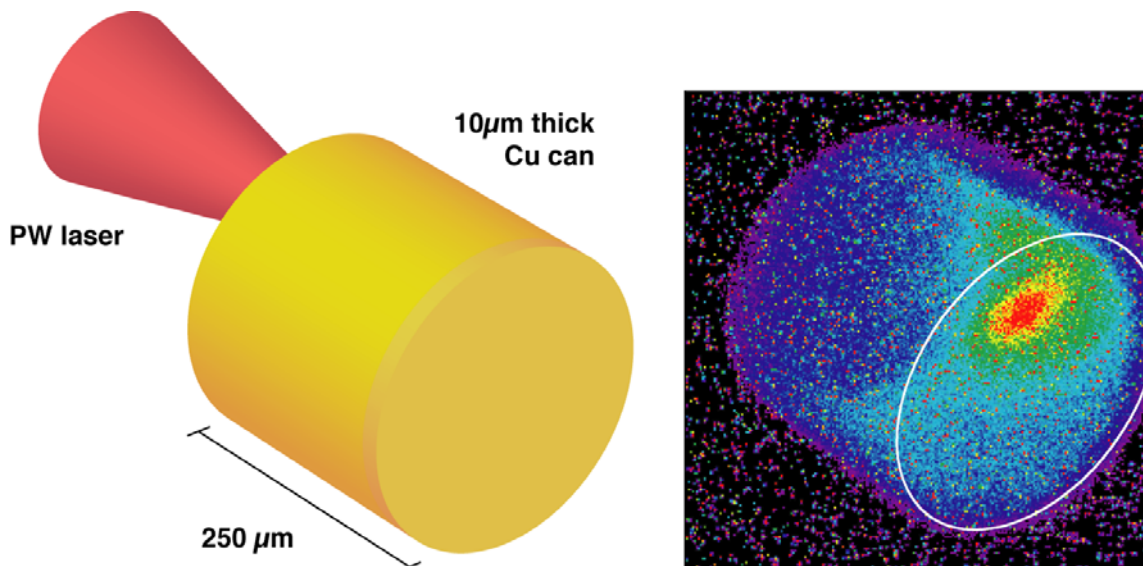


Figure 9. Schematic of laser fired into the open end of a 250 μm diameter, 250 μm long, 10 μm thick Cu can (left), and image of can in Cu K α x-rays on a 240 J shot.

In both cases a near-circular emission region is observed at the rear of the target with a 100-110 μm FWHM diameter—though the longer pulse shot exhibits a factor of 4 higher signal. The XUV emission most likely arises from isochoric heating of the rear surface by hot electrons propagating through the target.⁵⁾ If one assumes that the emission is initially blackbody one can use the absolutely calibrated monochromatic XUV measurement to estimate the rear surface temperature. Preliminary analysis indicates that temperatures are above 50 eV at the rear of the 20 μm thick Cu foil.

Cu K α imaging

Finally, we illustrate one of the benefits of running multiple secondary diagnostics on every shot of the experiment. One series of shots in the experiment—aimed at developing short-pulse thermal x-ray sources—included firing the PW laser into 250 μm diameter cylindrical Cu cans (through the opening at one end). The primary diagnostics were two von Hamos x-ray spectrometers measuring the Cu L-shell emission from the can. Additional, and very interesting, information was obtained from another diagnostic—a Cu K α imager—fielded for the electron transport studies. This instrument used a spherically-bent crystal to selectively diffract and image x-rays at the Cu K α energy of 8.05 keV onto a 16-bit CCD⁶⁾. Figure 9 shows an image of the K α emission from a Cu can shot with 240 J incident laser energy. The can was mounted such that the entrance hole was tilted upward at an angle of 25° to the horizontal. The laser was aligned to focus at the top of the inner rear wall. A bright x-ray signal is seen at this position, indicating that most of the laser energy reaches the inside rear wall. Also interesting to note is that the entire can emits Cu K α x-rays. Since K α x-rays are produced by the non-thermal electrons present only during a few picoseconds around the main pulse this image essentially provides a temporally-resolved snapshot of the hot electron transport throughout the walls of the can.

Conclusion

We have presented a brief overview of a large-scale experimental campaign performed on the Vulcan Petawatt laser in November 2003. A total of 19 diagnostics were fielded with most diagnostics operational on every shot. This strategy enabled an extensive data set to be collected with simultaneous measurements of optical light, XUV emission, soft x-rays, hard x-rays, protons, electrons, and neutrons. Analysis of the data is ongoing.

Acknowledgements

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Pumping laser energy absorption in X-ray laser experiments

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Introduction

With picosecond pulse pumping of X-ray lasers, the irradiances on target are much greater (up to 10^{16} Wcm⁻²) than needed with experiments using higher energy, longer pulse pumping lasers (typically up to 2×10^{14} Wcm⁻²). In addition, the high irradiance pulses are incident into long scale-length plasmas due to the use of a pre-pulse which means that although the laser absorption is high, parametric processes may cause some of this absorbed energy to produce fast electrons that will not efficiently collisionally excite the population inversion. We examine this indirect effect of parametric processes on the production of population inversions in X-ray laser experiments in this article.

Fluid simulation codes help understand the laser-plasma interaction, plasma expansion and atomic physics issues in X-ray laser experiments¹. The codes also aid the design of experiments and have helped studies to improve the efficiency and output of X-ray lasing².

Simulations of X-ray laser experiments sometimes require a reduction of the assumed pump laser energy absorbed to obtain agreement with experiment^{3,4}. A correction factor, $f \leq 1$, is utilized to multiply the actual incident laser energy to give a laser energy for use in the code simulations. In this article, we determine the necessary value of f needed to model X-ray laser experiments involving picosecond duration pumping by comparing the fluid and atomic physics code EHYBRID¹ output with experimental results. To understand the cause of the reduced “effective energy” absorbed in the experiment, we model the laser energy absorption and resulting electron energy distribution using a particle-in-cell (PIC)⁵ code. The electron energy distribution calculated by the PIC code is used to calculate collisional excitation rates for comparison to the rates used in EHYBRID where Maxwellian distributions are used.

Experiment

X-ray lasing was produced in Ne-like nickel at 23.1 nm ($2p^5 3p \ ^1S_0 \rightarrow 2p^5 3s \ ^1P_1$) by irradiating solid nickel slabs with two beams of wavelength 1.06 μ m from the Vulcan glass laser. A pre-plasma was formed with a controlled pre-pulse of duration 280 ps and peak irradiance 2×10^{13} Wcm⁻² in a line focus of length 16 mm and width 100 μ m. The main pulse irradiance had a duration of 1.2 ps and peak irradiance 7×10^{15} Wcm⁻² in a line focus of length 12 mm and width 100 μ m. The peak-to-peak delay between the pre-pulse and main pulse was 300 ps for Ne-like nickel. The main pulse was incident at travelling wave speed equal to the speed of light c along the horizontal target length and was polarized vertically. The experimental set-up and diagnostics have been described by Abou-Ali *et al.*⁶.

The X-ray laser output was recorded using a flat field grating spectrometer with either a time integrating CCD camera or an Axis Photonique streak camera positioned at the spectrometer detection plane. The temporal resolution of the flat field spectrometer with streak camera detector is estimated at 1.1 ps. The peak-to-peak delay between the pre-pulse and main pulse was varied to optimize the X-ray laser output. To measure gain coefficients, the length of the X-ray laser medium was varied. Another simple streaked slit diagnostic⁷ was developed to estimate the duration of the X-ray laser gain by temporally resolving spectrally integrated continuum and resonance line

emission from states near in energy to the upper lasing levels. A KAP crystal spectrometer was used to record the time integrated resonance line emission of Ne- and F-like germanium produced with similar irradiance (as indicated above) incident onto 100 μ m wide and 3.8 mm length germanium stripe target (except that the separation between pre-pulse and main pulse was 100 ps).

Simulation

Numerical simulation of X-ray laser outputs obtained at the Rutherford Appleton Laboratory (RAL) are obtained by post-processing the space-time output of the fluid and atomic code EHYBRID using a 3D RAYTRACE code^{2,8} to give information on the X-ray laser output and a code^{3,9} to create artificial resonance line spectra. Laser absorption is assumed to be by either inverse Bremsstrahlung absorption or resonance absorption at the critical surface. For resonance absorption, a fraction, 30%, of the laser energy reaching the critical density is dumped in the critical density cells and the remainder of the energy is reflected back into the low-density region for possible further inverse Bremsstrahlung absorption. Radiative energy losses through recombination, Bremsstrahlung emission, and line emission processes are taken into account.

In the simulations discussed here, a pre-plasma formed by a deliberate laser pre-pulse is irradiated to produce X-ray lasing. The EHYBRID fluid code, however, does not explicitly model laser scatter and parametric processes which may be expected to be important with such long scale-length plasmas. The effect of these mechanisms is taken into account by introducing the correction factor, $f \leq 1$, which is used to multiply the experimental laser energy to correctly simulate experimental observations.

To understand the laser energy absorption (including parametric processes) and the resulting electron velocity distribution, a PIC code is used to model the 1.2 ps pulse interaction with the pre-formed plasma. The PIC code has been described by Sheng *et al.*⁵. The code assumes one-dimension in space and three dimensions for the electron and ion velocities with the laser pulse incident normally to the density gradient. Collisions between electrons and ions are modelled as described by Cadjan and Ivanov¹⁰. The interaction of the 1.2 ps pulse with the plasma density profile produced by a 280 ps duration pre-pulse incident 300 ps earlier is modelled.

PIC code simulations

The PIC code simulated the 1 ps pulse interaction with a pre-formed plasma of profile and temperature as predicted by the EHYBRID code for the experimental conditions. An initial exponential density profile with an e⁻¹ scale-length of 30 μ m and temperature of 150 eV is used. For pumping laser irradiances greater than 10^{15} Wcm⁻², the PIC code shows the production of a two-temperature electron energy distribution (Figure 1) with laser energy absorbed dropping with increasing laser irradiance. The electron phase-space distribution calculated by the PIC code indicates that the laser absorption at irradiances above 10^{15} Wcm⁻² is due to inverse Bremsstrahlung and parametric instabilities around the region of the quarter critical density. These two processes produce the lower and higher temperature electron groups respectively.

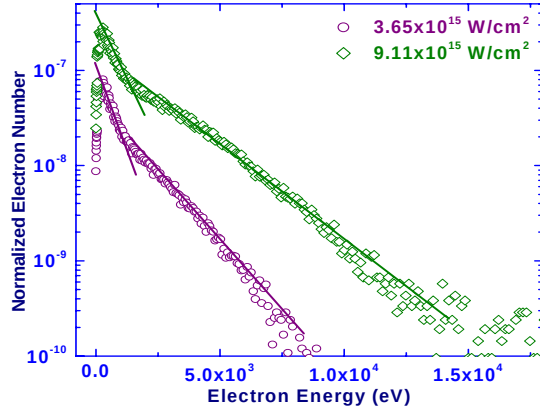


Figure 1. Electron energy distributions calculated by the PIC code showing the two-temperature structure for two different pumping laser irradiances.

For a specific electron energy distribution $f(v)$, the collisional excitation rate coefficient from the ground state to the upper lasing level of the Ne-like ion can be expressed as:

$$K = \langle \sigma(v)v \rangle = \int_{\Delta E}^{\infty} \sigma(v)f(v)v dv \quad (1)$$

where $\sigma(v) = \Omega/E$ is the collisional excitation cross-section, Ω is the collision strength of the transition, while E and v are the energy and the velocity of electrons. ΔE is the excitation energy and $f(v)$ is the electron energy distribution function.

With the Maxwellian distribution used in the EHYBRID code, the calculated collisional excitation rates are higher than the values calculated with the two-temperature electron distribution calculated in the PIC code. An estimate of the f -factor can be obtained from Figure 2 by comparing $\langle \sigma(v) \rangle / \Omega$ from the PIC and EHYBRID codes. The ratio of irradiances required to produce comparable $\langle \sigma(v) \rangle / \Omega$ gives the value of f .

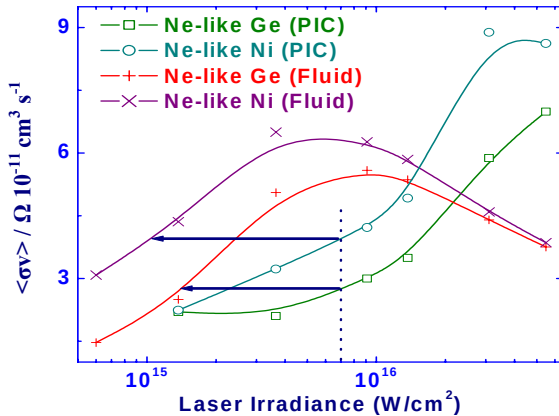


Figure 2. The reduced collisional excitation rate coefficient of the upper lasing energy level for Ne-like Ni and Ge calculated assuming a Maxwellian electron distribution from the EHYBRID code and the electron distribution from PIC simulations at the end of the 1 ps pulse.

It can be seen that an irradiance of $7 \times 10^{15} \text{ Wcm}^{-2}$ implies an f -factor of 0.22 and 0.16 for Ne-like Ge and Ne-like Ni respectively (see the arrows in Figure 2). Figure 2 is applicable for time at the end of the 1 ps pumping laser pulse. At later times, the number of hot electrons will reduce and the values of $\langle \sigma(v) \rangle / \Omega$ calculated by the EHYBRID and PIC codes will be closer leading to higher f -factors.

Fluid code simulations

To determine the correction factor f applicable for our experiment, a comparison of the simulated output of the EHYBRID code with different values of f and experimental results is made. A comparison of the simulated output and experimental results for the temporal variation of X-ray lasing at 23.1 nm for Ne-like nickel, the spectrally integrated time-resolved transverse emission in the 0.6-1.8 nm spectral region emitted from a nickel plasma, the time-integrated Ne-like nickel X-ray laser output as a function of target length and delay between the pre-pulse and main pulse and the Ne-like and F-like germanium resonance line emission in the wavelength range 0.7 – 1 nm is made.

For comparison of temporal variation of the Ne-like nickel output at 23.1 nm and spectrally integrated time-resolved transverse emission for nickel see Abou-Ali *et al.*¹¹⁾ which used correction factor $f=0.3$ for the simulations.

A sequence of shots on 4.3 mm long nickel targets was taken to determine the optimum delay between the pre-pulse and the short pulse (Figure 3). The measurement of X-ray laser output assumes a grating efficiency of 1%, a CCD quantum efficiency at 23.1 nm of 0.47 photons per count and the tabulated filter transmission of aluminium from Henke¹²⁾. Figure 3 also shows the Ne-like Ni X-ray laser energy output dependence on the arrival time of the peak of the main pulse relative to the peak of the pre-pulse from a numerical simulation with RAYTRACE post-processing of the space-time output from the EHYBRID code superimposed. Different values of the correction factor f equal to 0.2, 0.3 and 0.5 have been used in the EHYBRID code. The best agreement has been obtained for $f=0.3$ (Figure 3).

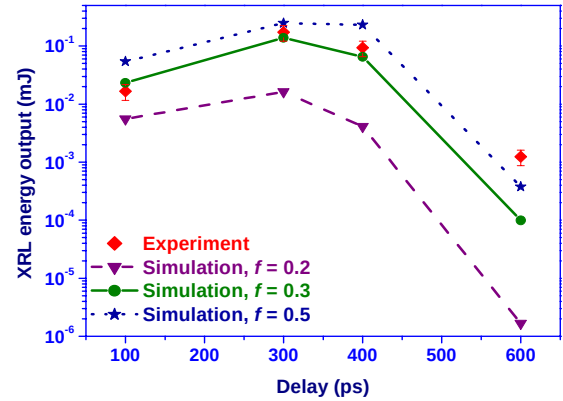


Figure 3. The simulated energy output of the Ne-like Ni X-ray laser at 23.1 nm after ray tracing for a target length 4.3 mm as a function of the peak-to-peak separation between the CPA main 1.2 ps pulse and 280 ps pre-pulse with correction factor $f=0.2, 0.3$ and 0.5 superimposed on the experimental time integrated energy output of the Ne-like Ni X-ray laser line at 23.1 nm recorded using a flat field spectrometer and CCD camera.

Figure 4 shows the simulated output of the Ne-like nickel X-ray laser with different values of f equal to 0.2, 0.3 and 0.5 superimposed on some single shot experimental Ne-like nickel X-ray laser outputs. Good agreement between the simulations and the experimental points within the estimated experimental errors is obtained with $f=0.3$ (Figure 4). The error bars shown on the experimental points of Figure 3 and 4 arise due to relative errors between the data points in integrating the output recorded with the flat field spectrometer and the uncertainties of different filter thicknesses.

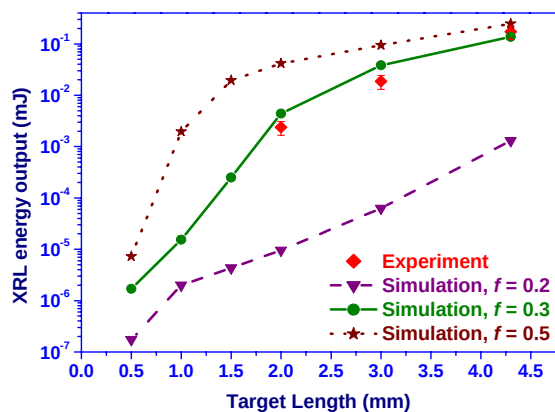


Figure 4. Ne-like Ni X-ray laser energy output from a numerical simulation with RAYTRACE post-processing of the space-time output from the EHYBRID code as a function of target length with $f=0.2, 0.3$ and 0.5 superimposed on the experimental Ne-like Ni X-ray laser output recorded using a flat field spectrometer with CCD camera.

A comparison of the time integrated resonance line emission from the Ne-like germanium X-ray laser with the predictions for the same emission from the hydro-atomic code EHYBRID has been made using the ratio of emitted intensities of F-like to Ne-like ions. The particular lines chosen for analysis were the 3d-2p F-like lines at 0.856 and 0.861 nm, and the 3p-2s Ne-like lines in the 0.839–0.846 nm region. These ratios tend to be sensitive to changes in the electron temperature. The specific spectral lines chosen are spectrally close together whilst still being clearly resolved. The post-processor⁹⁾ to the modified EHYBRID code has been used to simulate F-like and Ne-like germanium spectra with different values of f equal to 0.2 - 0.7. Figure 5 shows a comparison of the experimental ratio of intensity of the F-like and Ne-like lines to simulations of the ratio as a function of the f -factor value used in the simulations. Figure 5 indicates the value of the correction factor f to be 0.4-0.46.

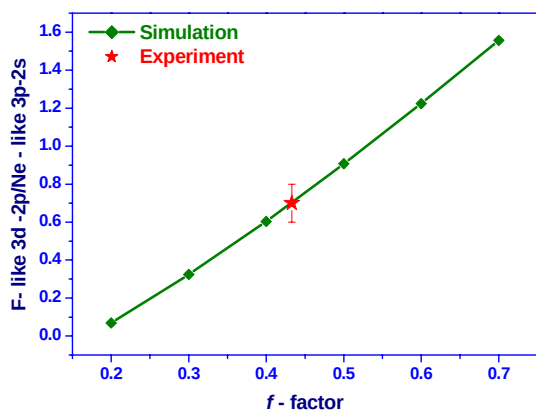


Figure 5. The simulated intensity ratio of 3d-2p F-like lines at 0.856 and 0.861 nm and the 3p-2s Ne-like lines in the 0.839–0.846 nm region, as a function of correction factor f for germanium. The experimental data points are marked.

Simulated time integrated Ne-like and F-like germanium spectra with $f=0.4$ superimposed on a time-integrated spectrum measured with the KAP crystal spectrometer are shown in Figure 6. The experimental absolute intensity is approximately equivalent to the absolute simulated intensity see Figure 6. The absolute experimental intensity is determined assuming an integrated reflectivity of 4×10^{-5} radians for the KAP crystal used in the crystal spectrometer (as given by Burek¹³⁾).

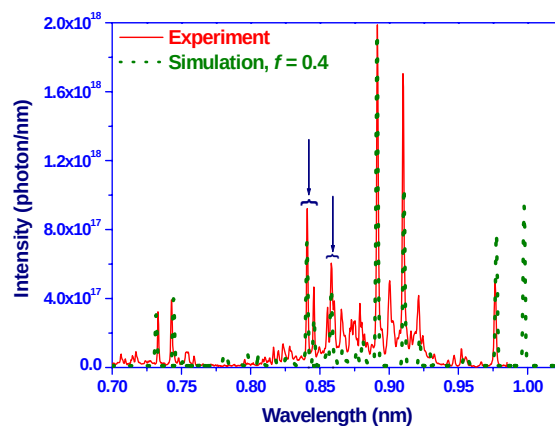


Figure 6. Time integrated theoretical Ne-like and F-like germanium spectra superimposed on a time-integrated spectrum measured with a KAP crystal spectrometer for $f=0.4$. The lines used in Figure 5 are marked by arrows.

Conclusion

The EHYBRID fluid and atomic physics code has been used to compare simulations with experimentally measured Ne-like nickel X-ray laser output at 23.1 nm and emission from nickel and germanium plasmas produced by irradiation into a pre-formed plasma with 1.2 ps pulses of 1.06 μm wavelength with peak irradiance $7 \times 10^{15} \text{ W cm}^{-2}$. A particle-in-cell (PIC) code has been used to simulate the laser energy absorption and resulting electron energy distribution. Some of the absorbed energy is distributed to fast electrons that do not produce collisional excitation of the population inversion. We have shown that the pumping laser energy employed in the EHYBRID code needs to be reduced to ≈ 0.3 of the experimental laser energy for the simulated results to agree with experiment. The fast electron production predicted by the PIC code explains the need to reduce the laser energy absorbed in the fluid code. It can be concluded that X-ray lasers created from pre-formed plasmas can be more efficient if the driving laser irradiance is kept below $10^{15} \text{ W cm}^{-2}$ so that the effect of fast electrons on gain is reduced.

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Experiment on collisionless plasma interaction with application to supernova remnant physics

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Introduction

High-power lasers have been used widely during the recent years to simulate aspects of astrophysical objects in laboratory plasma experiments^{1,2)}. The relevance of these studies relies on a scaling analysis and an assumption that the same fluid or magneto-hydrodynamic (MHD) models describing the evolution of the astrophysical system also describe the laboratory experiment. Invariant properties of these models then ensure that the two systems will behave identically if the relevant dimensionless parameters are matched. This scaling is independent of time or spatial differences.^{3,4)}

A particularly interesting feature of supernova remnants (SNRs) is the formation of a shock when the ejected matter of the exploding star (the supernova) interacts at high speed with the interstellar medium (ISM). Since ISM densities are extremely low, these shocks are collisionless. The formation relies on wave-particles processes involving a magnetic field rather than Coulomb interaction. The physical processes central to the formation of these shocks are also believed to result in the acceleration and production of cosmic rays with energies up to 10^{15} eV⁵⁾.

In a previous publication⁶⁾, we outlined the principle of a scaled laser-plasma experiment designed to simulate aspects of reverse shock formation in a young SNR. The aim of this study was to access the collisionless shock regime through the interaction of two laser-produced supersonic colliding plasmas immersed in an external magnetic field. Numerical simulation indicated that plasmas created from laser-exploded thin plastic foils could result in a collision-free interaction when used in a colliding geometry. With the addition of a magnetic field it should be possible to create conditions suitable for studying a collisionless interaction, and by careful choice of the experimental parameters a scaling to a 100-year-old SNR was possible at approximately 500 ps into the experiment. As in a SNR plasma, the role of magnetic field was to introduce new experimental scale lengths that are shorter than the particle mean-free-paths (MPF). If these scale lengths, the electron, r_{Le} , and ion Larmor, r_{Li} , radii are sufficiently small then a collisionless shock should form. This is interpreted as an increase in the *effective* collisionality of the plasma, compared to that due to Coulomb collisions.

Scaling

Dimensionless scaling parameters for a young SNR⁷⁾ and those derived from our scaled experiment⁸⁾ 500 ps after laser irradiation, are compared in Table 1. The collisionality parameter, ζ , is defined as the ion collisional MPF normalised to the size of the system, L . In a collision-free system, ζ must be larger than 1, which is the case for a SNR. In the colliding plasma experiment, ζ is determined for the counter-streaming ions and must be larger than 1.

MHD similarities between the SNR and the experiment can be ensured if they are ideal fluids and that the Euler number, Eu , and the plasma beta parameter, β , are matched in the two systems. The SNR parameter β is large indicating that the magnetic field will not dominate macroscopic fluid motion.

Similarly the experimental beta, denoted by β^* , should be large. In this paper, an asterisk indicates that the kinetic energy of macroscopic plasma flow rather than the thermal kinetic energy of the ions was used to derive the quantity. The ion localisation parameter defined as r_{Li}/L , is much smaller than 1 in a SNR (see Table 1). This parameter indicates that a collisionless SNR plasma exhibits fluid-like behaviour and the evolution is described by fluid equations. The amplitude of the magnetic field in the laboratory must also be sufficient to localise the ions (i.e. ensuring that $r_{Li}/L < 1$) and the electrons ($r_{Le}/L < 1$) whilst $\beta^* > 1$.

Parameters	SNR: 100 yrs	Exp: 500 ps
Collisionality parameter, ζ	2×10^6	3×10^2
Euler number, Eu	18	21
Plasma beta	$\beta = 5 \times 10^2$	$\beta^* = 4 \times 10^2$
Ion localization, r_{Li}/L	10^{-9}	10^{-1}
Reynolds number, Re	10^{13}	10^7
Péclet number, Pe	10^{11}	10^{10}
Mach number, M	16	12
Alfvén Mach, M_A	3×10^2	20

Table 1. Comparison of the scaling parameters for the reverse shock in a young SNR and the experimentally derived values measured at 500 ps.

The application of Euler equations assumes that plasma behaves like an ideal fluid. In an ideal fluid the dissipative processes such as thermal conductivity and viscosity are negligible; this approximation hold if the Péclet, Pe , and Reynolds, Re , numbers are very large. Finally, to form a shock it is necessary to ensure that the sonic Mach number, M , and the Alfvénic Mach number, M_A , are larger than unity; strong shock formation is expected when these parameters exceed 10.

The last column of Table 1 shows the scaling parameters extracted from experiment; these measurements are discussed in the remainder of the paper.

Experimental results

Details of the experimental set-up and results can be found in References 8 and 9. Plasmas are formed from 100 nm thick plastic foils. Measurement indicates that a single exploding foil 500 ps after laser irradiation has a low electron density of around 10^{18} cm⁻³, and expands supersonically. Results also

indicate that the hydrodynamics of a single expanding foil is not affected by a 7.5 T magnetic field when applied transverse to the plasma flow. Colliding experiments use two similar plastic foils placed in an opposing geometry and separated by 1 mm. Results obtained 500 ps after laser irradiation in a magnetic field-free experiment indicate that the plasma interaction is collision-free and that these opposing plasmas interpenetrate. When the same experiment is repeated with a 7.5 T magnetic field the plasma interaction is altered. The plasma density profile is observed to have a 300 μm wide region of low-density. Within this region there is electron density structure, which only appears when the magnetic field is present.

Discussion

Details on how scaling parameters are inferred from the experimental results are reported in Reference 8. In this section, some of the experimental scaling parameters are compared to numerical results using the one-dimensional hydrodynamic model Med103.¹⁰ The large dots and solid lines in Figures 1 - 4 correspond to experimental and numerical results respectively. Dotted lines indicate the influence of varying the laser energy and foil thickness in the numerical modelling by $\pm 10\%$; this is to account for experimental uncertainty. The experimental scaling parameters will be compared to those believed to be typical of a young SNR.

Figure 1 shows the Mach number M of a single exploding foil for a magnetic field-free experiment. M is shown as a function of time and at position 0.5 mm from the target foil surface.

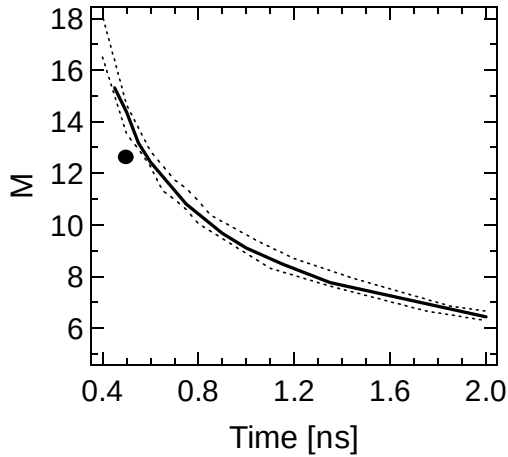


Figure 1. The experimental Mach number, M , (solid dot) at 0.5 mm and 500 ps compared to simulated M (thick solid line) at 0.5 mm and from foil target surface versus time. Thin dotted lines are discussed in the text.

Time zero corresponds to the peak of the 80 ps duration laser pulse. Experimental results show that the Mach number 500 ps after the peak of laser irradiation is 12. Numerical results broadly reproduce this result and indicate that the plasma expansion will stay supersonic for at least another 2 ns. High Mach number is necessary for strong shock formation.

Figure 2 illustrates how the collisionality parameter ζ of two opposing plasmas at the experimental midpoint and without magnetic field varies with time. Again, experimental and numerical results agree and indicate that ζ is around 300 at 500 ps. However, numerical results indicate that ζ decreases quickly with time and approaches unity around 1.4 ns. A large ζ is important to ensure the plasma interaction is collision-free. A collision-free interaction at 500 ps is also indicated by other interferometry data, where the inferred electron densities extracted from the magnetic field free experiments show no evidence of collisions.

Figures 3 and 4 show how a 7.5 T magnetic field may affect the plasma. The experiment shows that the magnetic field alters the

interaction of two opposing plasmas, yet the magnetic field does not retard the expansion of a single plasma. Here it is assumed that the magnetic field penetrates the plasma; the basis for this assumption is discussed more in detail in Reference 8. Figure 3 illustrates how the experimental parameter β^* at 500 ps varies with position in a single plasma. Position 0 corresponds to the initial foil target position; the laser beam approaches from the left to the right.

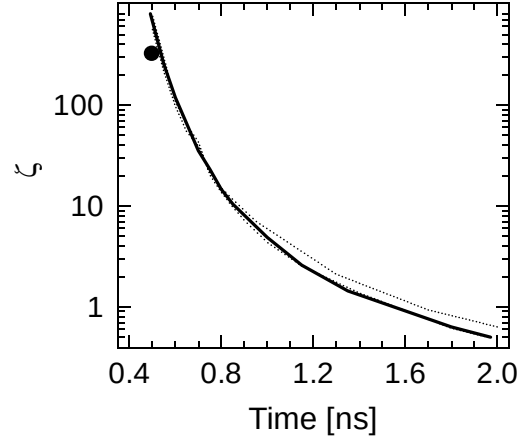


Figure 2. The experimental (solid dot) collisionality parameter, ζ , at 500 ps and 0.5 mm from foil surface compared with simulated (thick solid line) versus time. Thin dotted lines are discussed in the text.

Experimental results show that β^* is equal to 400 at 0.5 mm from the foil surface, a slightly low value, but $\beta^* > 100$, is predicted by numerical calculation. The large value of β^* indicates that the magnetic field pressure is low and is not expected to affect the plasma expansion dynamics for distances and times exceeding 1 mm and 750 ps respectively as observed in the experiment. The calculations show that the magnetic field is attenuated inside the plasma; this results in a very high β^* close to the initial foil surface, which decreases towards the plasma leading edge.

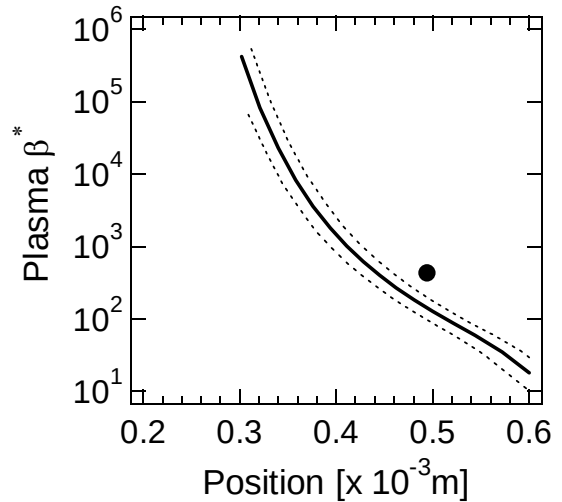


Figure 3. The experimental (solid dot) plasma beta, β^* , at 0.5 mm and 500 ps, compared to the simulated β^* (thick solid line) versus distance from foil target surface. Thin dotted lines are discussed in the text.

The ion localisation r_{Li}/L in a single exploding foil, at 500 ps, is shown in Figure 4 as a function of the position relative to the initial foil target surface. The r_{Li}/L inferred from experiment based on the thermal kinetic energy of the ions, is approximately 0.1 at 0.5 mm. Numerical results show that r_{Li}/L increases inside the expanding plasma, due to the

attenuation of the magnetic field, and approaches unity 150 μm from the position 0.5 mm. The ion localisation parameter $(r_{Li}/L)^*$ can be estimated using the ion flow kinetic energy; this is around unity at 0.5 mm and 500 ps. Although $(r_{Li}/L)^*$ is not localised, it is smaller than the collisional MFP. In both cases the electrons remain localised with r_{Le}/L and $(r_{Le}/L)^*$ around 10^{-3} . Charge neutrality is likely to ensure that the ions are localised.

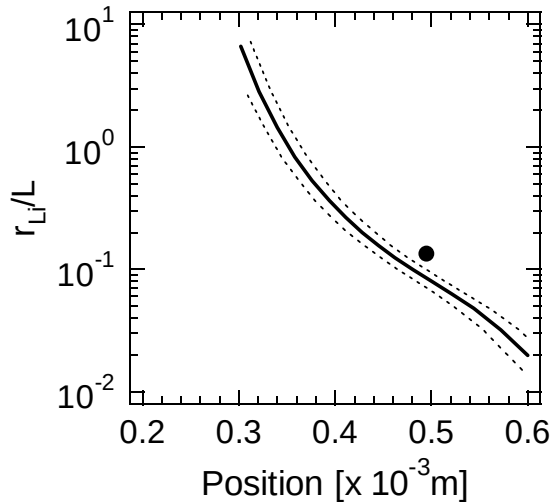


Figure 4. The experimental ion localisation parameter, r_{Li}/L , (solid dot) at 0.5 mm and 500 ps, compared with simulated r_{Li}/L (thick solid line) as function of distance from the foil target surface. Thin dotted lines are discussed in the text.

Experimental results show that the interaction of colliding plasmas is affected when a 7.5 T magnetic field is applied transverse to the plasma flow. The inferred electron density profiles between the foil targets are altered and show important differences from those obtained in magnetic field-free measurements. The electron density profiles show steeper gradients close to the initial foil target position and a low-density plateau approximately 300 μm wide centred on the collision area. We believe these results cannot be explained in terms of the magnetic field directly retarding the plasma flow or magnetic field compression between the leading edges of the two plasmas. The experiment is designed with a large β^* and the experimental geometry, with approximately 1 mm diameter plasmas should allow any compressed field to escape. A possible explanation for these observations is that the magnetic field has penetrated into the plasmas and indirectly altered the physics of the interaction by introducing the ion and electron Larmor radius as additional scale lengths that are shorter than the MFPs. If this occurs then fluid-like behaviour may occur at these new scale lengths and increase the effective collisionality of the experiment: a possible consequence is a collisionless interaction. Figure 4 suggests that an external 7.5 T magnetic field may diffuse into the plasmas to localise the ions, i.e. $r_{Li}/L < 1$, to approximately 150 μm from the position 0.5 mm. The penetration length based on single foil measurements is consistent with the extension of the low-density region observed when plasmas collide in a magnetic field.

In Table 1 the young SNR scaling parameters are compared to those inferred from the experiment at 500 ps. These results show that the collisionality parameter is much larger than unity for both systems. The Euler number and plasma beta are similar. This indicates that MHD similarity between the SNR and the laboratory experiment is accessible. The large Mach and Alfvén Mach number ensure that if a shock forms then the strong shock regime is accessible. Finally, large Reynolds and Péclet numbers ensure dissipative effects are negligible and so

ideal fluid equations are applicable. The results suggest that a SNR plasma and shock can be scaled and reproduced in a laser plasma experiment. Finally, if collisionless coupling between the counter-propagating plasmas has occurred, there is no evidence of collisionless shock formation. It is possible that shock formation requires a highly localised plasma with r_{Li}/L and $(r_{Li}/L)^*$ below 10^{-2} .

Conclusion

The dynamics of exploding plasmas from thin plastic foil targets have been studied with and without a 7.5 T magnetic field. Experiment and numerical results show that the expansion is supersonic and unaffected by the magnetic field. The densities are sufficiently low to ensure a collision-free interaction between two similar and opposing plasmas. The dynamics of two opposing plasma experiments was studied without and with this magnetic field; the inferred electron density profiles showed important differences. These differences cannot be interpreted in terms of the magnetic field directly retarding the plasma expansion, or by field compression between the plasmas. It is suggested that the magnetic field penetrates the plasmas and indirectly alters the interaction physics by introducing the particle Larmor radii as the shortest relevant scale-lengths. The plasma is expected to exhibit fluid behaviour at the Larmor radius, i.e. $0.1L$. Shock formation was not observed; this is probably due to the fluid scale being too large. It is suggested that shock formation may occur if Larmor radius is further reduced to $0.01L$. This condition may be achieved by increasing both the magnetic field and the size of the experiment. The difficulty remains keeping β^* high and r_{Li}/L or $(r_{Li}/L)^*$ low. It has been possible to extract the key scaling parameters from experiment. These parameters compare favourably to those determined for a young SNR and suggest that experimental simulations are possible. Numerical simulation supports this conclusion and indicates that the experimental design is robust.

Acknowledgments

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Hot electron generation and production of high magnetic field in a Helmholtz coil

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Introduction

Early studies showed that the interaction of an intense laser beam with a solid target increases the target electric potential to high values, of up to several hundred kV¹⁾. Other studies have demonstrated that these potentials can be used to drive large return currents in single loop targets and generate large magnetic fields²⁾. Magnetic fields up to 60 tesla were reported when a 2 mm diameter coil was driven by a CO₂ laser (10.6 μm) with resulting focused intensity of $1.3 \times 10^{14} \text{ W/cm}^2$ and $I\lambda^2 \approx 1.5 \times 10^{16} \text{ W/cm}^2 \mu\text{m}^2$. Under these conditions a hot electron temperature of 15 keV is inferred²⁾. The field persisted for $\sim 7 \text{ ns}$ with peak field value maintained for $\sim 1 \text{ ns}$. This represents a useful technology for generating high magnetic fields in the laboratory. There are many potential applications for this and of particular interest to us is the study of collisionless shocks in laser-produced plasma where pulsed magnetic fields of 10-20 tesla are desirable^{3, 4)}. The method is of particular interest to the Vulcan laser if field generation can be demonstrated at the shorter wavelengths of the Nd:glass gain medium. We experimentally investigated the behaviour of this technology with drive-laser wavelengths of 527 nm and 1054 nm.

Field generation mechanism

The field generation mechanism is illustrated in Figure 1, which shows a schematic of the laser-driven loop target. A laser pulse incident on the rear plate of the cavity heats and ionises the copper—ablating material, forming a plasma. The plasma expands into the cavity. At laser intensities where $I\lambda^2 > 10^{15} \text{ W/cm}^2 \mu\text{m}^2$ a significant proportion of energy is absorbed by the electrons through resonance absorption resulting in hot electrons with a temperature of $\geq 10 \text{ keV}$ ⁵⁾.

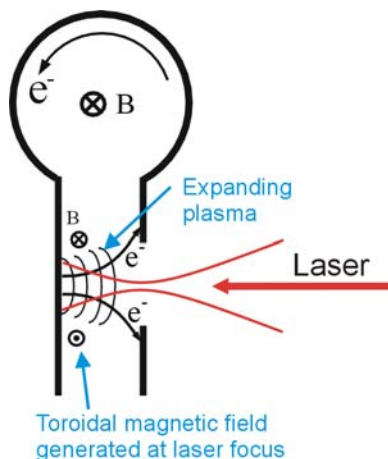


Figure 1. Showing a schematic diagram of laser-driven target, the hot electron trajectory, and the magnetic field generated in the plasma and the magnetic field generated in the wire loop.

These hot electrons travel to the front plate ahead of the expanding plasma resulting in a build up of negative charge on the front plate. This potential difference drives a strong (reverse) current in the coils resulting in a strong magnetic field. The experimental work of Daido *et al.* showed that the field produced varied with the plate separation, finding an optimum gap size of 0.6 to 0.7 mm²⁾. An optimum gap separation is

expected because the hot electrons have a maximum excursion distance from the expanding plasma. At the focus of a laser on a solid target a strong localised magnetic field is produced⁶⁾. Hot electrons travelling toward the second plate deviate in this field, this is illustrated in Figure 1. If the gap size is larger than the excursion distance the plates will not become electrically charged and no current is driven through the loops.

Design of Targets

In a previous article we looked at the design of a millimetre scale Helmholtz coil electromagnet⁷⁾. The use of a Helmholtz pair shown in Figure 2 produces a magnetic field with better uniformity than that produced in a single loop. Additionally, the use of two loops provides greater access to the experimental volume allowing laser probe diagnostics access in two directions. These targets are formed from a single sheet of photo-etched copper with thickness of 50 μm . Bending the sheet in a series of mechanical formers forms the loops and cavity. The loop diameter was 2.5 mm, loop width is 0.75 mm and the gap between loops is 2.5 mm. The cavity plates measured $8 \times 4 \text{ mm}$ with a variable parallel separation of between 0.25 and 0.75 mm. The incident drive laser beam is focused by $f/2.5$ lens through a hole of diameter 0.5 mm etched in the front plate.

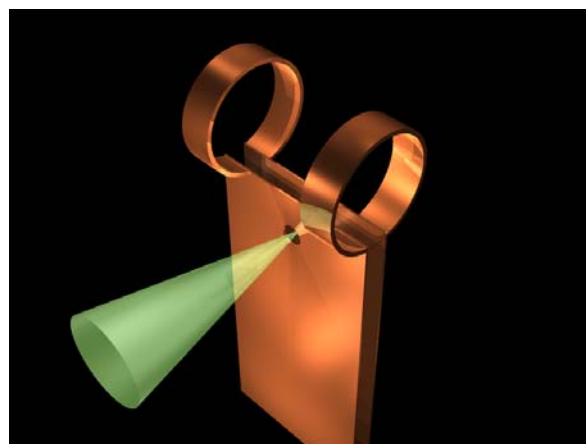


Figure 2. Illustration of the Helmholtz coil target showing the hole into a cavity formed by two Copper plates and the two loops of the electromagnet, and the focus laser beam.

Measurement of magnetic field

Single loop pickup coils (1 mm diameter) placed around the target and connected to a fast digitising oscilloscope provided time resolved, point, measurements of the magnetic field.

Measurement of hot electron temperature

The X-ray emission spectrum between 5 keV and 30 keV from the copper plasma was measured using the single photon counting method¹⁰⁾. The hard X-ray component is due to bremsstrahlung from the hot electrons. Emission from the plasma is incident on a CCD camera after being attenuated by stacks of filter material to the extent that single photons impacts are distinguishable. The energy of the photon can be deposited into either one or more adjacent pixels of the CCD chip, with a single photon recorded in up to six adjacent pixels in these

results. The total exposure of a group of pixels is proportional to the photon energy. Appropriate processing and calibration of the CCD data leads to an estimate of the X-ray power spectrum produced by the target plasma. In our work a 16 bit front-illuminated open electrode CCD camera (Marconi CCD30-11) with 1024×256 pixels was used. This was placed at 1.35 m from the Helmholtz coil target. A series of baffles ensured that only X rays from the laser focus propagated to expose the CCD camera. Filters were made from Mylar ($C_{10}H_8O_4$), Al, Cu, and Be sheets for which the X-ray spectral transmission is well known. Hot and cold electron temperatures were calculated from the X-ray emission spectrum of the laser-plasma formed in the target cavity.

The X-ray power spectral density Q_ν due to bremsstrahlung emission as given by Zeldovich and Raiser⁸⁾ is,

$$Q_\nu = \left(\frac{8\sqrt{2}}{3} \right) \frac{\pi^{3/2} Z^2 e^6 n_i n_e}{m_e^{3/2} c^3 \sqrt{K_B T_e}} \exp\left(\frac{-h\nu}{K_B T_e} \right) \quad (1)$$

This suggests that a model of the X-ray power spectral density $S(E)$, for a plasma described by two electron temperatures would take the form,

$$S(E) = C_0 + \frac{C_c}{\sqrt{T_c}} \exp\left(\frac{-E}{K_B T_c} \right) + \frac{C_h}{\sqrt{T_h}} \exp\left(\frac{-E}{K_B T_h} \right) \quad (2)$$

Here C_0 , C_c , C_h are constants and T_c , T_h are the cold and hot electron temperatures. A non-linear fit between expression (2) and the X-ray power spectrum of the plasma provides estimates of the hot and cold electron temperatures.

Results

Figure 3 shows the time evolution of the inferred magnetic field, B , at the centre of the Helmholtz coil. The peak field is around 7 tesla and decays over 30 ns. The laser delivered a single, 1 ns, 300 J pulse at 1054 nm, with $I\lambda^2 \approx 10^{16}$ W/cm² incident on the back plate of the target.

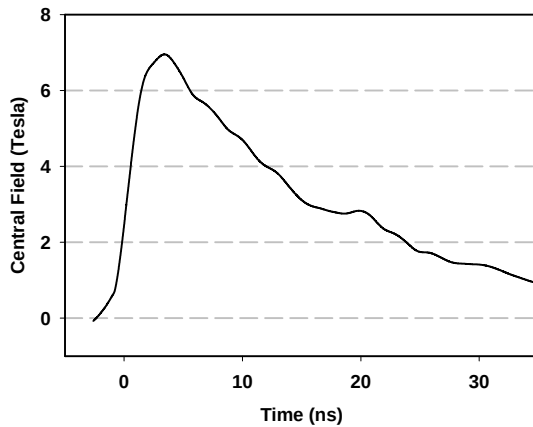


Figure 3. Magnetic field inferred at the centre of the Helmholtz coil from pickup coil measurements.

The spontaneous field generated by the interaction of the laser on the back plate of the target acts in the same direction as the field generated by the return current in the Helmholtz coils as shown in Figure 1. This field has a rapid decay. Also, the measurement of B by single loop pickup coil proved difficult because of electrical interference present during the laser shot in the target area. For this reason the magnetic field generated by the Helmholtz coil itself has been extracted by taking a series of shots where the laser was focused alternatively on the front and back plates of the target.

An example of the X-ray emission spectrum measured in the cavity by the single photon counting diagnostic is shown in

Figure 4 along with the best fit to the model described by Equation (2).

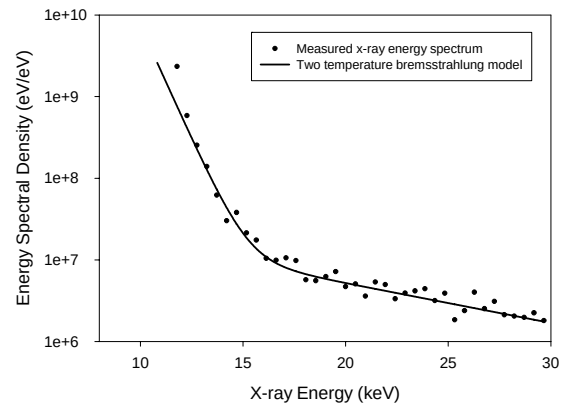


Figure 4. X-ray emission spectra for a single shot with laser intensity of 1.7×10^{16} W/cm², at 527 nm. Solid line shows fit to two-temperature bremsstrahlung emission model.

By this method estimates of the hot electron temperatures were made. These are presented along with the laser conditions in Table 1. These are in agreement with those calculated from empirical relations based on particle code simulations⁹⁾.

Drive Wavelength (nm)	Pulse length	Focused intensity (W/cm ²)	Hot electron temperature (keV)
1054	1 ns	6.4×10^{15}	14 ± 7
527	1 ns	1.7×10^{16}	7 ± 3

Table 1. Estimates of the hot electron temperature derived from the single photon counting measurements.

Conclusions

The generation of high magnetic field by a laser-plasma return-current was investigated using the Vulcan laser. The results obtained support the findings of previous work with this technology. Similar hot electron temperatures to those of Daido²⁾ were obtained at 1054 nm and a lower magnetic field is expected since the magnetised volume of our targets is larger. The magnetic field amplitude and decay time of ~ 30 ns are as expected from calculations presented in a previous paper, where we calculate a decay time of 25 ns⁷⁾. Measurement of electron temperatures shows agreement with accepted empirical models taking into account the laser conditions.

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Observation of hydrostatic-like shock compression in copper using *in-situ* X-ray diffraction from multiple crystal planes

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Introduction

Plastic deformation occurs in materials which are shock compressed beyond their Hugoniot elastic limit. The generation and motion of dislocations in the crystal structure are responsible for relieving the stresses that build up in the crystal, and consequently in plastic deformation. We are interested in studying the formation and motion of the dislocations and how these dislocations affect the crystal structure of a material.

The measurement and study of these dislocations associated with plastic deformation requires knowledge of the atomic positions. This can be done using x-ray diffraction. In this experiment we use *in-situ* x-ray diffraction to measure the compression of the unit cell while the crystal is being shock loaded¹⁾. Experiments of this sort require a large laser system such as the Vulcan laser to generate a large enough shock pressure to cause plastic deformation, and to simultaneously provide the x-ray backlighter for x-ray diffraction.

This report describes the preliminary analysis of data from an experiment using *in-situ* diffraction recorded on two wide angle film packs. The x-ray diffraction signal was measured in the Bragg and Laue geometry on wide angle film detectors²⁾. Using the diffraction from these two geometries hydrostatic-like compression is observed in a uni-axially compressed copper single crystal.

Background

There are different methods for inducing a shock wave in a solid material. In these experiments we use one beam of the Vulcan laser on a aluminized plastic coated crystal target. The hydrodynamic flow of plasma from the target will generate a shock wave into the target by conservation of momentum. The compression will be maintained as long as the drive lasers are producing plasma. Once the laser stops the pressure is released. While the laser is applying pressure the region between the compressed and uncompressed parts of the crystal is separated by a propagating shock wave. This shock wave will initially cause crystal compression along the direction of shock propagation. The compression along one of the axes in a crystal causes the generation of a large shear stress normal to the direction of shock propagation. If the compressing force is maintained long enough the shear stress will cause the atoms to compress in the lateral directions as well, leaving the crystal with the same crystal structure as the initial crystal except compressed in all three dimensions (Figure 1). This is called hydrostatic compression.

The time scale required to reach hydrostatic compression is material dependent. In this report we show that on the time scale of the experiment, 2 ns, we can observe the hydrostatic compression in a thin (10 μm) single Copper crystal.

Experiment

The experiment was performed in target area east of the Vulcan laser system. The main 6 beams were frequency doubled to 527nm and focused to a tight focal spot using f/10 lenses onto a copper backlighter foil. The He- α transition in the copper plasma from the backlighter foil produces 1.48 $\text{\AA}$ x-ray radiation. The copper crystal was shocked by a single backlighter beam with a maximum energy of 40J for a

maximum intensity of $1.6 \times 10^{11} \text{ W/cm}^2$. A varied shock pressure profile was generated on the crystal surface by placing a filter in the near field of the beam with the transmission shown in Figure 2. The beam was defocused such that the beam covered the entire crystal.

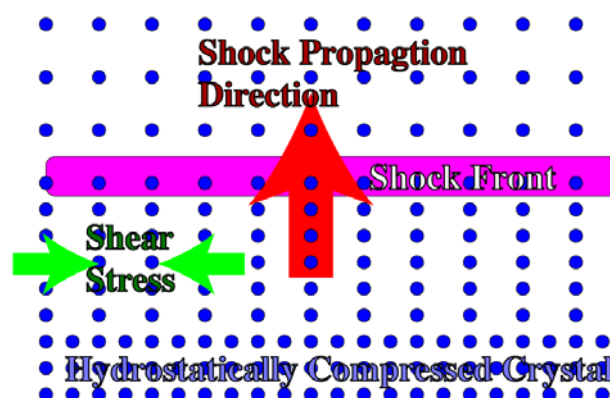


Figure 1. Schematic diagram of the propagation of a shock wave through a crystal and the eventual hydrostatic compression.

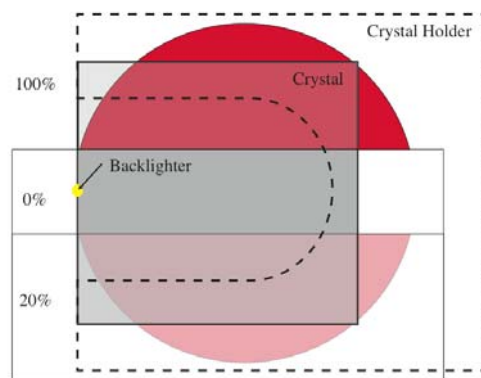


Figure 2. Schematic diagram of the shock intensity profile at the crystal, showing the outline of the crystal holder and the location of the backlighter.

The backlighter design is more complicated than ones used in the past because not only do we require a direct x-ray block for the Bragg film pack, but one for the Laue as well. This design uses an Ag-Pd (Silver Palladium alloy) tube outer diameter 1000 μm and inner diameter 800 μm to hold the backlighter foil, with a 25 μm thick gold shield providing protection for the Bragg film pack. The angle of the gold foil is set to 45° with respect to the backlighter foil, with the shape to the gold foil cut to give an edge near normal to the backlighter foil.

The crystal holder is designed to hold the crystal on three sides in a cut out hole similar to a horse-shoe. The crystal was 10 μm thick fixed by the corners in an aluminum mount, such that the

entire crystal is exposed to the shocking beam and the central 2x2 mm is open to the x-rays, Figure 2. The crystal and backlighter are held in separate mounts with six degrees of freedom each to allow flexible positioning of the x-ray source relative to the crystal.

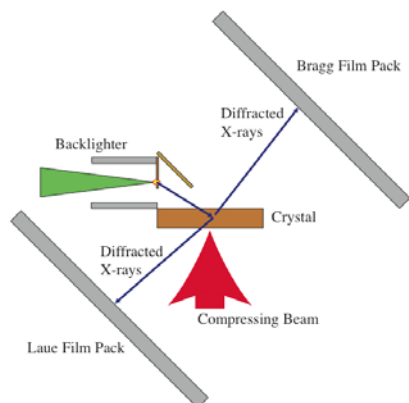


Figure 3. A schematic cross section of the target and diagnostic geometry.

The diffraction data was recorded on two film packs placed in the so-called Bragg (off the surface of the crystal) and Laue, (through the crystal) geometries. The Bragg geometry records diffraction from planes whose reciprocal lattice vectors are not parallel to the crystal surface, while the Laue geometry records diffraction from planes whose reciprocal lattice vectors are not normal to the crystal surface. Since both film packs cover a wide range of angles there will be multiple diffraction lines recorded on both. A schematic representation is shown in Figure 3, where in the real experiment the shocking beam was not normal to the surface. The two film packs record the diffraction signal on Fuji BAS-MS-type image plates.

Diagnostics

The main diagnostics were two wide angle film packs. The film packs consist of a large rectangular section and two triangular wings each. A single film pack covers an effective solid angle of π -steradians. Using a point x-ray source close to the crystal surface means that there will be a large range of incident angles of x-rays on the crystal. When these angles satisfy the Bragg condition,

$$\cos\theta = \frac{\lambda}{2d},$$

there will be a maximum in scattered intensity where θ is measured with respect to the crystal plane, λ is the wavelength of the diffracted radiation and d is the crystal plane spacing. Given that there are many different planes with different orientations and spacing in the crystal there will be many different lines from different conic sections in the plane of the film pack which satisfy the above condition.

In a previous report we discussed the importance of being able to know the orientation of the unshocked crystal to perform the data analysis³⁾. The varied shock front helps by providing a fiducial to orient the crystal with because that region will remain unshocked. Allowing diffraction measurements to be taken at later time, when potential the shock front has propagated to the end of the crystal and the diffraction from the unshocked crystal is too small to record.

Results

The diffraction from the central film pack for both the Laue and Bragg diffraction are shown in Figure 4. Both film packs show scattering from multiple diffraction plans, but on the Bragg pack the (002) plane is highlighted because it shows the

compression along the z-axis of the crystal, the direction of shock propagation. On the Laue film pack the (200) plane is highlighted because it shows the compression along an axis perpendicular to the direction of shock propagation. The filter on the shocking beam results in the uncompressed regions in the centre for the (002) and (200) planes. Analysis is still being undertaken to determine the amount of compression in the lateral direction, but it is obvious that over the time scale of the experiment that the crystal structure has under gone some hydrostatic compression due to the shear stresses in the crystal.

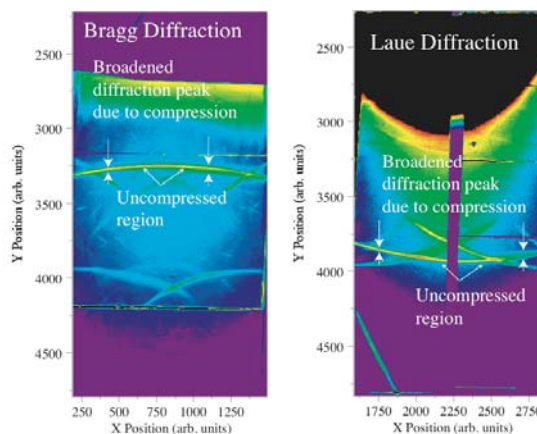


Figure 4. The central rectangular film pack from both the Laue and Bragg film pack. The 002 peak is isolated on the Bragg film pack while 200 is isolated on the Laue film pack.

Discussion

Using the two wide angle film packs makes it possible to study the plastic response of the crystal structure in multiple directions independently. The hydrostatic compression can be observed in different planes, ones where h,k,l are all non-zero, but the planes observed on the different film pack simultaneously give a measurement of the compression in two perpendicular directions. As the results are analyzed for these different planes we will gain a better understanding of the change in the crystal structure as it undergoes plastic deformation. With the establishment of this technique it will be possible to test different materials for their response to uniaxial shock compression.

Acknowledgements

We would like to thank the staff of the CLF at the Rutherford Appleton Laboratory for their help in making this experiment possible, and in particular Martin Tolley and Donna Shepherd for their work in manufacturing and dealing with our difficult targets.

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Preliminary investigations into the magnetic field topology of multiple-beam produced plasmas

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Introduction

The realization of inertial confinement fusion has been the primary motivation behind the investigation of plasma interactions with high-power, nanosecond pulse duration lasers for over thirty years¹. Inertial confinement fusion relies upon the rapid implosion and low-entropy compression of a thermonuclear fuel pellet. Central to the conventional *indirect* drive approach is the use of a laser heated, high-Z cavity - or hohlraum². The high-Z walls of the hohlraum allow the efficient conversion of laser energy into soft x-rays. The enclosed cavity rapidly forms a thermal radiation field sufficient for the ablation and compression of a centrally located fuel pellet.

Designs for ignition scale hohlraums include a low-Z gas fill to tamp the expansion of the laser-irradiated walls. Laser beams propagate through the gas-fill and deposit most of their energy into the hohlraum walls. The pressure of the heated gas prevents the walls from expanding and maintains a symmetrical radiation drive. Electron temperatures, though, of a few keV are expected with mean-free-paths of the order the hohlraum dimensions itself, capable of preheating the fuel pellet. The heat carrying electrons will also be strongly magnetized by the $\nabla T_e \times \nabla n_e$ magnetic fields that are convected into the gas.

The role of non-local electrons, self-generated magnetic fields and heat transport inhibition³ are important considerations in tuning the hohlraum environment for ignition.

Studying the hohlraum environment is complicated by its enclosed geometry, making diagnostic access troublesome. Investigations of laser-solid interactions with planar and curved targets in *multiple-beam* geometries on the Vulcan laser facility, though, can offer an approximate yet accessible environment for the study of hohlraum relevant physics.

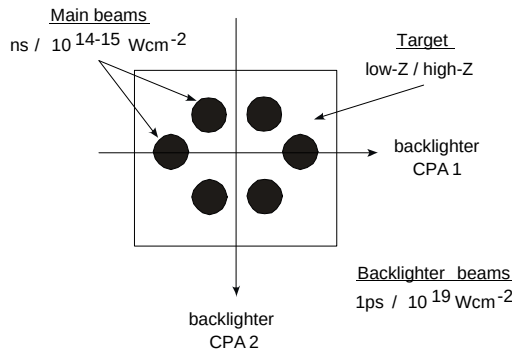


Figure 1. Approximating the hohlraum environment with the Vulcan laser system.

The Vulcan laser has the attractive capability of combining up to six, nanosecond pulse duration beams in a cone-cluster configuration at an intensity $\sim 10^{14-15} \text{ Wcm}^{-2}$ with a short, picosecond pulse duration CPA beam ($\sim 10^{19} \text{ Wcm}^{-2}$) for backlighting. The long pulse beams can somewhat approximate the hohlraum geometry in a planar hexagonal pattern and be simultaneously backlit from two orthogonal directions by splitting the CPA beam into two, Figure 1. The split CPA beam provides high spatial ($10 \mu\text{m}$ focal spot) and temporal resolution

for a range of simultaneous backlighter options, including x-rays, protons and electrons. Long scale-length plasmas can be simulated in front of the target with a gas jet.

Important questions about the role of self-generated magnetic fields in thermal transport, inner-wall interactions and inter-streaming plasma flows can be investigated in such an open geometry that provides excellent diagnostic access.

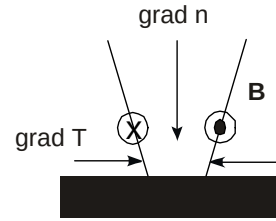


Figure 2. The $\nabla T_e \times \nabla n_e$ mechanism generated from a laser-solid interaction.

During the interaction of a single, nanosecond pulse duration laser ($\sim 10^{14-15} \text{ Wcm}^{-2}$) with a solid target, high-temperature blowoff plasma rapidly forms. Magnetic fields generated in the near-collisionless corona and the innermost dense, collisional plasma affect the transport of energy and the growth of instabilities⁴. In laser-solid interactions, the dominant source of magnetic fields is non-parallel density and temperature gradients, Figure 2. This arises from the electron pressure gradient, $\nabla P_e = -n_e e E$, where $P_e = n_e k_B T_e$, and Faraday's

Law, $\frac{\partial \bar{B}}{\partial t} = -\nabla \times \bar{E} \therefore$

$$\frac{\partial \bar{B}}{\partial t} = \nabla \times \left(\frac{\nabla P_e}{n_e e} \right) = \left(\frac{k_B}{n_e e} \right) \nabla T_e \times \nabla n_e \quad (1)$$

Megagauss level magnetic fields attributable to the $\nabla T_e \times \nabla n_e$ mechanism have been previously inferred experimentally in the corona of single ns-beam, laser-produced plasma from the Faraday rotation of an off-harmonic optical probe⁵.

The thermal plasma pressure dominates the hydrodynamic expansion of the blowoff plasma. The ratio of the thermal and magnetic pressure is defined by β :-

$$\beta = \frac{P_T}{P_B} = \frac{(n_e k_B T_e)}{(B^2 / 2\mu_0)} \approx 4 \left(\frac{n_e}{10^{20} \text{ cm}^{-3}} \right) \left(\frac{T_e}{\text{keV}} \right) \left(\frac{\text{MGauss}}{B} \right)^2 \quad (2)$$

For the blowoff plasma, $\beta > 1$, though the magnetic field *can* play a role in the plasma evolution by magnetizing the electrons. The Hall parameter, $\omega_c \tau_e$, quantifies the affect of the magnetic field on electron transport :-

$$\omega_c \tau_e = 0.6 \left(\frac{10}{Z} \right) \left(\frac{10^{20} \text{ cm}^{-3}}{n_e} \right) \left(\frac{10}{\log \Lambda} \right) \left(\frac{T_e}{100 \text{ eV}} \right)^{3/2} \left(\frac{B}{\text{MG}} \right) \quad (3)$$

where τ_e is the electron collisional time and $\omega_c = \frac{eB}{m_e}$ is the electron cyclotron frequency. When the Hall parameter is greater than one, the thermal conductivity $\kappa \approx (1 + \omega_c^2 \tau_e^2)^{-1}$ is reduced, affecting the temperature distribution. For megagauss magnetic fields, $\omega_c \tau_e > 1$ when $T_e > 500\text{eV}$ and $n_e > 10^{20}\text{cm}^{-3}$. Hydrodynamics, x-ray emission, parametric instabilities, filamentation and laser beam propagation are all affected by the change in the electron energy distribution.

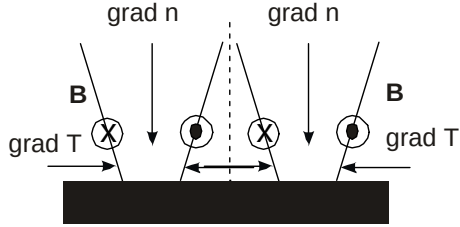


Figure 3. The $\nabla T_e \times \nabla n_e$ mechanism generated from a laser-solid interaction with two beams.

This report describes preliminary results relevant to our studies of multiple-beam produced plasma. The measurements presented here are of the magnetic fields generated by two long pulse (nanosecond duration) beams focused within a few spot diameters of each other on a solid target, Figure 3.

Of particular interest is the plasma evolution in the region between the two focal spots where the blowoff plasmas interact, marked in Figure 3 by the dashed line. Recent experiments by Beg *et al.* report studies of plasma formation between two parallel wire z-pinch⁶. Instability generation in the central plasma column ($m=1$) was observed, indicative of current transfer from the wires to the central plasma.

Experimental Details

The experiment was conducted in Target Area East at the Rutherford Appleton Laboratory and used the Vulcan Nd:glass laser (1054nm) facility. For ease of diagnostic access, the targets were 1.3mm diameter Al wires mounted vertically upon brass stalks. The target chamber was configured in a frequency doubled (527nm) six beam, f/10 cone-cluster orientation with a 13° half-angle. Only two of the main six beams were used in this experiment. The two beams (200J per beam in ω , 1ns square pulse and typical irradiance of $5 \times 10^{13}\text{Wcm}^{-2}$) were focused upon the target with spot diameters of approximately 20 μm and a vertical separation that varied between 50-100 μm , Figures 4 and 5.

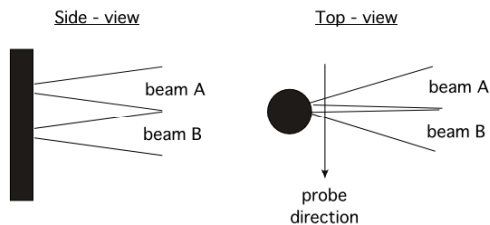


Figure 4. The target configuration and beam alignment.

The principal diagnostic used was a polarimetry channel measuring the Faraday rotation of a linearly polarized, frequency quadrupled (263.3nm, 80J in ω , 100ps duration) probe beam. The magnitude of the angle through which a linearly polarized probe beam is rotated due to the Faraday effect is given by:-

$$\theta_{\text{rot}} [\text{rad}] = 2.6 \times 10^{-17} \lambda_p^2 \int_0^L n_e \bar{B} d\bar{l} \quad (4)$$

where L is the path-length traversed by the probe inside the plasma (cm), B is the magnetic field (G), λ_p is the probe wavelength (cm) and n_e is the electron density (cm^{-3}). The probe beam will be rotated through an angle of the order of a few degrees due to magnetic fields in the megagauss range.

The probe beam was limited to approximately 5cm in diameter by an aperture and passed across the target in a direction orthogonal to the two main beams. A 30cm focal length lens was used to image the target interaction on a 16bit Andor CCD. The lens was placed a distance equal to its focal length away from the target. The total magnification and resolution of the imaging system was of the order of 1.5x and 15 μm . A polarizer (P1) and analyzer (P2) were placed before and after the interaction, respectively. A combination of neutral density filters and a 4 ω interference filter were used after the analyzer to reduce the detectable self-emission from the target.

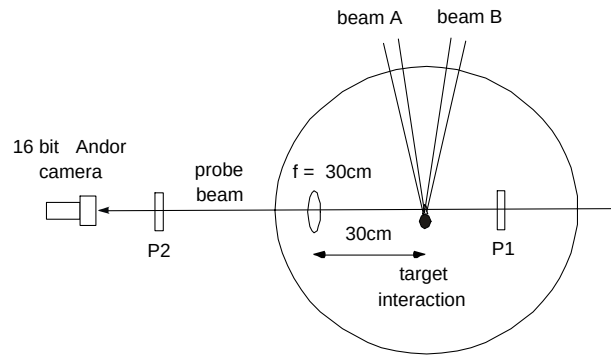


Figure 5. The experimental configuration.

Experimental Results

Figures 6, 7 and 8 are polarograms taken at varying intervals in time after the laser beams first strike the wire surface (time, t_0). Figure 6 shows the extent and evolution of the plasma produced from the interaction of the two laser beams with the wire at ($t_0 + 400\text{ps}$) with the analyzer at an angle of 6°.

The green horizontal lines indicate the positions of the focal spots of the two laser beams, propagating from the lower edge of the image to the top. At ($t_0 + 400\text{ps}$) the plasma has combined into a hemispherical structure with an asymmetry point appearing at the position marked A. Four regions of varying brightness are identifiable in the polarogram along the curve BC, two on either side of the cusp, indicative of magnetic fields. Growth of the plasma structure has occurred to a distance of approximately 100 μm implying an expansion velocity of the order of $2.5 \times 10^7\text{cms}^{-1}$.

The region, D, is inaccessible by the probe. The probe beam was limited to the periphery of the expanding plasma to densities $< 10^{20}\text{cm}^{-3}$ due to refractive effects and limitations in the acceptance angle of the imaging lens. The ring structures surrounding the expanding plasma are due to diffractive effects.

Figure 7 is a polarogram taken at ($t_0 + 450\text{ps}$) with the analyzer at an angle of 10°. The cusp has begun to evolve separately from the two blowoff plasmas on each side and exhibits, compared to the surroundings, a well-localized, bright spot.

The polarogram in Figure 8, taken at ($t_0 + 500\text{ps}$) with the analyzer at an angle of 10°, shows the growth of a region of plasma expulsion. In this image, the right blowoff plasma has dominated the evolution of the left blowoff plasma, accounting for the asymmetry in the ejecta. The velocity of the plasma flow being ejected in the blue region is of the order of $(6.0 \times 10^7) - (8.0 \times 10^7)\text{cms}^{-1}$.

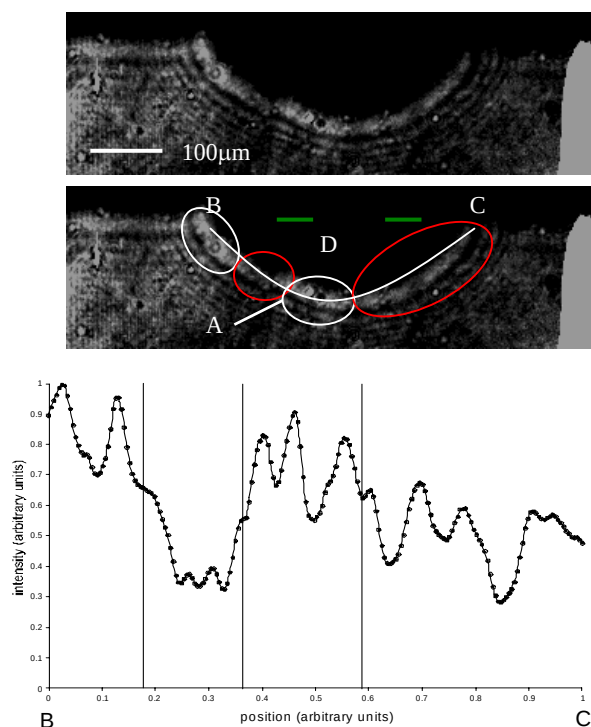


Figure 6. A polarogram taken at $(t_0 + 400\text{ps})$. The lineout is taken along the curve BC. (The white region on the right of the image is filter damage).

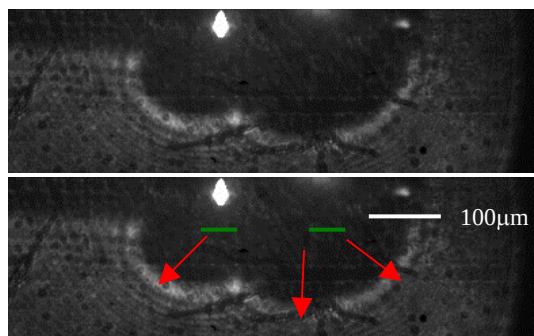


Figure 7. A polarogram taken at $(t_0 + 450\text{ps})$.

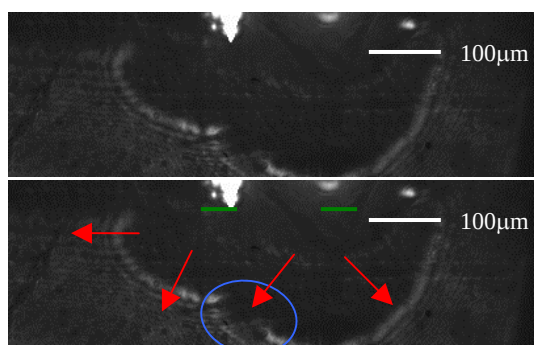


Figure 8. A polarogram taken at $(t_0 + 500\text{ps})$. (The lower edge of the image is just below the extremities of the CCD chip).

Discussion

We have undertaken preliminary investigations into the interaction of merging blowoff plasma generated from two laser spots in a solid-target interaction. A region of plasma ejecta has been observed. The open question concerns the origin of this ejected plasma. Is it a result of the interaction between the two ablating plasmas that form a shock? Is it directly related to the reorientation of the magnetic field topology during the spatial and temporal evolution of the combining plasma? Or could it be a combination of the two to some extent?

Further interrogation of the multiple-beam produced plasma environment is required to be conclusive, particularly in the vicinity between the two laser spots, of the source of the plasma ejecta, and improve the signal-to-noise measurements from the polarograms and quantify the magnitude of the magnetic fields.

Acknowledgements

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High efficiency K-alpha production with second harmonic light on Astra

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Introduction

Short bursts of K- α emission from solid targets continue to be of significant interest to researchers¹⁻⁸⁾. This interest is in part driven by the potential of these sources to be generated with sub-picosecond duration²⁾. The efficiency of such sources (typically 10^{-6} - 10^{-3}) may be attributed primarily to the distribution of hot electrons generated at the front plasma surface of the target in the presence of the incident laser beam. The generation of hot electrons and their energy distribution in turn depends on several parameters that include target material and surface properties, laser beam intensity, pulse length, pre-pulse level, wavelength, polarization and angle of incidence. The experimental results and the Monte-Carlo simulation reported by Eder et al.³⁾ demonstrate an optimum value for the Cu K- α production as a function of the incident intensity. The theoretical model of Reich *et al.*²⁾ also suggests an optimal hot electron temperature for efficient generation of K- α photons. Our own previous work⁹⁾ with p-polarised 800nm radiation showed conversion efficiencies of $\sim 10^{-4}$ into Ti K-alpha photons, in broad agreement with others. However, in a recent small study with 400nm radiation that was designed originally to look at the thermal He-like line radiation we noticed significant conversion to K-alpha radiation. Although facility access time limited us to a relatively small data set of ~ 50 shots we present here a conclusive result that high K-alpha yield can be generated with frequency doubled light. An additional bonus was that the spectra were generated with a much lower background of hard x-rays.

Experimental arrangements

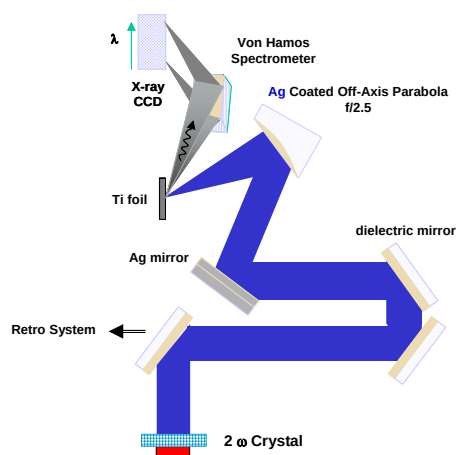


Figure 1. Schematic of experiment. The three dielectric mirrors dump the IR energy effectively.

The experiments (shown schematically in Figure 1) were carried out at the Rutherford Appleton Laboratory using the Ti:Sapphire based CPA system, Astra, delivering up to 150mJ on target in infrared (800nm), p-polarized pulses of 45($\pm$ 5)fs duration. In addition to the pre-pulse activity at ~ 13 ns ahead of the main pulse and having a contrast of 10^{-7} , the main pulse is superimposed on a residual uncompressed CPA pedestal and ASE. The contrast of the residual uncompressed pedestal is measured to be 10^{-6} at 10ps and rises to 10^{-4} at 1.5ps ahead of the main pulse. The ASE starts 2ns ahead of the main pulse and

rises linearly from a background of 10^{-8} of the main pulse to a level of 10^{-6} in 1ns and then stays constant until the main pulse arrives. In this experiment we made the pulse high contrast by using an 0.8mm thick type-I KDP crystal to convert the IR beam into second harmonic, 400nm (blue), S-polarised pulses. A beam splitter reflecting the blue and transmitting the IR, is used at 45° to relay the blue beam onto the target. The IR part of the beam was dumped at the back of the splitter. Two dielectric mirrors in the beam-path further reduced the IR component on target. Such a conversion immensely reduces the level of pre-pulse activity as well as the ASE and the CPA pedestal and a relatively clean pulse interacts with the solid target. The conversion efficiency to blue was about 20% and in excess of 30mJ was achieved on target. Evidence of solid density interaction was seen in the presence of emission of Li-like satellites to the He-alpha line as seen below. This is never seen in the 800nm case since the beam interacts with a low density pre-plasma and there is simply not enough time for ionization to reach this stage before the expansion and subsequent cooling of the plasma.

An f/2.5 off-axis silver-coated parabola was used to focus the 400nm beam at an angle of 20°-45° normal to the target plane. Focal spots at different positions were recorded in the low energy mode of the laser with the help of a retro-system making use of a leakage through one of the turning mirrors inside the interaction chamber. The full width at half maximum (FWHM) of the focal spot at the best focus, shown in Figure 2, was measured to be $\sim 5\mu\text{m} \times 5\mu\text{m}$. The FWHM contains about 57% of the total energy. This compares with the IR spot, which (using a gold f/2.5 parabola) gave a $3\mu\text{m}$ FWHM containing 55% of the energy. However, the blue beam spot was less uniform and contained hotspots as shown in Figure 2. The focal spot was varied by moving the parabola off the best focus position along the line-of-focus by a known amount with the help of a micro-controller, towards the target and away from the

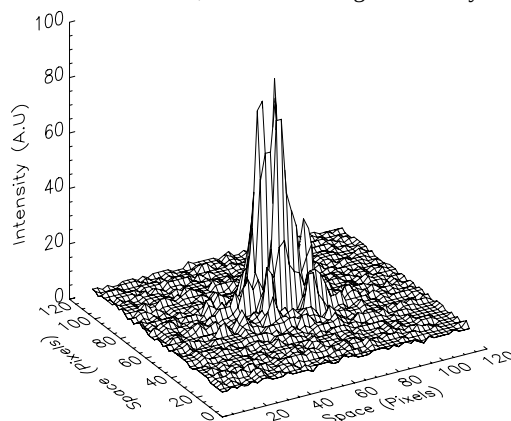


Figure 2. Beam Spot at Best Focus. Frequency doubled (400nm), 45fs (low energy mode) FWHM is 12pixels x 13 pixels (5.25micron x 5.68micron). Energy content in the FWHM is 55%.

target (referred to as positive off-set and negative off-set respectively). With the positive off-set a convergent beam interacts with the target while in the case of the negative off-set

the focus lies before the target and a divergent beam interacts with the target. As we go away from the best focus, the focal spot starts breaking up into numerous hotspots and, therefore, the energy distribution in the focal spot changes. The IR energy was monitored for every shot with a calibrated fast diode and this was cross calibrated with the blue energy at target focus using an energy meter. The maximum energy recorded on target was $\sim 37\text{mJ}$. At the best focus, the intensity on target reaches a maximum of $\sim 2 \times 10^{18} \text{W/cm}^2$ in blue.

Ti foils having thickness of $12.5\mu\text{m}$ were used as the target. After every shot, the foil was moved by 1mm with an external computer controlled micro-drive to get a fresh surface of the target for the laser interaction. In all cases, the beam was tight focused on the foil, using the retro viewing system, before moving the parabola to the desired offset position. A thin glass pellicle was used in front of the target to protect the parabola from the plasma debris. The time integrated K- α line emission of titanium (4510.84eV), was recorded with a Von Hamos (VH) spectrometer coupled with an x-ray CCD system⁹⁾ employing a curved LiF (200) crystal with a reflectivity of 0.042mRad . The He-like $1s^2-1s2p$ 1P line at 4.75keV was also within the spectral range of the spectrometer. The line of sight of the spectrometer (crystal centre and the source position) made an angle of $\sim 48^\circ$ with the horizontal plane.

Results

Figure 3 shows the absolute K- α yield for 400nm irradiance on bare Ti targets at 45° and 20° angles of incidence as a function of focus position. Most data points are an average of 3 shots and the error bars are the statistical error.

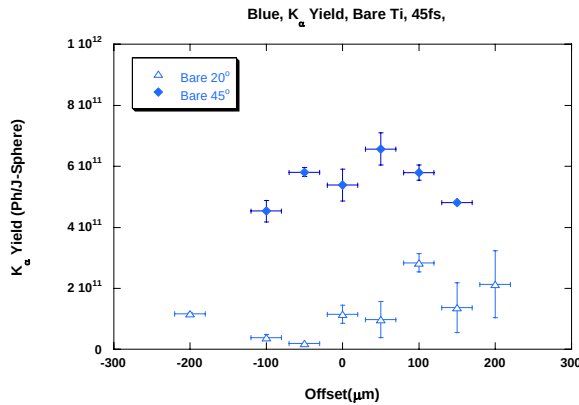


Figure 3. Yields of K-alpha for 400nm s-polarised radiation as a function of offset.

The error bar in the focal position is $\pm 20\mu\text{m}$. The most striking thing is that in the 45° case the blue light is 5-6 times more efficient in terms of photons/J/sphere than the P-polarised IR light⁹⁾. For the 20° case there is a much smaller difference between the blue and IR peak yield.

In the spectra gathered in this experiment there is always a background level on the CCD. Since magnets and lead shielding on the housing did not noticeably reduce this, we surmise that it is due to hard X-rays from the target causing fluorescence on the crystal. This was much less significant for the 400nm case, as may be expected. Figure 4 shows a spectrum from 400nm irradiance. We can note the emission lines, which are identified as Li-like satellites to the He-like $1s^2-1s2p$ 1P line. As we have stated before, this helps to confirm that the blue beam indeed interacts with a solid surface.

Discussion

Apparently we have a slightly puzzling situation. The 400nm beam is s-polarised and due to the spot size, energy and wavelength, $I\lambda^2$ is less than the 800nm case by a factor of ~ 40 .

Fast electron production and subsequent K-alpha emission is expected to be much less efficient than for the p-polarised 800nm case. Modelling with the HYADES hydrodynamic code¹⁰⁾ which incorporates a wave-solver routine, indicates absorption of $\sim 10\%$ which is broadly comparable to the data of Price *et al.*¹¹⁾ for Cu and Al targets at normal incidence.

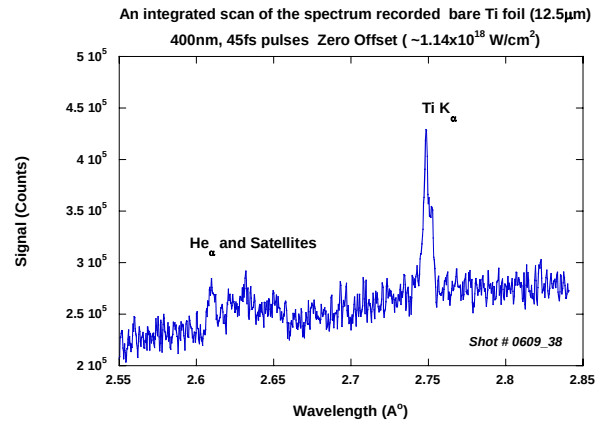


Figure 4. Spectrum taken with 400nm beam, integrated over 10 rows on the CCD.

In order to give an explanation of our data we propose two possible explanations. In the first model, we assume that at the tight focus, with a non-uniform focal spot, that the effective polarisation may not be so well defined. This means that a certain percentage of the light may be converted to fast electrons via resonance absorption in the steep gradients. For the 10% absorption case above, the scale length at the peak of the pulse is calculated to be $\sim 50\text{nm}$ and so $L/\lambda \sim 0.125$.

We further assume that the electrons created by resonance absorption stream into the target with a 1-D Maxwellian distribution and estimate the hot electron temperature given from the experimental data of Nishimura *et al.*¹²⁾:

$$T_{\text{hot}} = 29(I/10^{17} \text{Wcm}^{-2})^{0.74} \quad (1)$$

We also assume that a hot electron of a given energy E (in keV) creates K- α photons according to the data for Ti of Green and Cosslet¹³⁾:

$$N_{\text{gen}}(E) = 4 \times 10^{-5} (E - E_0)^{1.63} \quad (2)$$

where E_0 is the K-shell ionisation energy. We neglect absorption effects as we have a relatively thin foil. By combining Equations 1 and 2 in a numerical calculation we can estimate that a yield of $\sim 6 \times 10^{11} \text{ph/J/sphere}$ is possible with 20% of laser energy transferred to hot electrons.

There are other scaling laws for hot electron temperature for sub-picosecond pulses^{2,12,16)}. These tend to give temperatures for our irradiance of $50\text{--}150\text{keV}$. These are generally either calculated or experimentally determined for first harmonic radiation in pre-formed plasmas and so which best suites the case of a frequency doubled beam hitting a solid surface is not clear. We can estimate the range of the electrons in the foil due to electric field inhibition using the equation below, which comes from the work of Bell *et al.*¹⁴⁾ and is presented in this form by Pisani *et al.*¹⁵⁾:

$$z = 3 \times 10^{-3} \sigma T_h^2 (f I / 10^{17} \text{Wcm}^{-2})^{-1} \mu\text{m} \quad (3)$$

where σ is the conductivity in $10^6 \Omega^{-1}\text{m}^{-1}$, f is the fraction into fast electrons and T_h is in keV. We find that for cold Ti, the range at $T_{\text{hot}} = 150\text{keV}$ is about equal to the foil thickness and thus for all the cases considered we do not expect many electrons to escape the rear surface and re-enter by being pulled back by electrostatic forces.

This model has the merit of allowing enough K-alpha production and the angular variation is expected since the simulated scale length dictates a significant rise in absorption as we go to higher angle, as seen experimentally. However, the precise mechanism by which the polarisation becomes mixed is uncertain. The targets are quite smooth on the wavelength scale as evinced by the fact that they are quite mirror-like. The generation of large magnetic fields in such short scale-length high intensity interactions is quite well known and perhaps they may affect the laser polarisation, although this would have to happen on the timescale of the laser pulse itself and seems a little unlikely at first glance.

In our second model, we assume that ponderomotive heating is the responsible mechanism. The energy of an electron ejected from the focal spot region is given by, for example, Amiranoff¹⁷⁾ as

$$U \sim 1\text{MeV} (I\lambda^2/10^{19} \text{ Wcm}^{-2}\mu\text{m}^2) \quad (4)$$

This means for our peak irradiance we have an effective hot electron temperature of $\sim 120\text{keV}$, enough to create our K-alpha signal if again about 10% of energy is absorbed in this way. The reason for the difference between the two angles of incidence would need to be explored more fully with a 2-D consideration.

As stated, we have simulated the interaction of the laser with the foil using the HYADES hydrodynamic code. This code uses the SESAME equation of state library and a Helmholtz wave solver routine to calculate the absorption. From this we estimate the absorption is 10% and that the plasma temperature rises to about 1.5keV , not enough for significant fast electron numbers to penetrate into the cold solid. For p-polarised an absorption of $\sim 20\%$ is predicted and the heated region is wider but at similar temperature. This solver does not of course give resonance absorption heating results. By post-processing the hydrodynamic data with a 1-D time dependent collisional radiative model we can predict the emission of the He-like lines and their satellites. This is illustrated in Figure 5, where we can see that the FWHM of the emission is predicted to be very short ($\sim 0.2\text{ps}$) but there is a significant tail of emission lasting over 1ps .

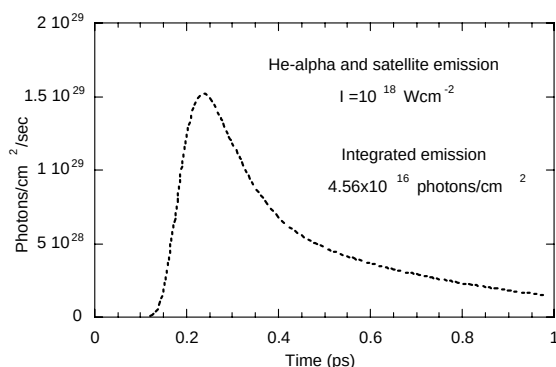


Figure 5. Predicted emission history of He-alpha and satellites for 400nm irradiation.

The overall emission yield is predicted to be $\sim 6.5 \times 10^{11}$ photons/J which is about a factor of 2-3 higher than seen experimentally.

Acknowledgements

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Ultrafast dissociation of H_2^+ as compared to the ionisation and dissociation of H_2

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Introduction

The hydrogen molecular ion is the simplest of all molecules, and thus attractive from a theoretical standpoint as the Schrodinger equation may be solved, even in the intense electric fields generated in a laser pulse¹⁾. Experimentally, however, the hydrogen neutral molecule (H_2) is far more appealing, given the ease in which it may be prepared as a target. As a consequence, a limited number of experiments have been performed on an H_2^+ target^{2,3)}, as compared to a plethora in the case of an H_2 target. Irrespective of the target however, a number of complex phenomena have been observed in the molecular hydrogen system, including bond-softening⁴⁾, bond-hardening⁵⁾, laser-induced reorientation⁶⁾ and Coulomb explosion from a critical internuclear separation⁷⁾.

The accepted mechanisms for the laser- H_2 interactions can be summarised by the following steps:

- | | | |
|----|-------------------|--|
| 1) | Ionisation | $\text{H}_2 \rightarrow \text{H}_2^+$ |
| 2) | Dissociation | $\text{H}_2^+ \rightarrow \text{H} + \text{H}^+$ |
| 3) | Coulomb Explosion | $\text{H}_2^+ \rightarrow \text{H}^+ + \text{H}^+$ |

Step 2 can be subdivided, according the net number of photons absorbed, or by the vibration levels from which H_2^+ dissociates:

- | | |
|-----|----------------------------|
| 2a) | One-photon / $\nu = 5 - 9$ |
| 2b) | Two-photon / $\nu = 0 - 4$ |

Theoretical treatments of the dissociation of H_2 have invoked the principle of light-dressed potentials (LDPs), alternatively referred to as light-induced potentials. The lowest order bound $1\sigma_g$ and unbound $2p\sigma_u$ states of the H_2^+ molecular ion are dressed by the field, and the adiabatic avoided crossings define the dissociative pathways, see the theoretical review of Giusti-Suzor and co-workers⁸⁾ for discussions.

In the following report, the ionisation and subsequent dissociation of the neutral hydrogen molecule will be investigated using Intensity Selective Scanning (ISS) coupled with a deconvolution technique, allowing for the focussing of a slightly diffracted (i.e. non-Gaussian) laser pulse. New experimental results are presented, where the variation the amount of ionisation generated by the distribution of laser intensity throughout the interaction region is removed: volume-independent ionisation of a molecule is observed for the first time. Furthermore the direct dissociation of an H_2^+ molecular ion is measured. These experiments employ a novel experimental technique, where the step-1 ionisation rate is matched in linear and circular polarisations by varying the relative intensities of the light. Clearly this ionisation rate can only be matched in the case of an H_2 target – we only measure the dissociation of H_2^+ , and exclude the Coulomb explosion by detecting the neutral fragment. It is also acknowledged that the ionisation mechanism may be dependent on polarisation, however, we have found this to be an informative tool in the case of atomic ionisation⁹⁾, justifying its application to a molecular system. It is also stressed that this article presents very recent data, and as a consequence, the analysis presented is preliminary.

Experimental

The experiments are performed using TA1 of the Astra Laser Facility, which provides 50 fs 790 nm laser pulses at a repetition rate of 10 Hz and typical pulse energy of 25 mJ. These laser pulses are f/11 focussed into the interaction region of either the UCL time-of-flight mass spectrometer (TOFMS), or the QUB plasma-discharge ion beam and parallel plate system (PDIB). Both experimental systems are described in detail in this⁹⁾ and previous CLF Annual Reports¹⁰⁾, thus for brevity will be omitted. By employing both time-of-flight mass spectroscopy and ion beam techniques, we are afforded the ability to compare the response of neutral and ionic targets to identical focal conditions, thus the $\text{H}_2 / \text{H}_2^+$ system is chosen for its bearing as a simple molecular system.

The processes under consideration require focussed laser intensities between 10^{13} and 10^{15} Wcm^{-2} , affording new experimental freedom, as the 50 fs laser pulses from the Astra facility need only be loosely focussed to generate peak intensities in excess of 10^{17} Wcm^{-2} . Intensities of the order of 10^{13} Wcm^{-2} are generated over ± 10 mm either side of the focus. Sub-millimetre spatial restrictions in both experimental systems then allow the intensity at which the interaction occurs to be precisely defined through Intensity Selective Scanning¹¹⁾. In the case of the TOFMS, a 0.25 mm aperture performs intensity selection; in the PDIB the finite width (< 0.9 mm) of the ion beam defines the effective aperture.

A PC-based data acquisition is employed with both systems, where the optical conditions are defined by computed controlled wave-plates and lenses. The PC also controls the 10% intensity-gated shot-to-shot averaged data collection through a Tektronix TDS-744A Digital Storage Oscilloscope, and storage over the local area network.

Data Processing

Following the collection of a series of spectra as a function of lens position (focal detuning), it is necessary to remove the effect on the signal of the variation of confocal volume with lens position. This is performed through a development of the method suggested by Walker and co-workers¹¹⁾, and will be discussed in a future publication. In essence, the volume-free intensity dependence of the ionization / dissociation processes is deconvoluted from the raw ISS data by generating an on-axis intensity distribution $I(z)$, then performing a series of numerical differentials of both the ISS signal and $I(z)$.

Given that the diameter of the temporally compressed Astra beam is comparable to that of the final transmission optics (a pair of retardation plates), the laser focus is Gaussian only to a first approximation due to the effects of diffraction. When a comparison is made between the ISS data and theoretical predictions resulting from a Gaussian focus, the differences are negligible. However, as the deconvolution technique relies on the differential of both the signal and intensity distributions, any difference is unacceptable. As a consequence, a new analytical technique has been developed which allows the on-axis intensity of the focussed laser beam to be calculated for an arbitrary ABCD optical system. Importantly, the ingoing laser

beam distribution and final limiting aperture are taken into account, resulting in a physically realistic $I(z)$, where diffracted or non-Gaussian focussing are possible. The volume-independent intensity response can now be measured through a coupling of deconvolution and an analytical optical model, the results of which are presented in the following section.

Results

I. $H_2 \rightarrow H_2^+$: observation of ionisation mechanisms

In step 1 the electron may be removed from the neutral molecule by three different mechanisms, namely multiphoton, tunnelling or field ionisation. Keldysh¹²⁾ originally defined the adiabaticity parameter, γ such that:

$$\gamma = \frac{\omega}{\epsilon} \sqrt{2E_i} \quad (1)$$

where ω and ϵ are the frequency and magnitude of the electric field generated by the laser, and E_i is the ionization potential of the target. Using the refined definition of Illkov and co-workers¹³⁾ a distinction may be made between these ionisation mechanisms depending on γ : the optical period of the light field is compared to the time for the electron to tunnel through the modified Coulomb potential into the continuum. If the tunnelling time is much less than the period of the light field, ionisation progresses via the non-resonant absorption of multiple photons via a laser-induced ladder of virtual states (Step 1a), when $\gamma > 0.5$. If the tunnelling time is comparable to the frequency of the light causing the reaction, the electron departs the molecule by tunnelling directly to the continuum (Step 1b), traditionally defined as $\gamma < 0.5$. Furthermore, if the frequency of oscillation of the light is slow enough, the electron undergoes field ionisation (Step 1c). For a fixed wavelength, such as that found in the present work, the intensity of the pulse defines the type of ionisation.

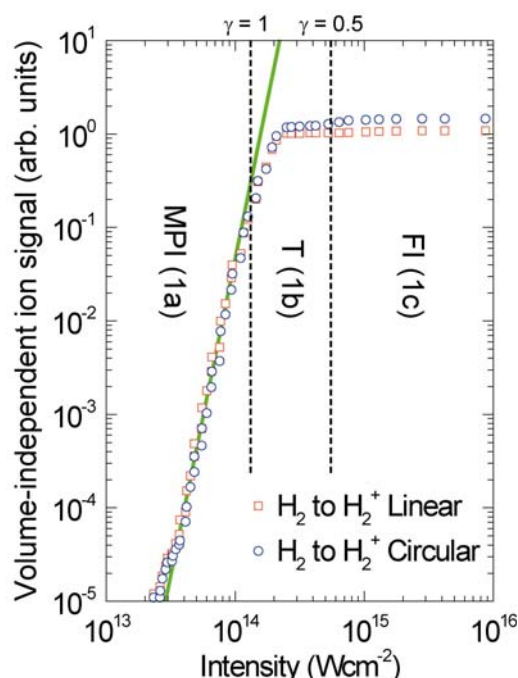


Figure 1. Volume-independent matched ionization-rate of H_2^+ from a H_2 gas target. The laser intensity has been adjusted to make the ionization rates for linear and circular polarizations comparable. The different ionization mechanisms are indicated 1(a-c), and are discussed in the text. The green line indicates ionization through the absorption of seven photons.

In Figure 1, these three different ionisation mechanisms are demonstrated. Starting at the lowest intensity, ionisation into H_2^+ appears at an intensity of $2.5 \times 10^{13} \text{ Wcm}^{-2}$, and proceeds via the multiphoton route up to an intensity $\sim 1 \times 10^{14} \text{ Wcm}^{-2}$, after which the tunnelling mechanism becomes more dominant, indicated by the deviation of the slope from linear. Above an intensity of $\sim 3 \times 10^{14} \text{ Wcm}^{-2}$, the laser intensity is sufficient to field ionise the molecule directly, hence the intensity dependence saturates, as all molecules exposed to this intensity are ionised. The boundaries indicated by the vertical dashed lines on Figure 1 ($\gamma = 0.5$ and $\gamma = 1$) appear to define the character of the ionisation of H_2 rather well, given that γ is defined in terms of ionisation potential. As a consequence, γ is a zero range potential, and does not take into account the length of the molecular bond. Despite the well-known approximate nature of the Keldysh parameter, it is clearly an informative guide to the origin of the hydrogen molecular ion when generated by a laser pulse. It is suggested that the ionisation mechanism of H_2 can therefore be redefined as MPI if $\gamma > 1$, tunnelling if $0.5 < \gamma < 1$ and field ionisation if $\gamma < 0.5$.

Importantly, it is possible to closely match the ionisation rate of $H_2 \rightarrow H_2^+$ over almost an order of magnitude in laser intensity and five orders of signal strength. The agreement between the circular and linear signal in Figure 1 only appears to separate at an intensity $> 2 \times 10^{14} \text{ Wcm}^{-2}$. At these intensities, dissociation via step 2 or Coulomb explosion via step 3 are expected to dominate.

An interesting conclusion from Figure 1 is that the multiphoton ionisation of H_2 does not appear to proceed through the absorption of nine or more photons as expected from the ionisation potential, rather seven photons appear to be sufficient to ionise the molecule. The underlying mechanism is probably a Stark-shifting process.

II. $H_2 \rightarrow H_2^+ \rightarrow H + H^+$: dissociative processes

Following the application of the deconvolution technique, the volume-independent response of $H_2 \rightarrow H_2^+$ (ionization rate matched linear-to-circular) followed by either dissociation ($H_2^+ \rightarrow H + H^+$) or Coulomb explosion ($H_2^+ \rightarrow H^+ + H^+$) is presented in Figure 2. As three different processes are presented (steps 2a, 2b and 3), step 2a is normalised to 10^2 , step 2b to 10^1 , and step 3 to 10^0 for the sake of clarity. In all cases, there is no normalisation of the signal strength between the linear and circular polarisation. It is therefore interesting that the one-photon process (step 2a) is almost polarisation independent, indicated by the similarity of signal strength over a large dynamic range. In Figure 2, the magenta line is a best fit to the signal in the multiphoton regime between the appearance of the signal and the point at which the H_2^+ data deviates from a linear response (Figure 1). The slope of this line indicates the absorption of eight photons, a remarkable fit given that step 1 has been observed to require seven photons, followed by one-photon dissociation. For the sake of comparison, the thin green line is the best fit to the H_2^+ step, as presented in Figure 1, and is clearly not in agreement with the data in the MPI region in Figure 2. At an intensity $\sim 10^{14} \text{ Wcm}^{-2}$, there is a decline in the quality of agreement between the data and the best fit line, an indication that the tunnelling process is increasing in strength. The deviation is larger than that in the case of the H_2^+ , indicating that the tunnelling process is involved not only in the generation of the molecular ion, but the dissociation as well.

As is apparent in Figure 2 from almost an order of magnitude difference in signal, the response of the two-photon dissociative process (step 2b) is strongly polarisation dependent. The orange line in Figure 2 is a best-fit to the two-photon signal for linear polarisation in the multiphoton regime. As with the one-photon process, seven-photon (green line) absorption does not agree well, rather the orange line is nine-photon absorption, continuing the remarkable agreement between this data and

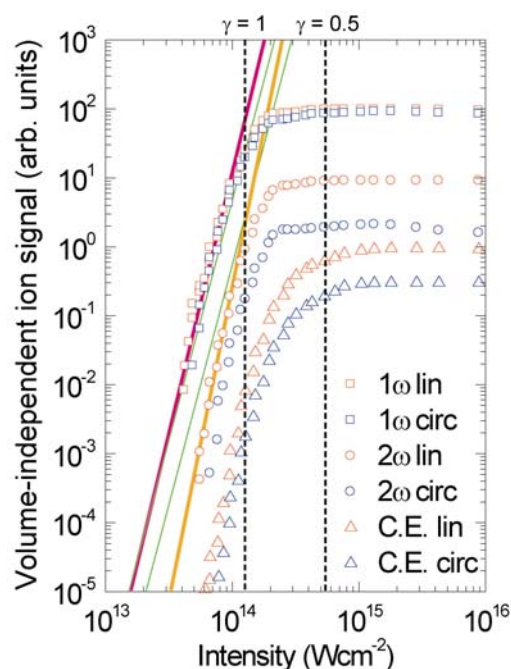


Figure 2. Volume-independent H^+ signal from one- and two-photon dissociation and Coulomb explosion of H_2^+ generated in a laser field. The vertical black dashed lines delineate the same ionisation regions as Figure 1, and the green lines have the observed slope of the 1a process. The magenta and orange lines are best-fits to the multiphoton region of the one- and two-photon signal respectively.

predictions from light-dressed potentials. Clearly there is major physical significance to the difference between the linear and circular polarisations, given the agreement presented in steps 1 and 2a. Although a preliminary analysis, it is suggested that this may be due to a combination of some type of polarisation sensitive ionisation / dissociation process such as rescattering¹⁴ and laser-induced reorientation⁶.

III. $H_2^+ \rightarrow H + H^+$: kinetic energy of dissociation

As informative as the data presented in Figures 1 and 2 clearly is, the ISS data is integrated at each focal position, hence information about the kinetic energy release is lost. To investigate the kinetic energy dependence with intensity, two surface plots are presented in Figure 3 for the reaction $H_2 \rightarrow H_2^+ \rightarrow H + H^+$, where the kinetic energy of the H^+ fragment is measured for (a) linear and (b) circular polarisation. Figure 3(c) illustrates the variation of on-axis laser intensity with focal detuning, allowing a comparison to be made with Figures 1 and 2. In converting from time-of-flight to dissociation kinetic energy in the centre of mass frame, flux conservation must be observed, the effect of which is to emphasise the low energy signal with respect to the high energy processes. Also, the same ionisation rate matching technique has been applied between linear and circular polarisations as with the data presented in Figures 1 and 2.

Comparing Figures 3(a) and (b), using (c) as a reference, the following observations are made regarding the dissociation of laser generated H_2^+ . A pair of processes are present: a low energy (peaked at 0 eV) and intermediate energy (peaked between 0.2 and 0.8 eV) peak is observed in both cases, attributed to one- and two-photon dissociation. The one-photon process manifests with almost identical distributions in kinetic energy and focal detuning, in agreement with Figure 2. The two-photon process shows a marked difference however: linear polarisation, Figure 3(a), is far more efficient at dissociating the molecule through this route. There is also a small polarisation dependence evident from the small increase in the dissociative

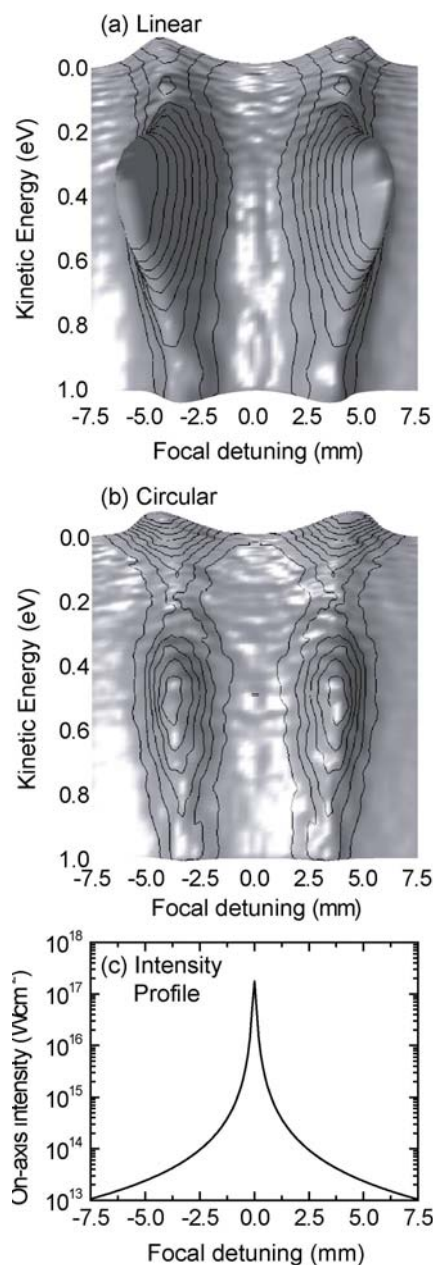


Figure 3. H^+ from laser generated H_2^+ for (a) linear and (b) circular polarisations.

kinetic energy between linear to circular. Also, in the circular case in particular, there is evidence of the kinetic energy of dissociation being loosely intensity dependent, indicated by the gradual shift of the two-photon peak to smaller focal detuning with increased kinetic energy.

The valley in the signal corresponding to zero focal detuning is the result of the cross-section of the confocal volume decreasing to the beam waist, thus illustrating the necessity of applying the non-Gaussian focussing deconvolution.

In stark contrast to Figure 3, Figure 4 is a pair of surface plots of the kinetic energy and focal detuning variation of the signal of H from the dissociation of a beam of H_2^+ as measured with the PDIB apparatus for linear and circular polarisation. As with the TOF data presented in Figure 3, a transformation is required between the laboratory time-of-flight frame to the centre-of-mass dissociation kinetic energy, via the fragmentation velocity in the lab frame. This conversion also includes flux conservation. The most striking difference between Figures 3 and 4 is the far broader range of laser intensities over which the dissociation signal is measured, a consequence of the molecule

being prepared in an ionised state. The dissociation therefore need only overcome the nuclear binding energy. There are important similarities as well – the distribution of signal irrespective of kinetic energy around the ‘valley’ around zero focal detuning is very similar to that observed with the laser generated H_2^+ in Figure 3, despite the circular signal, Figure 4(b), not quite falling to zero as in the linear case. This implies that above saturation in the dissociative processes, $2 - 3 \times 10^{14} \text{ Wcm}^{-2}$, results presented in Figure 2, the behaviour of $\text{H}_2 / \text{H}_2^+$ is similar, as we would expect. Another similarity is that there is a major enhancement of the dissociation signal for linear polarisation as compared to the circular case.

We now move on to the most important difference between Figures 3 and 4: the massive discrepancy between the distribution of kinetic energy. Rather than two well-separated peaks, a broad range of kinetic energies are observed, ranging from 0 eV to ~ 0.7 eV. There is some evidence that there are two processes generating the H signal in the circular case, Figure 4(b): the low energy peak at ± 5 mm is separate from the more energetic (~ 0.2 eV) peak centred around ± 12 mm. With

this in mind, the linear, Figure 4(a) distribution could be due to two processes. Firstly, a low energy peak around ± 5 mm, analogous to the one-photon peak in Figure 3 is seen, along with a second, more energetic component around 10 - 15 mm, peaked around 0.2 eV. The enhancement of the linear signal is therefore due to an intermediate intensity ($10^{13} - 10^{14} \text{ Wcm}^{-2}$) process appearing between 5 - 10 mm.

Conclusion

A deconvolution routine has been applied to the laser-induced ionisation and dissociation of the hydrogen molecule for the first time, aided by a new analytical model of focused, diffracted Gaussian laser beams. An interesting insight into the different ionisation mechanisms has been presented, based on the Keldysh parameter, allowing multiphoton, tunnelling and field ionisation to be clearly identified. The influence of these processes on the subsequent dissociation of the laser generated H_2^+ ion have also been presented, illustrating one- and two-photon absorption, along with an increase in the amount of tunnelling observed in the dissociative channel. The kinetic energy of the dissociative products has also been compared for H_2^+ generated in a laser field and a plasma discharge source and significant differences observed. The analysis of the presented data is ongoing.

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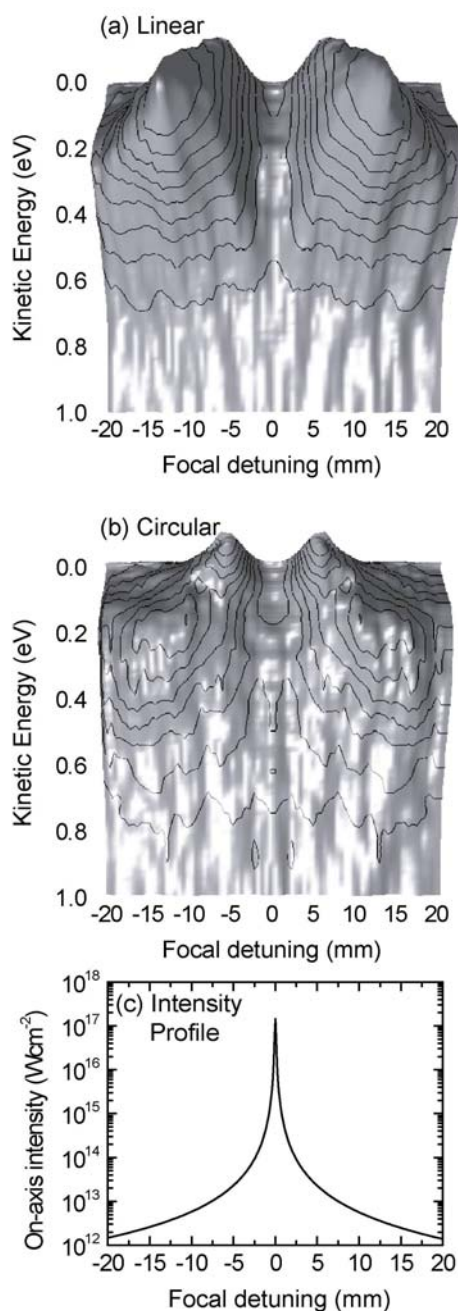


Figure 4. H from a beam of H_2^+ for (a) linear and (b) circular polarisations.

Observing momentum and intensity selective processes in the ultrafast ionisation of carbon dioxide

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Introduction

Ultrafast laser-matter interactions have been studied in physics, chemistry and materials research, and have led to the discovery of interesting multiphoton and nonperturbative effects. These include above threshold ionisation and dissociation, and the study of high-order harmonic generation. Long-term goals of research include the generation of attosecond laser pulses and coherent control: the ability to control atoms and molecules with light.

Results from the ionisation of CO₂ in an intense laser field are presented here, collected using an intensity selective scanning technique¹. Although some other studies of CO₂ exist^{2,3,4,5}, shown here is a first analysis of new results from the molecule, including a study of O²⁺ production.

Experimental Configuration

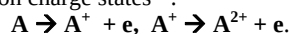
A time-of-flight mass spectrometer (TOFMS) was used to measure ionisation resulting from the intense laser field. The laser is focussed into the TOFMS interaction region, from which the ions are extracted via a positive potential and accelerated into a 110mm drift tube. Ions are then detected by a pair of channel plates, and can be identified by their mass to charge ratio. The TOFMS has a Wiley-McLaren geometry⁶, ensuring that the total flight time for ions is independent of initial position within the interaction region. This configuration permits good energy resolution of the numerous ion fragments, although the spatial resolution is reduced. The design also incorporates an aperture before the detector, to limit the spatial acceptance region to a 0.25mm slit, giving spatial resolution.

The laser used was the Ti:Sapphire (55fs, 790nm, 10Hz) at RAL (UK) Astra, with a focussed peak intensity of $8 \times 10^{16} \text{ Wcm}^{-2}$ and Rayleigh range 0.234mm. Intensity selective scanning was achieved by translating the focussing lens (f/11) along the beam propagation axis, moving the entire confocal volume through the interaction region. As the lens is moved, a different slice of the confocal volume and therefore a different intensity is exposed to the detector.

Ionisation of CO₂

In Figure 1, the different charge states resulting from ionisation of CO₂ in a linearly polarised laser field can be seen as the confocal volume is scanned past the detector. There is evidence of Coulomb explosion, a high kinetic energy release mechanism describing the electrostatic repulsion between the resulting nuclei when a molecule is ionised. If Coulomb explosion occurs parallel to laser polarisation and detector axis, forwards (f) and backwards (b) peaks will be formed. Middle peak (m) ions detected between the f and b peaks are due to low energy photodissociation processes.

The multiphoton ionisation of CO₂ occurs via the sequential production of ion charge states⁷:



However, non-sequential ionisation ($A \rightarrow A^{2+} + 2e$) has also

been observed over a small, low intensity range. The current explanation for this mechanism is the Recollision model⁸.

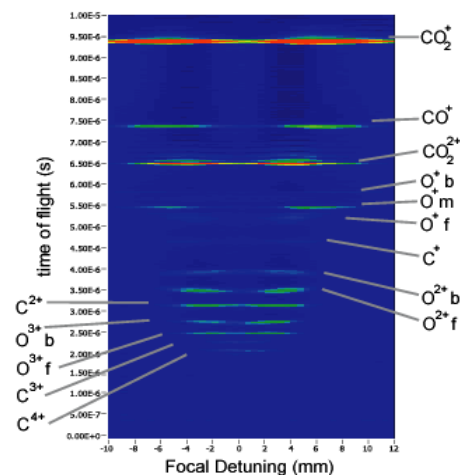


Figure 1. Time of flight z-scan matrix showing ion fragments.

In this model, the electron initially tunnels through the modified Coulomb potential, and is accelerated away from the ion by the laser field. As the field reverses during the next half-cycle of the pulse the electron is driven back, ionising the parent ion again. Clearly, the laser field must be linearly polarised to propel the electron back in the same direction. By comparing the data taken with linearly and circularly polarised laser fields, it can be seen if recollision effects are occurring. The lower signal detected for linear polarisation as shown in Figure 2 may indicate recollision leading to non-sequential ionisation.

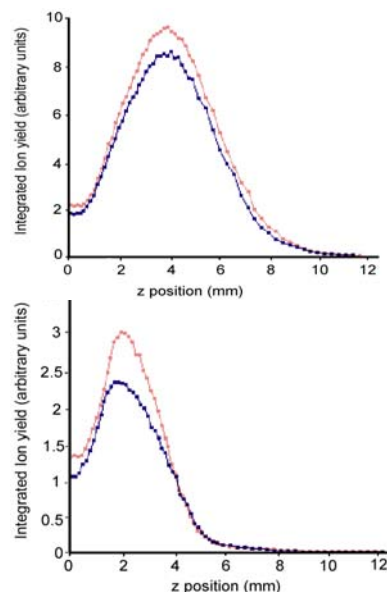


Figure 2. Comparison of data taken with linearly (blue) and circularly (red) polarised laser fields.

O²⁺ Production from CO₂

In a diatomic molecule there are few ionisation channels, which can be observed on a time of flight spectrum⁹. In the complex triatomic case there are many more possible channels, which can lead to overlapping. Intensity selective scanning permits resolution of the numerous ionisation channels in terms of their individual momentum and on-axis intensity.

Working from zero momentum time of flight (the central time of flight between the O²⁺ f and b peaks formed due to Coulomb explosion), the signal is converted into momentum using the equation $\mathbf{P} = qE\Delta t$.

The most probable channels can then be identified as ridges in momentum. These are labeled on the surface plots below, each with their exact momentum and transition energy. On-axis intensity can be obtained from the z position value.

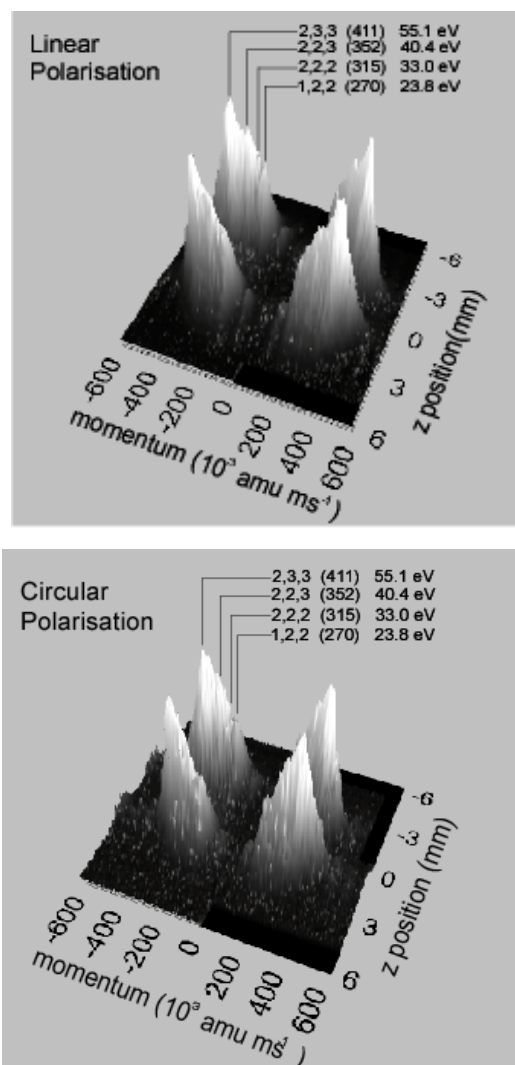


Figure 3. Surface plots of O²⁺ production from CO₂ showing signal in terms of momentum and z position (focus is at z = 0). High probability ionisation channels are labeled.

Conclusions

The plots show results for linear and circular polarisation, the ionisation rates having previously been matched. A comparison reveals lower signal overall for the circular data, (the same background noise appearing higher on this plot). This is as expected, considering the fact that molecular re-orientation is not observed in a circular field (laser-induced reorientation aligns the molecule so that it is parallel to the laser polarisation direction). The ion fragments resulting from Coulomb explosion are therefore less likely to reach the detector, producing a reduced signal.

The most probable ionisation channels are clearly visible as ridges in momentum, but slight shifts can be detected when the field polarisation is changed. The 2,2,3 channel at 352 10³ amu ms⁻¹ becomes less prominent in the circular plot, and a lower probability channel starts to appear (2,3,2 at 371 10³ amu ms⁻¹). Also, the lower momentum channel at 270 (1,2,2) appears to be enhanced by a circular field.

This may be an indication of different ionisation processes occurring, for example it is possible that the enhancement of the 1,2,2 channel is due to an increase in low energy photodissociation. Work is in progress to interpret the full significance of these surface plots and the differences that have been observed. Further analysis may include comparisons with covariance mapping techniques¹⁰, and the calculation of exact intensities, rather than using on-axis intensity represented by z position.

Analysis of the results from ionisation of the parent molecule shown in Figure 2 is also in progress. The ionisation rates for linear and circular polarisation were previously matched (to account for the lower electric field strength for linear polarisation), so the fact that fewer ions reach the detector in a linearly polarised field suggests that there may be ions remaining in the interaction region undergoing non-sequential ionisation. Recollision effects are usually observed at the outer edge of the CO₂²⁺ graph (~6mm) as an increase in linear signal. It is not clear from the graph if this is occurring; although the linear signal appears to be slightly higher than the circular, the difference may not be significant. Further stages of analysis will be required to reach a definite conclusion.

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Nonsequential dissociation of N_2^+ via ultrafast strong laser field ionization of the N_2 molecule

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Introduction

The observation of enhanced ion yields in the double and multiple ionization of atoms¹⁻³) has been the topic of exciting new studies into intense laser field physics in recent years. Continuing experimental tests investigating the fundamental mechanism responsible for this nonsequential ionization stands to provide a greater understanding of the primary role of the parent atom and the initially removed electron in this ionization process. Such nonsequential ionization has also been reported for simple molecular targets⁴⁻⁶).

Whilst several models have been put forward as to how the nonsequential process proceeds, the model that generally holds most precedence is the recollision model. This model predicts a strong laser field ellipticity dependence and with this in mind we report on the double ionization of N_2 with direct comparison made between using linearly and circularly polarized laser fields. The added complexity of this diatomic system over a simple atomic structure makes it an interesting target to study because not just pure ionization but also dissociative ionization may proceed via a number of channels.

Experimental Method

The apparatus⁷) used for this experiment was a Wiley-McLaren-type⁸) time-of-flight mass spectrometer (TOFMS), which could also be operated in a spatially resolved geometry setup. It consists of a vacuum chamber with a background pressure of about 2×10^{-10} mbar into which Nitrogen gas may be introduced via a hypodermic needle. Following the focusing of the laser into this interaction region, product ions are extracted by a weak electric field through a 0.25 mm aperture to maximise spatial resolution. In the Wiley-McLaren-type setup the ions first pass through a field-acceleration region before drifting in a field-free region through to the detector. This setup has a desired focusing effect such that ions of the same mass/charge ratio and same initial momentum reach the detector simultaneously independent of the initial position of their production within the interaction volume. This allows good energy resolution of the forwards and backwards peaks produced from the Coulomb explosion channels of the molecule. The signal from the microchannel plate detector is fed into a fast digital storage oscilloscope with the time-of-flight information recorded allowing time resolution of the different product ions.

The source of the femtosecond laser pulses used for this experiment was the RAL (UK) Astra laser facility. This system, manipulating the CPA of the output of a 790 nm Ti:Sapphire laser system, generates 55 fs pulses, with an energy of 22 mJ per pulse, at a repetition rate of 10 Hz. The 22 mm diameter laser beam is focused into the interaction region by a 25 cm focal length spherical lens to give a peak focal intensity in excess of 4×10^{16} Wcm⁻². Utilizing the Intensity Selective Scan (ISS) technique^{9,10}), the ionization signal as function of axial position, z , with respect to the centre of the laser focus is measured. In this way we probe the ionization dynamics through different intensity slices of the confocal volume, with the added advantage of volume enhanced signal at the low

intensity regions. A 10 % gating is placed on the pulse energy so that any large shot-to-shot deviations are discarded. A quarter waveplate is also used to switch between linearly and circularly polarized light with the linear polarization direction aligned along the detector axis.

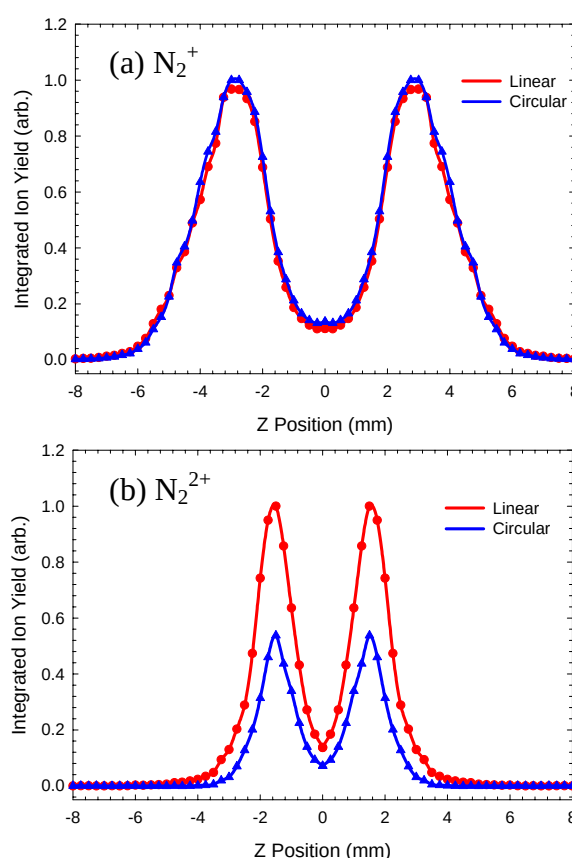


Figure 1. ISS signal measured as a function of focusing lens position, with respect to spectrometer axis, for linear (red curve) and circular (blue curve) polarizations (a) N_2^+ production and (b) N_2^{2+} production from the target N_2 molecule.

To carry out this experiment using a molecular target, the system required operation in Wiley-McLaren mode to obtain good resolution of forward and backward dissociation peaks. However, the difficulty which manifests itself in using the Wiley-McLaren setup is that information on the intensity distribution within the confocal volume is lost due to the lensing-like effect. In the Spatially resolved geometry mode, which is similar to Wiley-McLaren but without the added field-acceleration region, the intensity distribution of the interaction volume as a function of axial z -position from the centre of focus may be determined. Hence to calibrate the system we first introduced a simple atomic element, Ne, into the system and performed an ISS using both setups. The atomic target does not have the complication of dissociation peaks thus permitting a

direct mapping of the intensity scale from the Spatial to the Wiley-McLaren mode.

Results and Discussion

The direct comparison between using linearly and circularly polarized laser fields for the single and double ionization of the parent N_2 molecule is shown in Figure 1. The ion signal which is obtained through charge integration over the relevant time-of-flight window is plotted on an arbitrary scale. To compare these two extremes of ellipticity, the input pulse energy of the linearly polarized pulses is 0.63 that of the circularly polarized pulses. This slight deviation for molecular targets from the matching factor we have determined for atomic targets¹¹⁾ of 0.65 is detected through the extreme sensitivity to the confocal intensity distribution of the Intensity Selective Scanning technique. The general shape of the ISS curve for N_2^+ is typical for this technique where increased signal (despite decreasing intensity) either side of the focal centre ($z = 0$ mm) is representative of enhanced volume. The N_2^+ signal drops off at the extreme ends of the focus ($z > 6$ mm) where the intensity has decreased dramatically.

In the single ionization of the N_2 molecule, ionization will only proceed via a sequential process as only a single active electron is involved. Thus no distinct differences are anticipated between linearly and circularly polarized fields. Figure 1(a) shows the N_2^+ production from N_2 and it conforms to this expected behaviour. However it is clear from Figure 1(b), that over the entire N_2^{2+} production range, the linearly polarized laser field enhances the N_2^{2+} signal by about a factor of two and this can be attributed to nonsequential ionization. It has recently been shown¹²⁾ through electron momentum correlation experiments that such nonsequential double ionization of N_2 may be explained by the recollision model. Following ionization of the first electron, it returns to the ionic core upon reversal of the oscillating linearly polarized electric field. Over a number of laser cycles, the electron may collide with the core electron resulting in the double ionization of the parent molecule. With circular polarization this effect is reduced as the initial electron is driven away from the core region.

C.E. peaks	Channel	Dissociation mechanism	KER/ion (eV)	
			Expt.	Calc.
N^+	(1,1)	$N_2 \rightarrow N^+ + N^+ + 2e^-$	3.8	6.6
	(1,2)	$\rightarrow N^+ + N^{2+} + 3e^-$	7.5	13.1
N^{2+}	(2,1)	$N_2 \rightarrow N^{2+} + N^+ + 3e^-$	7.8	13.1
	(2,2)	$\rightarrow N^{2+} + N^{2+} + 4e^-$	14.6	26.3
	(2,3)	$\rightarrow N^{2+} + N^{3+} + 5e^-$	20.9	39.4
N^{3+}	(3,2)	$N_2 \rightarrow N^{3+} + N^{2+} + 5e^-$	22.5	39.4
	(3,3)	$\rightarrow N^{3+} + N^{3+} + 6e^-$	30.8	59.1

Table 1. Coulomb Explosion channels identified from the dissociative ionization of N_2 . KER denotes the Kinetic Energy Release to each fragment ion for the given channels (experimental and calculated values).

The resolution of the TOFMS system is sufficient to temporally resolve the different Coulomb explosion channels through their time-of-flight (TOF). These dissociation channels for N^+ , N^{2+} and N^{3+} are described in Table 1. Also given in Table 1 are the Coulomb explosion energies per fragment ion for each of these channels. These are determined from the kinetic energy release in both the forwards and backwards direction along the detector axis through the TOF of the ion. As a comparison, the calculated theoretical energy release per ion within an electrostatic interpretation based on the molecular ion

dissociating with its fragment ions separated by the equilibrium distance is shown in the column adjacent to the experimentally determined values. It is clear that the experimentally determined energy release is consistently almost a factor of 2 less than the theoretical values for dissociation at the equilibrium separation. This would suggest that the molecules in fact dissociate at approximately twice their equilibrium bond length, which is in good agreement with previous experimental findings and predictions¹³⁾.

Figure 2(a) shows a plot of the TOF spectra for the N^{2+} signal as a function of z position (i.e. with respect to focus). There are three distinctly observable channels as indicated in Table 1. The shift of the N^{2+} channels towards higher intensity (i.e. towards $z = 0$ mm) for increasing channel order is consistent with the increase in the kinetic energy release through Coulomb explosion. For example, the (2,3) channel requires the highest ionization stage of the initial N_2 molecule (removal of five electrons) and thus is observed closest to the centre of the focus. When it Coulomb explodes via $N^{2+} + N^{3+}$, the repulsion between these ions is greater than for (2,1) and (2,2) channels thus releasing greater energy in the N^{2+} fragment. A similar effect is apparent in the N^{3+} forward and backward peaks, Figure 2(b). The two channels observed are given in Table 1 with again the shift of the (3,3) channel towards higher intensity consistent with the increased Coulomb explosion energy. There is good agreement between the Coulomb explosion energy per fragment ion determined from the N^{2+} forwards/backwards (2,3) channel and the N^{3+} (3,2) channel, as one would expect since upon dissociation both ions share the explosion energy equally. The same is found with the N^+ forwards/backwards (1,2) channel and the N^{2+} (2,1) channel. The (1,3) channel is not observed in either the N^+ or N^{3+} forwards/backwards peaks as this is a less energetically favoured explosion channel than the (2,2) channel.

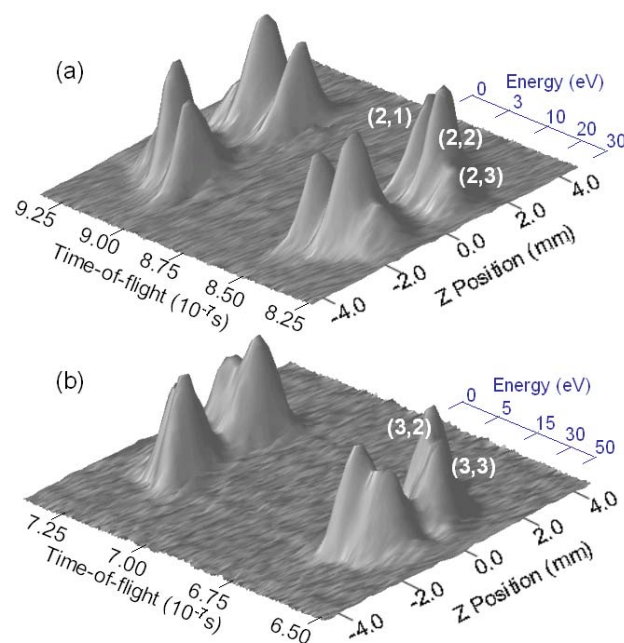


Figure 2. Time-of-flight spectra as a function of focusing lens position, with respect to spectrometer axis, using linearly polarized pulses for the Coulomb explosion channels of (a) N^{2+} and (b) N^{3+} via the dissociative ionization of N_2 .

Over and above the observation of the various Coulomb explosion channels of the nitrogen molecular ions, a weak dissociation peak of the N_2^+ ion via the (1,0) channel is also detected. This appears in the N^+ signal. From the TOF information for this ion, this channel proceeds with a dissociation energy of 0.9 eV. Of particular interest is the

comparison of the signal from this channel using linearly and circularly polarized light, see Figure 3. As the N_2^+ ion is produced by single ionization of N_2 , then no nonsequential effects, highlighted by the linear-circular comparison, are expected as was indicated by Figure 1(a). Hence when this ion dissociates one also would not expect to observe any difference in the linear and circular signal. This however is not the case as Figure 3 clearly shows.

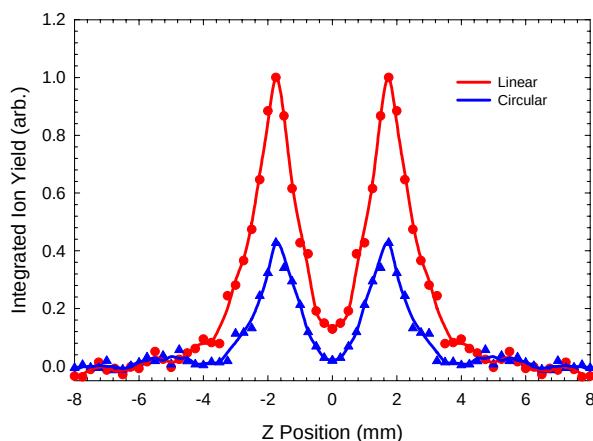


Figure 3. ISS signal measured as a function of focusing lens position, with respect to spectrometer axis, for linear (red curve) and circular (blue curve) polarizations for $N^+(1,0)$ dissociation channel from the target N_2 molecule.

The large difference between the linear and circular polarizations appears to be the signature of nonsequential dissociation of N_2^+ . In the analogous situation to the nonsequential ionization of N_2^+ , the first electron is removed from the parent N_2 target, producing N_2^+ . When the oscillatory linearly polarized laser field reverses its direction and drives this electron back, it can collide with the N_2^+ ion. Instead however of knocking free a secondary electron, thus ionizing it, it provides the energy to induce dissociation of the N_2^+ molecular ion. We hence observe a difference in the linear-circular signal as we did for N_2^{2+} production, Figure 1(b). We believe this to be the first observation of nonsequential dissociation of a molecular species in intense laser fields.

Conclusions

The intense field ionization of the simple diatomic molecule N_2 has been probed using linearly and circularly polarized laser pulses. A large enhancement of the double ionization of the parent molecule is observed and this is indicative of nonsequential ionization believed to proceed via recollision of the first removed electron with the newly formed molecular ion. Moreover, enhanced dissociation of the N_2^+ ion with linearly polarized pulses is also observed. This likewise is believed to occur via the recollision of the initially ionized electron. The different Coulomb explosion channels have also been identified and the kinetic energy release upon their dissociation is determined.

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Precise comparison of atomic ionization in linearly and circularly polarized intense femtosecond laser fields

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Introduction

The development of strong-field atomic and molecular physics has come through several distinct phases, characterized by the available intensity of lasers at the time. The electric field strength in the current phase of intense short laser pulses exceeds the Coulomb field strength binding atomic electrons. This gives rise to many interesting features in their interaction with atoms, molecules and ions. One such feature, non-sequential (NS) multiple ionization under the influence of elliptically polarized laser fields, is the subject of considerable contemporary interest¹⁻⁴. L'Huillier *et al.*⁵ first suggested the possibility of NS ionization following the observation of a much higher yield of multiply charged ions than expected according to a simple sequential ionization model.

The study of the influence that the polarization of the laser field has on the degree of NS ionization has been instrumental in determining the exact mechanism for this process. The most successful model in accounting for polarization effects has been the re-scattering model proposed by Corkum *et al.*⁶. It is well established that the NS ionization rate is much higher for linearly polarized light compared to circular, for which it is suppressed⁷⁻¹². However, to our knowledge, no one as yet has determined a precise value for the linear-circular laser intensity ratio at which the ionization rates for pure sequential tunnelling are the same. In fact, it is often assumed that by matching the peak electric field component for both polarizations (i.e. a linear-circular intensity ratio of 0.5) an adequate comparison may be made. As the non-sequential ionization process only begins after the removal of the first electron, it is important to perform the experiments with the laser intensities matched for both polarizations to give the same ionization rate for the sequential process, so that one can compare quantitatively the non-sequential component. In this report, we present a precise value for the matching linear-circular intensity ratio for the first time, and through intensity selective scanning¹³ we carry out an experimental study of both atomic and ionic Xenon targets interacting with intense ($\sim 10^{17}$ W/cm²) ultra-short laser pulses. Whilst experiments on gas targets have been carried out for some time, it is only recently that intense ultra-short laser pulses have been used with pre-ionized targets in the form of an ion beam¹⁴.

Experiment

A beam of Xe⁺ ions, was extracted from a discharge ion source and momentum selected by a bending magnet. The beam was then further focused and transported into a differentially pumped chamber to a diameter of 0.8 mm FWHM at the point of interaction with the laser beam. Following laser interaction, electrostatic fields were used to separate the initial and product ion beams. A channel electron multiplier was used to detect the product ions and the primary ion beam was collected in a Faraday cup. In a parallel experiment using the same laser conditions, Xe gas was effused into the vacuum chamber of a second instrument (TOFMS) via a hypodermic needle and the product ions extracted through a 0.25 mm aperture and detected using conventional time of flight techniques.

The laser system used in these experimental studies was the RAL (UK) Astra Ti:Sapphire laser (790 nm) utilizing chirped pulse amplification (CPA) with 50 fs pulse duration, 10 Hz repetition rate and 20 mJ per pulse. With an initial beam diameter of 22 mm, this was focused into the interaction region via a 25 cm focal length lens. A half-wave plate was used to attenuate the laser energy to suit our experimental requirements and a quarter-wave plate was used to change linear polarization to circular polarization or vice-versa. To reduce the effects of spatial averaging over the laser focus volume we used the restricted volume technique (Intensity Selective Scan, ISS). The interaction volume was defined by the aperture for the neutral gas experiment and by the beam diameter for the ion experiment. In this way, we limit the volume from which signal is collected. The lens was translated perpendicular to the aperture so as to probe the interaction at different intensity slices of the confocal volume. Pulse integrity was monitored using a frequency resolved optical gating technique and shot to shot fluctuations discriminated at a 10 % level.

Results and Discussion

In principle the normal sequential ionization of atomic targets is independent of the polarization of the external electric field. For a quantitative comparison of any non-linear differences that may arise through using linearly and circularly polarised pulses one must first match the ionizing rates in the direct sequential channel. A quasi-static tunnelling model, ADK¹⁵, which is based on the original formulations of Perelomov *et al.*¹⁶, predicts the strong field tunnel ionization rates of single and sequential multiple ionization as a function of field strength, including polarization ellipticity dependence.

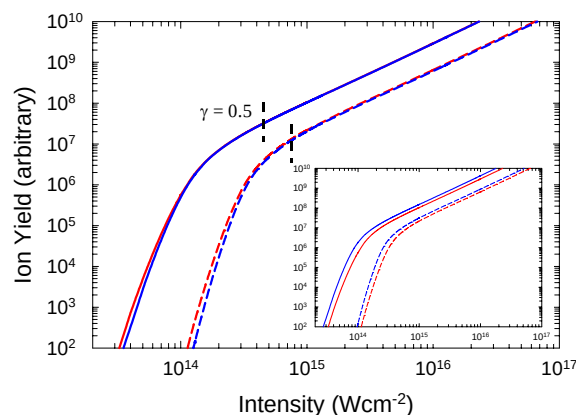


Figure 1. ADK curves for Xe⁺ (solid) and Xe²⁺ (dashed) production from Xe for linear (red) and circular (blue) polarizations. The inset shows unshifted curves whilst in the main figure the circular curve has been shifted upwards in intensity by a factor of 1.3.

From this model the total ion yield for a particular peak focal intensity is obtained by integrating these rates over the duration of the laser pulse and subsequently spatially over the interaction volume.

Within the limits of this model (Keldysh parameter $\gamma < 0.5$) the ion yield at an intensity I the circular polarization is found to match that of the linear at a higher intensity of $1.3I$, see Figure 1. Hence in terms of electric field vector, for a circular field strength E , the required matching linear field is $\sqrt{1.3}E$. This is understood if one considers that in the linear case the electric field sinusoidally oscillates between zero and the peak value. The width of the Coulomb barrier which the confined electron must tunnel across is therefore varying as a function of time. For circular however the electric field is constant over the optical cycle and hence the barrier width is fixed. The linear time-averaged barrier width over the period of a laser cycle is larger than for the stationary circular case⁸). Hence the tunnel ionization rate is lower for linear polarization.

For a given focused laser intensity, if the peak amplitude of the electric field vector for a linear pulse is E_0 , then the equivalent circular pulse will have an electric field vector $E_0/\sqrt{2}$. This derives simply from resolving the electric field components along the fast and slow axis of the quarter-wave plate. Hence as shown from the predictions of ADK theory, to obtain the same ionization rate as for circular, a linearly polarized pulse should have an electric field amplitude of $E_0/\sqrt{2} \times \sqrt{1.3}$, i.e. $0.81E_0$. As intensity is proportional to the square of electric field, this translates to comparing a circular intensity of I to a linear intensity of $0.65I$ (i.e. $(0.81)^2$).

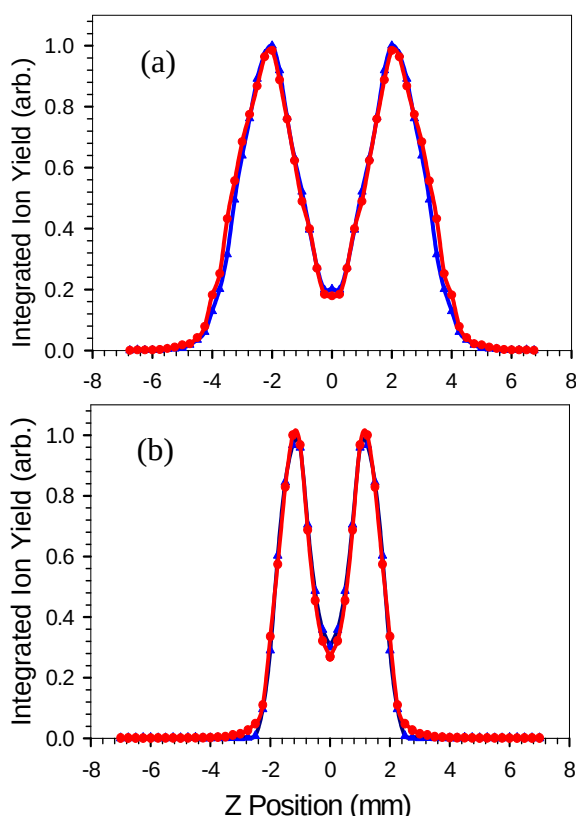


Figure 2. (a) Ne^+ and (b) Ne^{2+} production from neutral Ne, arbitrarily normalized to 1.0, as a function of focusing lens position with respect to spectrometer axis, for linear (red) polarization at $0.65I$ and circular (blue) at I .

We performed a rigorous experimental check of this theory using a Ne gas target in the TOFMS by measuring the resulting Ne^+ and Ne^{2+} signals, see Figures 2(a) and 2(b) respectively. The ion yield is displayed on an arbitrary scale. At $z = 0$ mm (centre of the focus) the laser peak intensity is maximum and decreases outwards either side from the centre of the focus. Ne is a good test target to use as previous observations have shown a low level of NS ionization from this element¹⁷). In both single and double ionization, near-perfect overlap in the linear and circular signals is obtained when the peak intensity of the laser beam with the linear setup is at the predicted factor of 0.65 times that of the circular case. This factor was experimentally verified to an accuracy of 0.65 ± 0.01 . The ISS technique proved particularly sensitive in accurately determining this ratio.

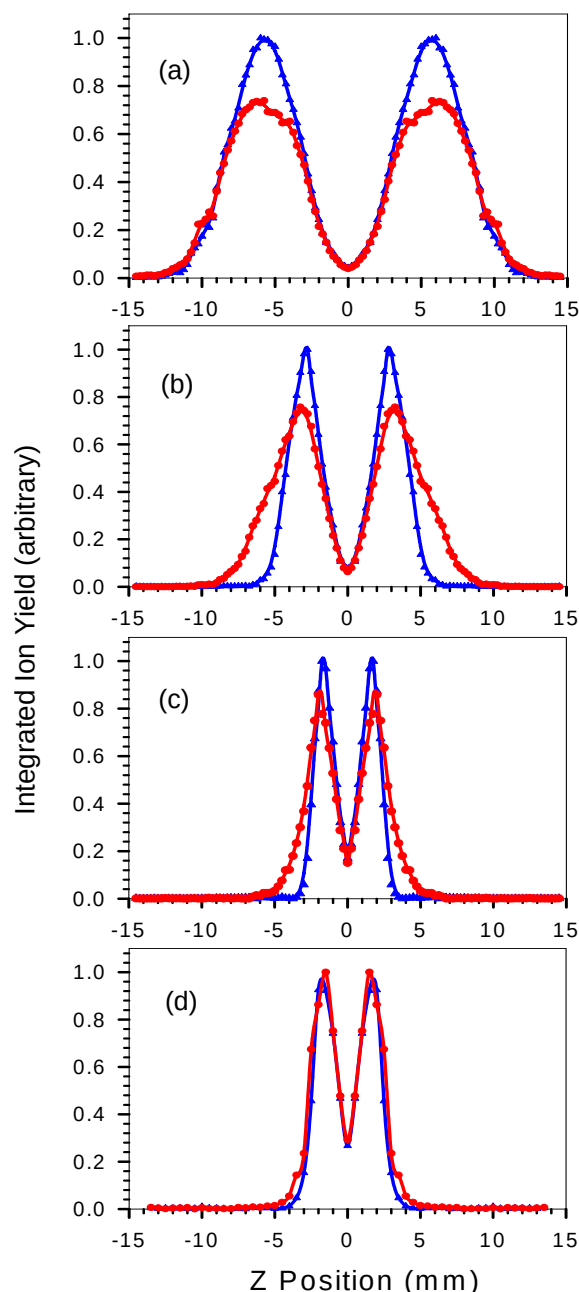


Figure 3. ISS ion yield of (a) Xe^+ (b) Xe^{2+} and (c) Xe^{3+} from Xe target, and (d) Xe^{3+} from Xe^+ target, by linearly (red) and circularly (blue) polarized laser fields.

In a similar study by Guo and Gibson⁷), also looking at the ADK tunnelling rates, a shift of the linear ADK rate curve by a factor of $\sim 1.6 - 1.7$ to match the circular rate is reported. This

however is with the ADK curves plotted as a function of average intensity, and not peak intensity. As a function of peak intensity this relates to a shift of the circular curve by 1.18 - 1.25 along the intensity axis. This is slightly lower than the value of 1.3 reported in the present study. However Guo and Gibson looked for agreement between linear and circular rates in the cross-over intensity region between the multi-photon and tunnelling regimes, where the ADK approximation begins to break down. Auguste *et al.*⁸⁾ also performed multiple ionization studies on ps laser pulses and from experimental data reported shift factors for the circular polarization of 1.4 - 1.7 in order to match the ionization threshold intensities. This corresponds to a laser intensity ratio of between 0.59 and 0.71, in good agreement with the present measurement of 0.65 ± 0.01 .

Figure 3 shows the comparison of single (a), double (b) and triple (c) ionization results for a Xe target and double ionization of a Xe^+ target (d) using circular and linear polarizations with intensities in the ratio 0.65. If the ionization process is purely sequential then ion yields by both linear (red) and circular (blue) polarizations should be the same at all interaction positions along z , independent of the intensity. The observed higher ion yields for double ionization with linear polarization at lower intensities, from $z = 4$ mm to $z = 9$ mm in Figure 3(b) and around $z = 4$ mm in Figure 3(d), and triple ionization, around $z = 4$ mm in Figure 3(c), are a measure of the non-sequential ionization contribution. The enhanced ionization in the double and triple ionization of Xe can account for the loss of flux in the peaks of the Xe^+ yield where no non-linear effects are anticipated. Likewise, the linear signal is lower than the circular signal for Xe^{2+} in the range $z = 2$ mm to $z = 4$ mm corresponding to the enhanced linear Xe^{3+} production in the same region. The same applies to the Xe^{3+} peak where Xe^{4+} linear yield is enhanced. Summing over all charge states observed (up to Xe^{8+}), the total ionization flux is found to be comparable for linear and circular at each z position. It is interesting to compare double ionization from the primary Xe^+ target (Figure 3(d)) to that from the neutral Xe target, Figure 3(b). It is clearly observable that the non-sequential ion yield of Xe^{3+} from Xe^+ is significantly less than that of Xe^{2+} from Xe. It is even small compared to the similar ratio for triple ionization of Xe, Figure 3(c). Non-sequential multiple ionization is much more apparent when using the neutral target than the ionic target and confirms our previous finding with Ar^+ where the NS ionization was found to be suppressed¹⁴⁾.

Conclusion

We have reported and detailed, for the first time, the precise linear-circular intensity ratio needed for a direct comparison of intense laser field ionization from both polarization states. Using this ratio in studies of Xe a clear enhancement of non-sequential ionization is observed for linear polarization. In the first ever linear-circular comparison experiment for an ionic target, the measurement of double ionization of Xe^+ shows suppression of NS effects by comparison with double and triple ionization of neutral Xe target. The volume restricted intensity selective scanning technique has proved particularly valuable in these studies where sensitivity to the confocal intensity distribution is of key importance.

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Production of mono-energetic electron beams on Astra

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Introduction

Since the 1970's, it has been noted that electron plasma waves fulfil many of the criteria required for compact particle acceleration. In particular, their ability to support acceleration gradients ~ 100 GV/m makes them an attractive prospect. As such, the production of relativistic electron bunches from laser-produced plasmas has been well documented both theoretically¹⁾ and in experiment²⁾. It is important to note that such experiments indicate an electron energy spectrum that is quasi-thermal. It is only recently that attention has been focused on the possibility of producing high quality beams. If plasma accelerators are to be considered as a viable alternative to conventional structures, it must be shown that the beam produced can have a short temporal duration, small energy spread and have low divergence.

Recently some computational work³⁾ has suggested that a high quality beam may be produced from a laser-produced plasma if certain criteria are fulfilled. Here we present some of the first experimental results showing a high quality electron beam being produced using the Astra laser system at the Rutherford Appleton Laboratory.

Experimental Set up

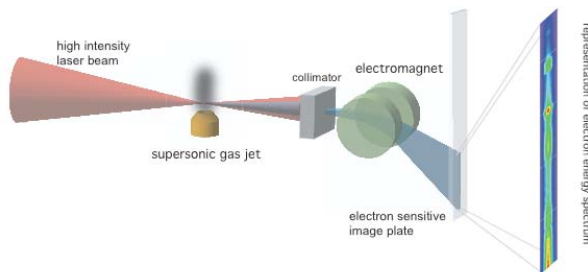


Figure 1. Experimental Schematic.

The experiment used the high power Titanium:Sapphire Astra laser system. The laser pulses ($\lambda = 800$ nm, $\tau = 40$ fsec with energy ≈ 0.36 J on target) were focused with an $f/16.7$ off-axis parabolic mirror onto the edge of a 2 mm long supersonic jet of helium gas to produce peak intensities up to 2.5×10^{18} Wcm⁻². The experimental setup is shown in Figure 1.

The plasma density was varied from $n_e = 3 \times 10^{18}$ cm⁻³ to $n_e = 5 \times 10^{19}$ cm⁻³. The wavelength of a relativistic plasma wave is given by Equation (1).

$$\lambda_p = \frac{2\pi\omega_{pe}}{c} \quad (1)$$

So in our case λ_p ranged from 2 down to 0.33 times the laser pulse length ($c\tau = 12$ μ m). Over this range of conditions, a plasma wave is generated due to the ponderomotive push at the front edge of the laser pulse on the plasma electrons. The restoring force due to the stationary ions causes these electrons

to start oscillating around their initial longitudinal displacement. This generates the plasma wave as illustrated by Figure 2.

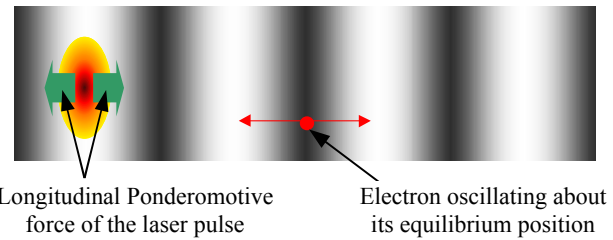


Figure 2. The electron density variation produced by the oscillation of electrons caused by the ponderomotive force.

This process should be most efficient for pulses where $\lambda_p = 2c\tau$, so that the backward push of the rear of the pulse coincides with return of the electrons. Recently it has been found that at higher densities, where this condition is not met, non-linear modification of the laser pulse by the plasma wave can force this resonant condition⁴⁾.

Once established, the laser-plasma wave can then grow until wavebreaking occurs⁵⁾. This is where, at very large plasma wave amplitude, the wave motion becomes so non-linear that wave energy is transferred directly into particle energy. Electrons that reach relativistic energies from wavebreaking of a plasma wave can become trapped such that they are further accelerated in the space-charge field of the plasma wave.

In our experiment, the electron energy spectrum was measured using an on-axis magnetic spectrometer. A high-resolution image plate detector (Fuji BAS1800II) was used to obtain the electron spectrum. The electrons were also simultaneously measured using a lower resolution array of diodes situated behind the image plate in order to calibrate the image plate response. This set-up was able to measure the spectrum over a wide energy range in a single shot.

Experimental Results

Electron acceleration was observed over a range of electron densities. With the plasma density below 7×10^{18} cm⁻³ no energetic electrons were observed (this corresponds to $\lambda_p = c\tau$). In this classical wakefield regime, the growth rate of the plasma waves is too slow to reach wavebreaking amplitudes.

Increasing the density above 1×10^{19} cm⁻³ produced a sudden change with the detection of electrons with energies up to 100 MeV. Measurements of the beam divergence using radiochromic film detectors show that the FWHM of the electron beam was less than 5°. More interestingly, it is found that in this regime, the electron energy spectra were exceptionally non-Maxwellian. Indeed they generally consisted of one or more narrow spiky features, each having an energy bandwidth of less than 20% (see Figures 3a and 3b). This is in contrast to the electron spectra of all previous laser acceleration experiments in which 100% energy spreads are observed. As the density was increased, the peak energy of the electrons was

observed to decrease and the spectra began to assume a broad Maxwellian shape, as reported in previous experiments (see Figures 3c and 3d).

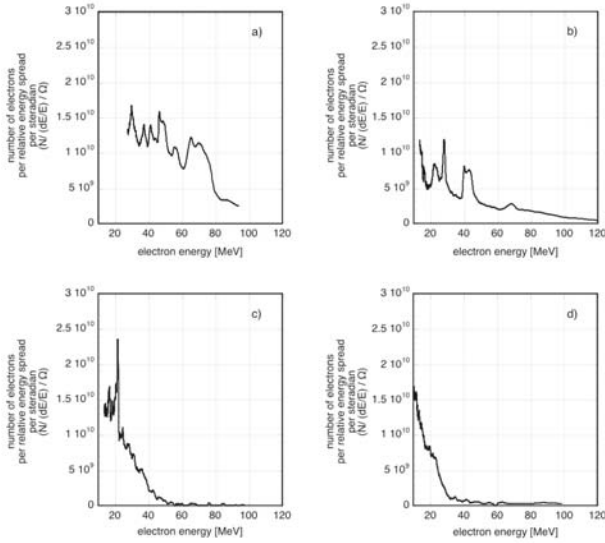


Figure 3. Number of electrons per relative energy spread per steradian as a function of electron energy.

The difference observed in these spectra can be attributed to the timing of the injection of electrons into the relativistic plasma wave. Evidently wavebreaking places the electrons to be accelerated at a precise phase within the plasma wave. In this way, all the electrons experience an almost identical acceleration gradient. Since the wakefield is several plasma wavelengths long, with its amplitude decreasing away from the laser pulse, successive plasma periods will accelerate trapped electron bunches to different energies producing multiple spikes in the spectrum.

For the right conditions, the mono-energetic structure was even clearer. For example with higher laser energy ($\approx 0.55\text{J}$) often only one very narrow single peak was observed in the spectrum. This is clearly illustrated by the result shown in Figure 4.

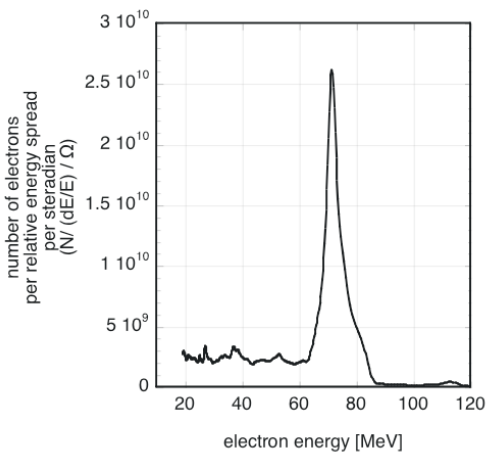


Figure 4. Measure electron energy spectrum showing a single mono-energetic peak.

For these mono-energetic features to be transported out of the plasma, the electron bunches cannot be dephased (i.e. outrun the plasma wave), since then they would be decelerated by the leading edge of the plasma wave. The distance over which the electrons outrun the plasma wave, or the dephasing length (L_d), is given by Equation (2).

$$L_d \approx \frac{2\pi\omega^2}{\omega_{pe}^3} \quad (2)$$

This means that the combination of the length after which wavebreaking occurs plus the dephasing length needs to be less than the interaction length. Indeed, the conditions which showed the clearest, most reproducible evidence of these narrow energy spread beams were those in which the dephasing length and the observed interaction distance were both roughly 1 mm. In contrast, at higher densities the dephasing distance is shorter than the interaction distance and so a quasi-Maxwellian distribution of electrons emerges from the plasma, Figure 3d.

Figure 5 illustrates some of the important parameters. It demonstrates how the dephasing distance and cold wavebreaking amplitude vary with plasma density. The circles indicate the dephasing lengths and wavebreaking amplitudes corresponding the spectra shown in Figure 3. Those in the red region correspond to the spectra which exhibited mono-energetic features, while those in the blue shaded region correspond to those spectra exhibiting Maxwellian-type distributions. The green line indicates the interaction length observed by shadowgraphy during the experimental run.

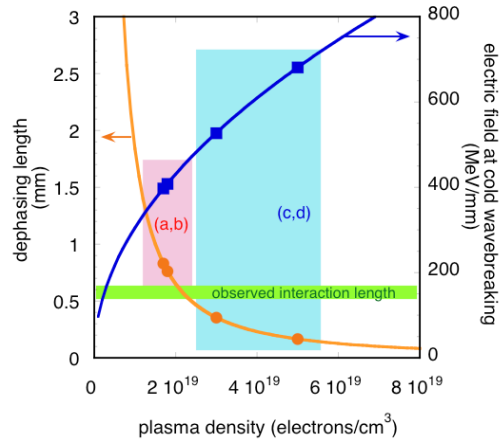


Figure 5. Comparison of experimental parameters.

2D3V particle-in-cell code simulations of the interaction performed using the code OSIRIS⁵⁾, support this picture of the acceleration process. Simulations of this particular experiment show good agreement with these experimental results⁶⁾. A complete experiment and analysis of the mechanism is due to be published in the peer-reviewed press shortly⁷⁾.

Acknowledgements

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All optical injection laser wakefield accelerator

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Introduction

Exciting new results to be published this year demonstrate production of monoenergetic ($\Delta E/E < 10\%$) electron bunches, highly collimated ($< 2^\circ$ angular divergence) at high energies ($> 50\text{MeV}$) using a single short ($\sim 40\text{fs}$) laser pulse focused in a gas jet.¹⁾ This is a giant leap towards laser-plasma based accelerators of electrons becoming viable as sources for medical purposes and possibly even as a replacement for conventional RF LINAC's. Issues can be raised, however, about the level of control in electron characteristics produced by the intrinsically non-linear wavebreaking phenomenon.²⁾ Although it may in principle be possible to use a single beam to create a usable particle source³⁾, it might prove necessary to move to a more complex geometry.^{4,5)}

Presented here are proof of principle observations demonstrating that using a two collinear beam geometry can transform the wakefield produced electron spectrum from an essentially Maxwellian distribution, to a monoenergetic electron beam at around 15MeV . The two beams are focused with differing focal lengths, therefore creating a small intense focal spot and a long flat focal region respectively. The intense spot creates a burst of electrons via wavebreaking, as its intensity is just above the Akhiezer and Polovin cold wavebreaking threshold;⁶⁾

$$E_{\text{max}} = \sqrt{2(\gamma_p - 1)}E_0$$

where $E_0 = m\omega_p c/e$, and it is assumed that the wakefield is produced by a temporally Gaussian pulse;⁷⁾

$$E_{\text{max}}/E_0 = (a_0^2 \sqrt{\pi}/4) \tau \exp[-\kappa^2/4]$$

where τ is the laser pulse length normalized to the plasma wavelength and $a_0 = eA/mc$ is the normalized vector potential. The threshold intensity $\sim 10^{19}\text{Wcm}^{-2}$, at $n_e \sim 10^{19}\text{cm}^{-3}$ corresponding to an a_0 of ~ 2 for wavebreaking is significantly higher than the large f -number region ($a_0 \sim 0.8$), and it therefore creates a classical wakefield with phase velocity close to the group velocity of light in the plasma. Electrons with velocities close to the wave velocity are trapped in the wave potential and accelerated - as shown in Figure 1. The ratios $E_{\text{max}}/E_0 \sim \delta n/n_0$ for the two wakefields are 0.2 for the $f/20$ focus in used in this experiment and 4 for the $f/3$ both at $n_e \sim 10^{19}\text{cm}^{-3}$.

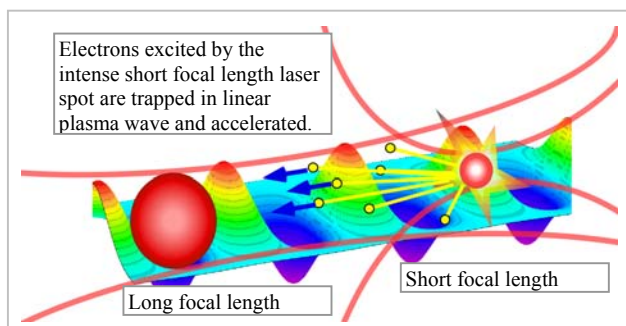


Figure 1. Two beam electron trapping.

Experiment

Figure 2 shows the experimental setup of the target chamber for the experiments performed on the 800nm , $40 \pm 5\text{fs}$ pulse length (FWHM) Astra laser. The beam, of 50mm diameter, enters horizontally polarised into a mechanically isolated vacuum chamber and is either split into two equal energy beams of around 250mJ - B1 and B2 in Figure 2 - using a thin (5mm) $50:50$ beam-splitter. B1 was directed onto an $f/20$ parabolic mirror and focused 1mm above a supersonic gas jet nozzle of 2mm diameter. B2 was incident on an $f/3$ parabolic mirror with a 10mm central hole, the purpose of which was to allow the two beams to focus collinearly on the same point above the gas jet. A timing slide in the B2 beam-line allowed variation of the arrival times of the two pulses on target. Helium gas was used at a backing pressure of 50bar , corresponding to a number density of $1 \times 10^{19}\text{cm}^{-3}$. The whole experiment took place in an isolated vacuum chamber at 10^{-2}mbar .

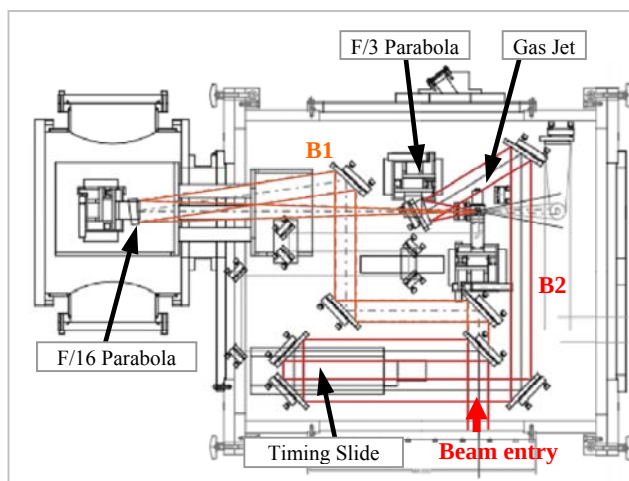


Figure 2. Experimental Setup.

The energy spectrum of the accelerated electrons was obtained using a custom-built magnetic electron spectrometer with image plates as the electron detector. Image plates are polymer sheets doped with Europium atoms that can be excited to metastable states by electrons or high-energy photons. They are read with a He:Ne laser, which stimulates emission of blue light with intensity proportional to the original incident radiation. Image plates have an excellent dynamic range and resolution. They allow single shot, full spectral acquisition, which is essential for diagnosing non-Maxwellian energy distributions, as features may be "washed out" in any statistical averaging scheme. An optical spectrometer looking at the forward scattered light allowed calculation of the electron density via Raman satellites in the spectrum.

Results

With the $f/20$ beam alone, no electron signal above noise level was detected. The $f/3$ beam produced Maxwellian electron energy distributions, as found frequently in previous experiments. These are shown in graphs (a) and (b) of Figure 3.

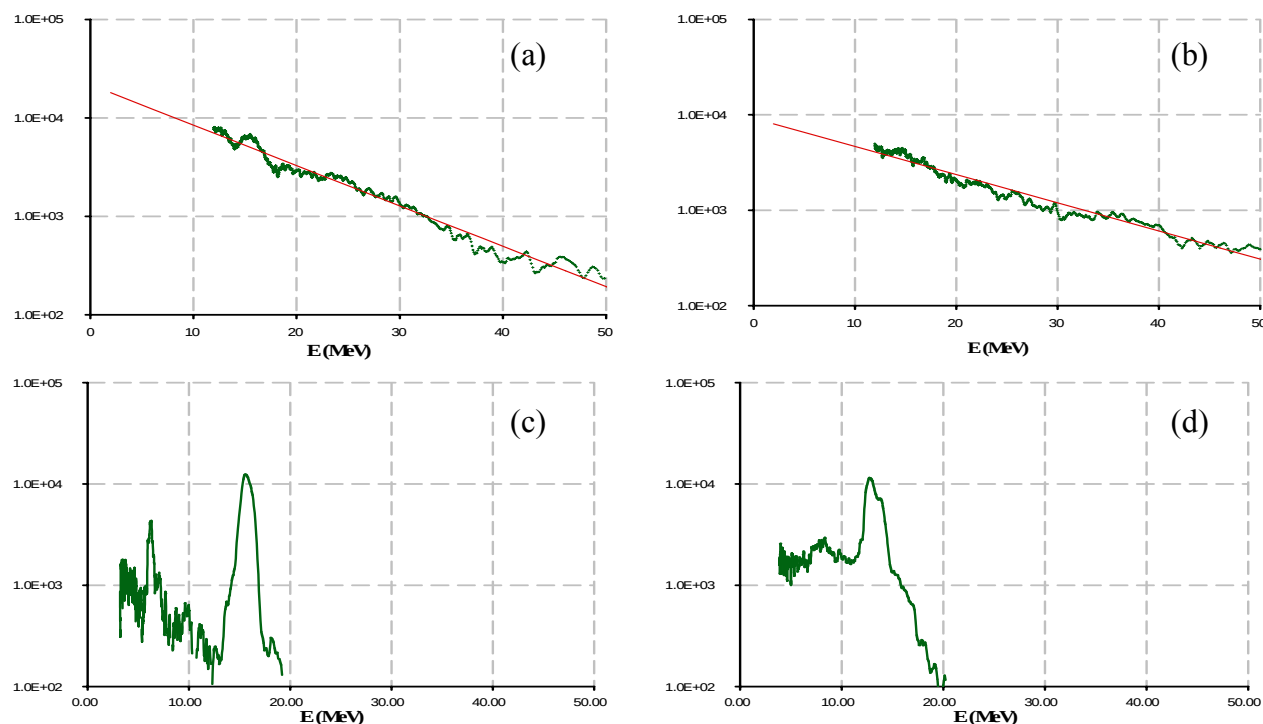


Figure 3. Examples of electron spectra for the 2 beam experiments plotted on a logarithmic scale. (a) and (b) show Maxwellian spectra and correspond to f/3 only shots (c) and (d) show a clear electron beam due to the combination of f/3 and f/16 beams.

The red lines show an exponential curve fit of the form $N(E) \sim \exp[-E/T]$.

In the case of the two beams together a scan of the timing between the beams was performed. Qualitatively, the spectra obtained fell into three categories. Firstly there were a limited number of exponential spectra. These could be due to misalignment of the two beams – the error in f/20 transverse position was more than its spot size – or due to incorrect phase injection. The second type was plateau like or multiple spiked spectra. These seemed to be congregated about the nominal zero position of the timing – i.e. with the beams arriving at the same time. This may well have to do with the complex intensity profile of the overlapping beams. Certainly the maximum energies obtained in this region are far higher than with the beam timing being far apart.

The third were quasi-monoenergetic spectra, two examples of which are shown in graphs (c) and (d) of Figure 3. The electron yield in the spikes seems to be higher than would be obtained by simply filtering a section of the spectrum by, for example, using magnets. This suggests some sort of trapping on the part of the f/20 wakefield, bunching electrons close in energy to the wave velocity into a peak. When the energy of these peaks is plotted against beam timing, as in Figure 4, a distinctive peak is found in the data. When points are added for the multiple spiked data, they seem to cluster around the nominal zero position.

This could well represent a region where the beams are adding together, and driving the wave strongly to breaking. As the pulse length (FWHM) is 40fs, it seems feasible that the overlap region would extend to 100fs; represented by the yellow region in Figure 4. The blue line on the graph, representing a qualitative minimum energy threshold, is higher than the energy associated with the phase speed of the wakefield; represented by the red line. This suggests some acceleration has been done by the f/20 wakefield, although for the monoenergetic spectra it would only be slightly over 10MeV at most.

Further experiment is needed to determine precisely by what mechanism the different spectrum types are obtained. Although outside of the critical region the energy fluctuations seem lower, they still represent a relatively large ($\sim 20\%$) error. However, the process is likely to be highly sensitive to transverse beam

overlap, which in the experiment had a very high error. This will also need to be improved in a future experiment so that this innovative approach to electron acceleration can be pursued.

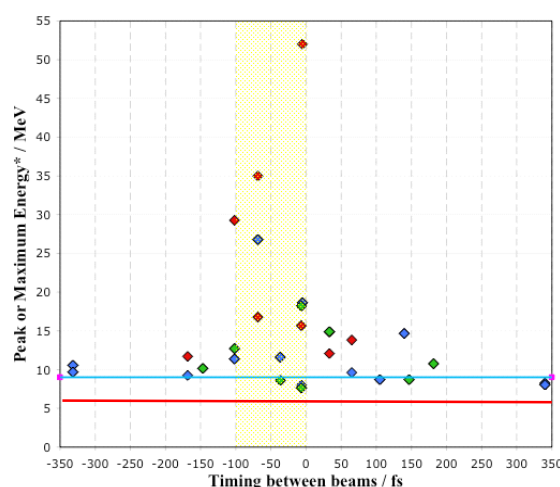


Figure 4. Relationship between beam timing and electron energy. Green points depict monoenergetic electron beams whereas blue are spectra with one prominent spike among other features. The peak energy is taken for these points. Red points are plateau or multiple spiked spectra and the high energy cut off is taken.

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Multiphoton processes in noble-gas atoms using R-matrix Floquet theory

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Introduction

Over the last decade, there has been a strong interest in studying the influence of electron-electron interactions on the dynamics of atoms in strong laser fields. In particular, experimentalists have demonstrated, that, when He is subjected to 780 nm light with an intensity in the order of 10^{14} W/cm², double ionization is several orders of magnitude more likely than could be expected from purely sequential models¹. This has led theorists to develop new theoretical approaches to describe He atoms in strong laser fields including electron-electron interactions^{2,3}. Electron-electron interactions are, however, also important in other processes, such as two-photon double ionization⁴.

While at present many time-dependent methods have been developed for two-electron systems, the R-matrix Floquet method has been developed to describe the behaviour of general atoms in strong laser fields⁵. The approach combines the R-matrix approach for scattering and photoionization, one of the main tools for theoretical atomic physicists, with the Floquet-Fourier expansion.

Over the last 10 years, the R-matrix Floquet approach has been applied to a wide variety of atomic systems. Recent examples include studies of multiphoton ionization⁶ and harmonic generation⁷ in the noble gases, and multiphoton ionization of Ca⁸ and K⁹ using B-spline based model potential descriptions. The accuracy of the R-matrix Floquet approach has been demonstrated through comparisons with state-of-the-art time-dependent calculations¹⁰. This comparison found differences between the two entirely independent approaches well within 10% for six-photon ionization at a wavelength of 248.6 nm.

In the present report, we investigate the application of the R-matrix Floquet approach to few-photon ionization in the noble gases. We present recent results obtained for three-photon ionization of He, and for two-photon ionization of Ar⁶. Both studies involve frequencies in the XUV regime, which is of current interest due to the development of new laser sources in the XUV regime, such as attosecond lasers¹¹ and free-electron lasers¹². The interaction of atoms with intense lasers in this frequency region has not yet been investigated extensively, but new developments will soon open this area to experimental investigation.

Three-photon ionization of He

Helium has attracted significant interest in atomic physics, as it is the simplest two-electron system. It thus forms the simplest atom to study the influence of electron-electron interactions. While our understanding of these interactions for single-photon absorption has improved dramatically over the last 10 years, for multiphoton absorption our knowledge is significantly less.

At present, few-photon ionization of He is of strong topical interest. Several new types of radiation sources have become available to generate coherent radiation sources in the XUV regime. One of these, the use of a superposition of 7th to 13th harmonics of a Ti:Sapphire laser, has been applied to the study of helium photoionization¹³. In order to develop these new radiation sources, and to obtain good estimates of the laser intensities achieved, experimentalists require accurate few-photon ionization rates at high intensities.

From a theoretical perspective, while few-photon ionization of He has been investigated from a perturbative viewpoint¹⁴, few accurate results are available at high intensities. A good overview of multiphoton ionization cross sections of He in

lowest-order perturbation theory has been provided by Saenz and Lambropoulos¹⁴. However, at high intensities, the laser field distorts the atomic structure, and these perturbative results no longer describe the full behaviour of the He atom. One thus needs an approach, which goes beyond perturbation theory. As only a few photons need to be absorbed for ionization, the R-matrix Floquet approach is ideally suited to provide cross sections at high intensities.

In order to apply the R-matrix Floquet approach to the study of three-photon ionization in He, we have used the B-spline based R-matrix Floquet approach^{8,9}. We use three target states, 1s, 2s and 2p. For intensities of 10^{13} W/cm² and $2 \cdot 10^{13}$ W/cm², we combine this target-state basis with a Floquet expansion of 6 absorption blocks and 2 emission blocks and all angular momenta up to $L = 6$. For an intensity of $5 \cdot 10^{13}$ W/cm², we use the same Floquet expansion, and include angular momenta up to $L = 7$. For an intensity of 10^{14} W/cm², we employ a Floquet expansion of 8 absorption blocks and 3 emission blocks and include all angular momenta up to $L = 7$. In order to get results suited for comparison with experiment, we shift the field-free ground-state energy of He to its experimental position.

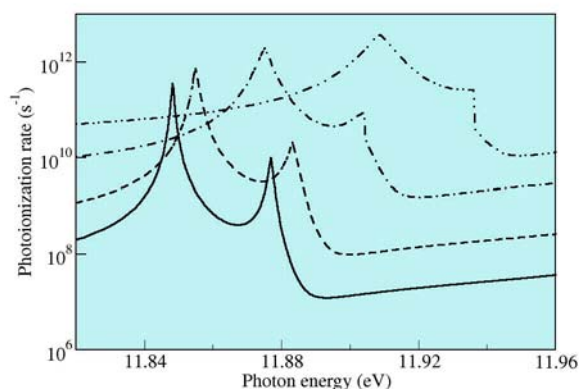


Figure 1. Ionization rates of He as a function of photon energy in the neighbourhood of the $1s4s\ ^1S^e$ and $1s4d\ ^1D^e$ resonances. Ionization rates are shown for intensities of 10^{13} W/cm² (solid line), $2 \cdot 10^{13}$ W/cm² (dashed line), $5 \cdot 10^{13}$ W/cm² (dot-dashed line), and 10^{14} W/cm² (dash-double-dotted line).

As an illustrative example of the photoionization rates we have obtained, we show in Figure 1 the photoionization rates of He near the $1s4s$ and $1s4d$ resonances. The $1s4s$ resonance is the dominant resonance, while the $1s4d$ resonance appears as a peak at low intensities and as a discontinuous shoulder at the higher intensities. The origin of the discontinuity is the interaction between the ground state and the $1s4d$ state, which leads to an avoided crossing. Hence, the $1s4d$ state and the ground state exchange character when the frequency is varied slowly. At each frequency, two states exist, one of which is associated with the field-free ground state, and one of which is associated with the field-free $1s4d$ state. However, at one particular frequency, the state associated with the ground state will jump from one of the adiabatic curves to the other. As Figure 1 shows, this jump leads to a discontinuous change in the photoionization rate. The actual change is relatively small for the $1s4s$ state, but quite significant for the $1s4d$ state.

Figure 1 demonstrates several ways how the presence of a laser field influences the ionization rates. First of all, off-resonance the ionization rates increase as expected following an I^3 law. On the other hand, at the peak of the $1s4s$ resonance, the ionization rates increase only linearly with intensity. This latter behaviour is due to the fact that on resonance the ionization rate is dominated by the ionization rate of the resonance. Secondly, we observe that the position of the resonances shifts to higher photon energy with increasing intensity. This is mainly due to the ponderomotive shift of the ground-state energy.

Figure 1 demonstrates that in order to get an accurate description of multiphoton ionization of He at 10^{14} W/cm², one cannot directly extrapolate the photoionization rates of He obtained at an intensity of 10^{13} W/cm² to this higher intensity. Non-perturbative aspects of the photoionization process grow increasingly important at higher intensities.

Two-photon ionization of Ar

It is also of strong current interest to investigate few-photon ionization of Ar. Recent experiments have investigated the break-up of Ar clusters when subjected to intense VUV light. The initial stage in the break-up is two-photon ionization of Ar. Intermediate- and final-state Ar resonances can enhance this ionization process.

From a theoretical perspective, there is also interest in investigating two-photon ionization of Ar. While the influence of intermediate resonances has been investigated in great detail¹⁵⁾, the influence of final-state resonances has so far not been included. However, the energy diagram of Ar shows that in two-photon ionization, both Rydberg series converging to the $3s^23p^5$ state and Rydberg series converging to the $3s3p^6$ threshold can enhance two-photon ionization. The former Rydberg series is reached after absorption of a single photon, while the latter is reached after absorption of two photons.

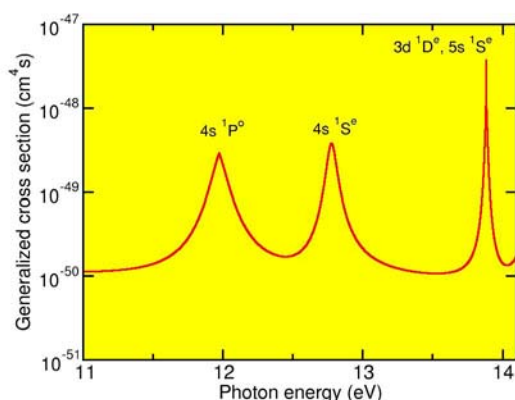


Figure 2. Generalized cross sections for two-photon ionization of Ar in the photon-energy region where resonances strongly enhance the photoionization cross sections. The resonance labeled $4s\ 1P^o$ is an intermediate resonance attached to the $3s^23p^5$ threshold. The $4s\ 1S^e$, $3d\ 1D^e$ and $5s\ 1S^e$ resonances are final-state resonances attached to the $3s3p^6$ threshold. The $3d\ 1D^e$ and $5s\ 1S^e$ resonances overlap.

Figure 2 demonstrates the influence of resonances converging towards the $3s^23p^5$ threshold and the influence of resonances converging towards the $3s3p^6$ threshold on the photoionization cross sections. As the latter threshold is reached at a photon energy of 14.6 eV and the former threshold at a photon energy of 15.8 eV, we observe a more densely packed Rydberg series for the Rydberg series converging to the $3s3p^6$ threshold.

The photoionization spectrum increases significantly in complexity for slightly larger photon energies than shown in

Figure 2. At a photon energy of 14.25 eV we find that 4 states are nearly resonant with the ground state: $5s$ and $3d\ 1P^o$ states converging to the $3s^23p^5$ threshold, and $6s\ 1S^e$ and $4d\ 1D^e$ states converging to the $3s3p^6$ threshold. The cross-section spectrum becomes quite difficult to interpret near this photon energy, and detailed interpretations of the cross sections are necessary to elucidate the ground-state behaviour. In order to limit the discussion, we have truncated the results shown in Figure 2 at a photon energy of 14.1 eV.

Conclusions

We have given an overview of recent multiphoton calculations carried out using the R-matrix Floquet approach. The R-matrix Floquet approach allows the detailed calculation of photoionization cross sections of general atoms in strong laser fields with good accuracy. We have demonstrated that atomic structure can significantly enhance ionization, and thus that it is important to obtain a complete description of the relevant atomic structure. We also demonstrate that in the intense-field regime, perturbative results no longer give a highly accurate description of the atomic properties. The present study focuses on transitions in the VUV regime, a regime in which important laser developments are currently taking place. We hope that our cross sections will be of benefit to workers in this area for the further development of their laser systems.

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Differential dynamics of protons and deuterons in laser plasma experiments

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Introduction

In any plasma the dynamics of different ion species are determined by their charge to mass ratio $Z e / A m_p$ where Z is the charge state, A the mass number and m_p is the proton charge. Protons have the largest value of $(Z/A) = 1$, deuterons and fully ionised light atoms have $(Z/A) = 1/2$ and other ions have $(Z/A) < 1/2$. In a fixed time interval and a fixed electric field protons will accelerate faster, travel farther and have more energy than other ion species. On the other hand in traveling through the same distance in a fixed electric field ions will simply acquire an energy equal to the potential drop $Z \Delta \Phi$.

Since the early ICF experiments with CO₂ lasers it has been known that there is a flux of energetic ions leaving solid targets and that protons constitute the fastest component of the ion emission. The protons are observed even from non-hydrogenous targets and are attributed to thin layers of surface contamination containing water and hydrocarbons. The acceleration is attributed to an electrostatic field created by the energetic electrons leaving the target which can maintain a non-neutral layer as long as the hot electron Debye length $\lambda_{D-hot} = v_{hot} / \omega_{p-hot}$ is greater than the density scale length. Protons have the highest velocity since they remain in the expanding Debye sheath longer than heavier ions which tend to experience a smaller field due to the screening effect of other ions. The same mechanism is observed on the front and particularly the rear surfaces of thin targets irradiated by CPA lasers where it is known as target normal sheath acceleration (TNSA).

In an equilibrium configuration where there are slowly varying potentials (either electrostatic or ponderomotive) there will also be a separation of the ion species of different Z since they have slightly different equilibrium Boltzmann distributions $n = n_0 \exp(-(\epsilon + Ze\Phi)/kT)$. In the process of relaxation to the equilibrium distribution, protons and deuterons will relax at different rates and again have different spatial distributions. Ions of different charge state of the same chemical species should not be included in this argument since the charge state of any individual ion will fluctuate in time due to ionisation and recombination processes. Ions of different chemical species will tend to separate since their distributions of Z will be different.

We have investigated two situations where these effects can be significant: transient proton acceleration in targets with differing fractions of protons relative to heavier ions (henceforth all lumped together as deuterons) and separation of species over long time scales in the presence of laser filamentation and Stimulated Brillouin Scattering.

Proton Acceleration

We have performed simulations with the OSIRIS Particle in Cell (PIC) code in 2-1/2 spatial dimensions of a laser with normalised intensity $a_0 = 8$ (10^{20} Wcm^{-2}) incident on a thin foil with peak density $10nc$ and thickness $30c/\omega_p$. The ions are divided into a fraction f of protons and $(1-f)$ of deuterons. Simulations have been carried out for $f = 1\%$, 10% and 50% .

The proton spatial distribution at $t = 401\omega_p^{-1}$ for $f = 10\%$ is shown in Figure 1. The figure shows the protons accelerated away from the rear surface of the target and the interior of the foil almost void of protons as they are accelerated through the foil by the shock generated by the laser at the front surface absorption region.

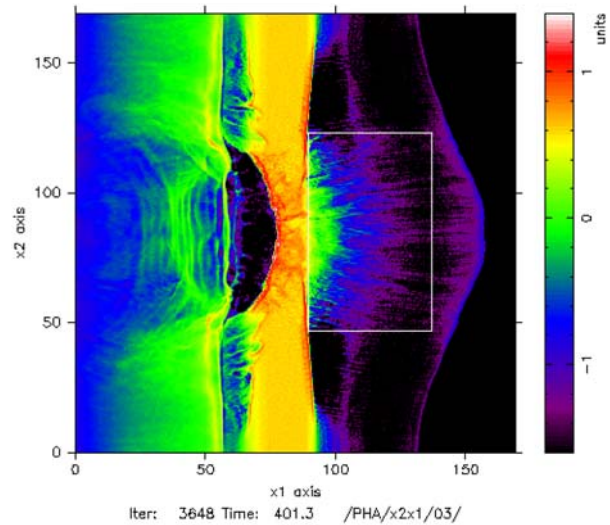


Figure 1. Proton distribution at time $401 \omega_p^{-1}$ in an OSIRIS simulation with 10% protons.

As the fraction of protons is increased we observe the maximum proton energy to decrease.

Proton Fraction	1%	10%	50%
Maximum proton energy	30MeV	25MeV	15MeV

This is to be expected since the larger numbers of accelerated protons that go with the higher concentrations also give more shielding of the space charge of the electrons.

Perhaps a more surprising observation concerns the ions which are accelerated by the piston-like ponderomotive pressure of the laser at the front side of the target. Where the protons are a minority species the lighter species can respond without significantly perturbing the charge balance of the plasma, i.e. they do not affect the screening of the potential in the wake of the shock front. As shown in Figure 1 the interior of the foil is almost devoid of protons at $t = 401 \omega_p^{-1}$.

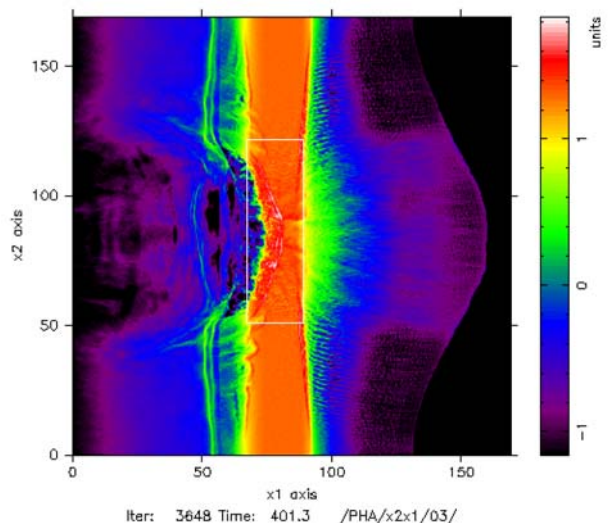


Figure 2. Proton distribution as for Figure 1 but with $f = 50\%$.

Figure 2 shows a similar situation to Figure 1 but with a proton fraction $f = 50\%$ and is dramatically different with the protons largely remaining in situ in the foil. For each of these cases we calculate the two dimensional p2p1 momentum distribution of the protons within the white rectangles and show these distributions in Figure 3 and Figure 4.

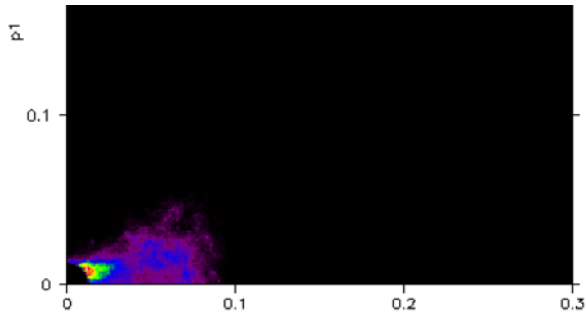


Figure 3. p2p1 momentum distribution for the protons in the white rectangle in Figure 1 ($f = 10\%$).

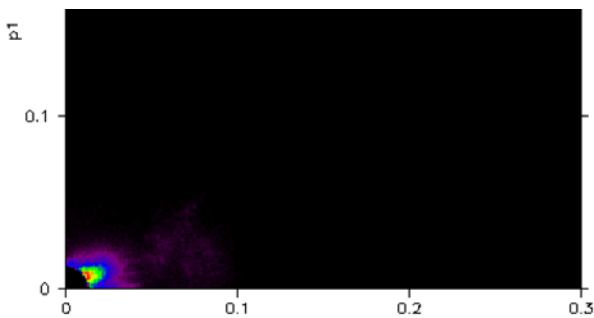


Figure 4. p2p1 momentum distribution for the protons in the white rectangle in Figure 2 ($f = 50\%$).

Comparison of Figures 3 and 4 shows a large increase in the numbers of protons with $\beta > 0.05$ ($E > 1\text{MeV}$) when protons are a minority species.

These results are significant if the aim of an experiment is to create protons above some threshold energy or if CH and CD targets are compared for the creation of neutrons. The CD target with a small percentage of protons present will produce significantly more energetic protons both internally and via the TNSA mechanism and these energetic protons may produce (p,n) reactions with other materials.

Ion Separation by Filamentation and SBS

In longer pulse experiments, when the laser pulse duration exceeds the ion plasma period there is time for SBS and ponderomotively driven filamentation to occur. The time scale for the ion distribution across a filament to reach a steady state is quite long since the ion transit time for a 2.5keV ion across a 20 micron filament is 60 psec and for times less than this the transient behaviour described in the introduction will give rise to a separation of species of the same Z but different (Z/A). In practice the filaments will probably move on a time scale less than 60 psec due to deliberate laser beam control through ISI or SSD or uncontrolled changes in the laser beam profile.

To model this longer term behaviour we have carried out an OSIRIS simulation with $a_0 = 0.1$ and $n_e/n_c = 0.3$ so that SBS may occur but not SRS. The ions in the simulation are 50% protons and 50% deuterons by number. The lighter protons are more effectively driven out of the filament than are the deuterons. Figure 5 shows the difference of the proton and deuteron densities and Figure 6 the magnetic field of the electromagnetic wave which shows evidence of both forward and backward scattering.

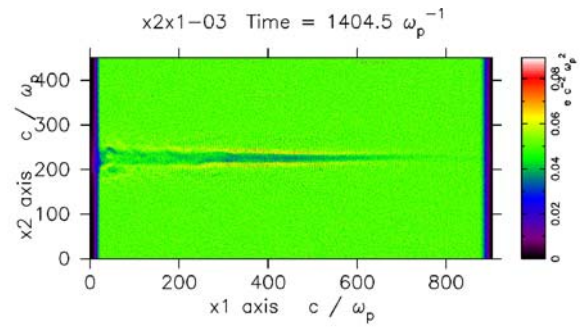


Figure 5. The difference in proton and deuteron densities around a ponderomotively driven light filament at $a_0 = 0.1$.

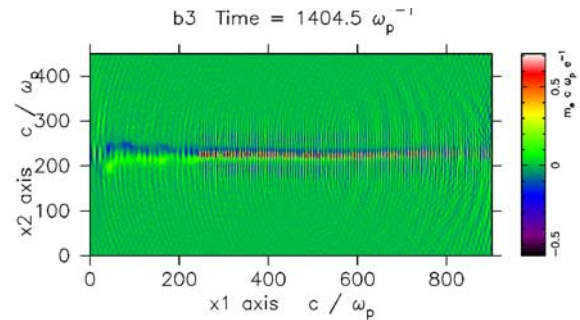


Figure 6. The transverse magnetic field of the laser and SBS scattered radiation from the simulation of Figure 5.

The significance of the separation of deuterons and protons is that the dispersion relation for ion acoustic waves $\omega_{ia}^2 = k^2(ZT_e/\langle m_i \rangle)$ is no longer uniform in space due to the variation of the average ion mass $\langle m_i \rangle$. This gives rise to a phase mismatch for any waves propagating at an angle to the filament and is a potential mechanism to reduce the amount of SBS to gain better agreement between codes and experiment⁴.

Conclusion

The low frequency forces in laser driven plasmas can produce a significant spatial separation of ions of differing Z/M and this leads to changes in the macroscopic behaviour of the plasma.

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Local electron acceleration by breaking Langmuir waves

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Introduction

Direct numerical simulations of electron dynamics in externally driven electrostatic waves have been carried out using a relativistic two-fluid one-dimensional Vlasov-Poisson code. When the driver wave has sufficiently large amplitude, ion density holes (cavitons) form. The interaction between these cavitons and other incoming Langmuir waves gives rise to substantial local acceleration of groups of electrons: fine jet-like structures arise in electron phase space. We show that these jets are caused by wave-breaking when finite amplitude Langmuir waves experience the ion density gradient at the leading edge of the holes, and are not caused by caviton burn-out.

The Relativistic Vlasov-Poisson System

The model used is a one-dimensional relativistic Vlasov-Poisson system of electrons and protons with no magnetic field. This fully nonlinear self-consistent system is governed by the Vlasov equation for the electron and ion distribution functions f_e, f_i

$$\frac{\partial f_{e,i}}{\partial t} + \frac{p}{m_{e,i}\gamma} \frac{\partial f_{e,i}}{\partial x} + q_{e,i} E \frac{\partial f_{e,i}}{\partial p} = 0 \quad (1)$$

and Poisson's equation for the electric field

$$\frac{\partial E}{\partial x} = -\frac{e}{\epsilon_0} \left(\int f_e dv - \int f_i dv \right) \quad (2)$$

The following dimensionless normalisation is adopted: $x = (c/\omega_{pe})\tilde{x}$, $t = (1/\omega_{pe})\tilde{t}$ and $E = (\omega_{pe}cm_e/e)\tilde{E}$, and all simulations use a mass ratio $M_r = m_i/m_e = 100$. The Vlasov-Poisson system is solved using a relativistic version of the code detailed in¹⁾. The initially Maxwellian distribution functions f_e, f_i are calculated on a fixed Eulerian grid periodic in space and quasi-infinite in momentum, and the solver is split into separate spatial and velocity space updates²⁾. These updates are one dimensional, constant velocity advections using the piecewise parabolic method³⁾. A large amplitude external driving field $\tilde{E}_d = \tilde{E}_0 \sin(\tilde{k}\tilde{x})\sin(\tilde{\omega}_{pe}\tilde{t})$ is added to the self-consistent electric field found from Poisson's equation. The system is driven at resonance ($\omega_0 = \omega_{pe}$, $\tilde{\omega}_0 = 1$ in normalised units), and the intensity of the perturbations corresponds to the high quiver velocity regime $v_q^2/v_{Te}^2 > 1$, where $v_q = eE_0/m_e\omega_0$. Hence $E_0 > m_e\omega_0 v_{Te}/e$, or equivalently $\tilde{E}_0 > \tilde{v}_{Te}$. This driving field, similar to the perturbation used in earlier work on the modulational instability⁴⁾, is necessary to drive the formation of cavitons and is only needed during the early stages of the simulation, between $\tilde{t} = 0$ and $\tilde{t} = 10$.

In Figure 1 fine jet-like structures in electron phase space are clearly visible, jets marked 'a' have recently formed on the inside edges of the two cavitons. The jets marked 'b' have formed in the same area at an earlier time and have since been advected through the system. The jets marked 'c' are at an intermediate stage, having formed on the outside edges of the cavitons. These jets are the result of Langmuir wave-breaking at the edges of the evolving density holes.

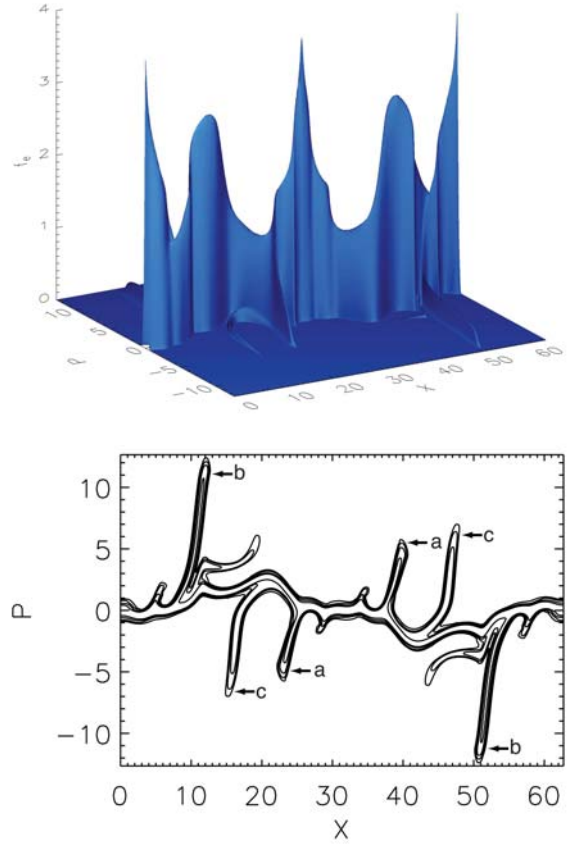


Figure 1. f_e (top) and contour plot $\log(f_e > 10^{-6})$ (bottom) at time $\tilde{t} = 40$ for a Vlasov-Poisson system driven from $\tilde{t} = 0$ to 40 at $\omega = \omega_{pe}$.

Cavitons and Phase Space Jets

Cavitons form in response to the ponderomotive force exerted on the electrons by the driving field $\tilde{E}_d$. At later times, populations of accelerated electrons appear in the contour plots of the electron distribution function, Figure 1 (bottom). These are the electron phase space jets. At $\tilde{t} = 20$, ten plasma periods after the driving field has been removed, there is no evidence of jet formation. However, between $\tilde{t} = 20$ and $\tilde{t} = 40$ a series of phase space jets forms on both edges of the deepening cavitons. In Figure 1, jets are highlighted at three separate stages of evolution. There are two jets (a) forming on the central edges ($\tilde{x} \approx 25, 37$) of the cavitons, as well as two old jets (b) which have been advected across the system, crossing the cavitons on whose edges they formed. Finally, there are two intermediate jets (c), on the outer edges ($\tilde{x} \approx 8, 55$) of the cavitons. The most energetic electrons within these jets have energies of 5 MeV, formed from a distribution with an initial temperature of 0.5 keV.

The appearance of these jets does not affect the development of the cavitons, which continue to deepen after the appearance of the phase space jets - this rules out caviton burn-out as an explanation for the origin of the phase space jets. The process of

jet emergence is seen from the evolution of the electron distribution function, focusing on a region where a jet develops, during its early stages. Figure 2 shows a reduced section of the electron phase space, the region $50 \leq \tilde{x} \leq 62$ where the rightmost jet (labelled ‘b’ in Figure 1) first appears. This region encompasses the right hand side of one of the deepening cavitons. The jet forms at the outer, right hand edge of this caviton at $\tilde{x} \approx 58$. The sequence of contour plots in Figure 2 shows that the jet then extends out from the edge of the main electron distribution, at $|\tilde{p}| \approx 2$, to momenta of $|\tilde{p}| \approx 8$ in only six plasma periods.

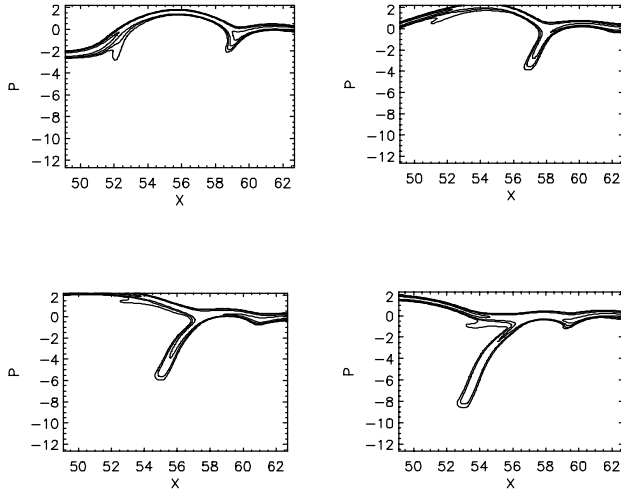


Figure 2. Contour plots of $\log(f_e > 10^{-6})$ in the region $62 > \tilde{x} > 50$ at times $\tilde{t} = 32$ (top left), $\tilde{t} = 34$ (top right), $\tilde{t} = 36$ (bottom left) and $\tilde{t} = 38$ (bottom right). These plots show a phase space jet developing at the outside edge of the caviton at $\tilde{x} \approx 60$. Electrons are accelerated from a compact region of the background distribution to form the jet which extends and advects across the caviton.

Wave Breaking

The key features of phase space jets are as follows:

1. Jets appear after $\tilde{t} \approx 20$, requiring some degree of caviton evolution.
2. Jets are not directly related to the external driver, appearing after the removal of the external driving field.
3. Cavitons persist long after the appearance of jets, indicating that jets are not associated with caviton burn-out processes.
4. Jets originate at the caviton edge. The direction of this acceleration (from the higher density region on the caviton edge towards the lower density region at its centre) indicates that phase space jets are the result of processes originating outside the caviton.

From extensive numerical simulations of the system, it is clear that the breaking of Langmuir waves moving into the density gradients at the edges of the cavitons is responsible for creating the phase space jets. Figure 3 illustrates the physical process schematically. The Langmuir wave first approaches the density hole. As it moves into the region of lower density, the phase speed at the front of the wave falls. If the phase speed declines rapidly enough to overcome the effect of Landau damping (which acts to damp the incoming wave energy, and thereby prevent it from breaking), then the wave will break. This creates a strong electric field localised at the wave crest within the caviton, which accelerates electrons in its vicinity away from the background population to form phase space jets.

Further numerical simulations, modeling simply the interaction of a Langmuir wave with a fixed density hole, confirm this

hypothesis. Furthermore, by considering the interaction of a Langmuir wave with a linear density ramp in the fluid limit, and adding additional terms to account for the kinetic effect of Landau damping, we obtain a breaking condition

$$\tilde{E}_{L0} \exp\left(\left(\frac{\pi}{2\tilde{T}_e\tilde{\eta}^2}\right) \exp\left(-\frac{3}{2} - \frac{3}{2\tilde{\eta}\tilde{x}}\right)\right) - \left(\frac{3\tilde{T}_e}{\tilde{\eta}\tilde{x}}\right)^{1/2} \geq 0 \quad (3)$$

where $\tilde{E}_{L0}$ is the initial amplitude of the Langmuir wave, $\tilde{T}_e$ is the electron temperature and $\tilde{\eta}$ is the gradient of the linear density ramp. This implies that a given Langmuir wave, of initial amplitude $\tilde{E}_{L0}$, moving down a density ramp of gradient $\tilde{\eta}$ and depth Δ will break, forming a jet, if Equation (3) is satisfied for some $0 < \tilde{x} < \Delta/\tilde{\eta}$. Finally, by assuming that the electrons which form the jet gain their kinetic energy directly from the potential of the Langmuir wave as it breaks, one can estimate the maximum energy within a jet as well as its energy spectrum - this is supported by the results from numerical simulations.

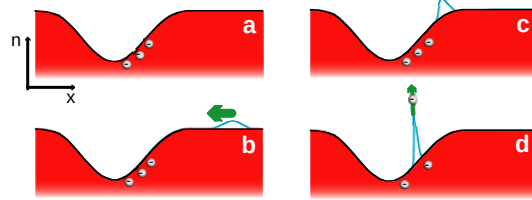


Figure 3. Diagrammatic representation of the process of Langmuir wave-breaking. a: Density hole with a few sample electrons highlighted. b: The crest of a Langmuir wave moves towards the density hole. c: As the wavefront moves down the gradient at the edge of the density hole, its phase velocity falls and the wavefront steepens. d: For a density hole of sufficient depth and steepness, the incoming wave breaks, forming a strong localised electric field which accelerates electrons from the inside edge of the caviton to create jets in electron phase space.

Conclusions

Shortly after exposing a fully relativistic Vlasov-Poisson system to a strong external driving field, at resonance, we observe the formation of fine structures in the electron distribution function corresponding to the acceleration of a small population of electrons to high energies (5 MeV). These phase space jets result from the interaction of Langmuir waves (initially excited by the driving field) with cavitons formed via the ponderomotive force exerted by the external driving field. We are able to explain the origin of the small populations of electrons which form the jets, derive a necessary condition for the formation of jets starting from a basic fluid treatment, and estimate the energy distribution of electrons within the phase space jet. This process may arise everywhere that Langmuir waves move through a density gradient, and is not limited to one dimension or to caviton formation. It may therefore require consideration in laser-plasma interaction contexts spanning inertial confinement fusion and particle acceleration.

Acknowledgement

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Extreme UV generation from molecules in intense Ti:Sapphire light

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Introduction

The use of ultrashort intense infrared light to study atomic and molecular dynamics on femtosecond timescales has been extremely successful. This technique, particularly in the pump-probe mode, has enabled an analysis in the time domain of molecular conformation changes and the study of excited-state vibrational dynamics. Very recently the prospect of resolving and manipulating electronic dynamics by creating high-frequency optical pulses has been advanced. To realise spatial and temporal resolution of electronic transitions within a molecule requires intense coherent light that switches on attosecond (10^{-18} s) timescales with wavelengths in the extreme ultraviolet or soft x-ray spectrum, $\lambda=0.1-10$ nm.

One of the most promising schemes for producing such light is through high-harmonic generation from intense Ti:Sapphire lasers interacting with gas-phase atoms and molecules¹⁾. The CCLRC-Central Laser Facility, Imperial College and Oxford are leading participants in a large UK consortium developing sub-femtosecond and attosecond pulses using the controlled generation of high-frequency light in atomic and molecular systems. The process of high-harmonic generation from IR light can be considered to have three distinct steps. Firstly, the initial molecular orbital is polarized and pulled away from the parent core by the external field to form a coherent continuum state, which then evolves within the laser field and finally, a few femtoseconds later driven by the field reversal, it returns to interact with the molecular core. In the ensuing collision the electron releases energy by bremsstrahlung during its passage across the molecule. Experiments have shown that the nonlinear medium, the molecule, has a critical role in forming, evolving and scattering the electronic wave packet, and hence in the generation of extreme UV light²⁾.

A feature of molecules that are hydrogenated or deuterated is that, for IR stimulation, the hydrogen vibrational relaxation time is comparable with the cycle time of the field, and hence the excursion time of the continuum wave packet. In previous work, we have shown that this vibration is extremely important for the process of ionization in light molecules³⁾ and in this work we show that it carries over to the process of harmonic generation. We study the quantal vibration effect in both long and short pulses and for both isotopes of hydrogen. In order to simplify the physics and isolate the important mechanisms, we consider the simple one-electron molecular ion and the single-molecule response for the spectral density.

Quantum vibration effects in 25 fs pulses

We simulate the dynamics of H_2^+ and HD^+ by direct solution of the time-dependent Schrödinger equation for the electronic and nuclear motion for the interaction of intense femtosecond pulses. On these timescales the rotational motion, even for such light molecules, is frozen. Therefore it is a reasonable assumption that the nuclear alignment is fixed during the pulse interaction and that rotation can be neglected. In terms of vibrational relaxation, and since the nuclei are light, vibration will be important over femtosecond timescales. Although homonuclear diatomics are IR-inactive, in an intense field one can create vibrational excitation through continuum coupling. To show the effect of vibration, consider a first approximation in which the nuclei are infinitely massive so they maintain their positions at a fixed bond length of $R=2$ a.u., throughout the process. A typical result for the single-molecule response for a 10 cycle, $\lambda=750$ nm pulse is shown in Figure 1. The spectrum has a characteristic plateau that is in rough agreement with the

classical cut-off. In the classical model the maximum photon energy depends on the ionization potential of the molecule ($I_0=31.7$ eV) and ponderomotive energy corresponding to an intensity of $I=4.5 \times 10^{14}$ W cm⁻² ($U_p=23.6$ eV). In this case, and under the assumption of fixed nuclei, only 1% of the molecules are ionized. A more realistic simulation, including quantal vibration, shows that 38% of the H_2^+ molecules are ionized. For the heavier isotope, HD^+ the yield is lower at 26% and closer to the infinite mass approximation. Our simulation shows that quantum vibration gives dramatically different results for ionization yields.

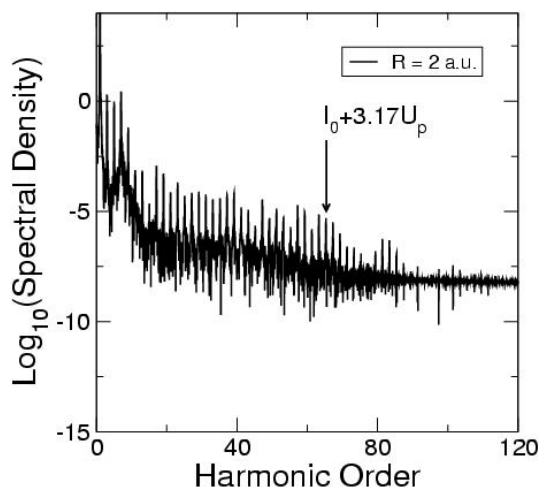


Figure 1. Simulation for frozen vibration showing the harmonic generation spectrum from the hydrogen molecular ion with fixed molecular bond length ($R=2$ a.u.). Indicated on the Figure is the classical cut-off frequency, which depends on the ionization potential (I_0) and ponderomotive energy (U_p). The incident pulse is 10 cycles, $\lambda=750$ nm, with intensity, $I=4.5 \times 10^{14}$ W cm⁻².

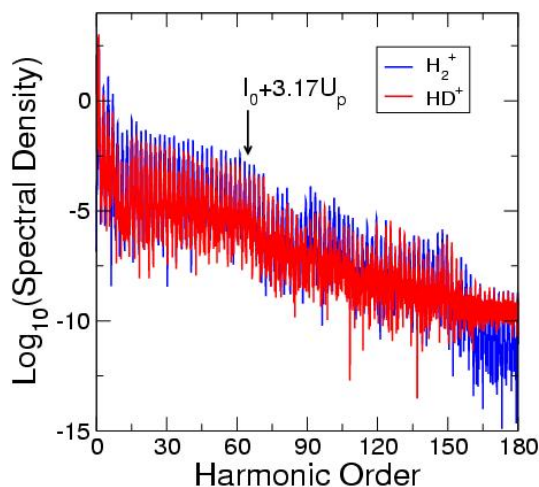


Figure 2. Simulation with quantal vibration. The harmonic generation spectrum from the hydrogen molecular ion including quantal vibration. The incident pulse is the same as that used for the results in Figure 1.

The corresponding harmonic generation spectrum including quantum vibration for the same 10 cycle, $\lambda=750\text{nm}$ pulse with intensity, $I=4.5\times 10^{14}\text{ W cm}^{-2}$, is shown in Figure 2. The spectrum of Figure 1 shows very significant inadequacies in the infinite mass approximation in qualitative and quantitative terms when compared with the quantum simulation (Figure 2). The molecule is much more efficient at high harmonic generation than one would conclude based on the infinite mass approximation. For example, around the 40th harmonic the quantum vibration amplifies the intensity by a factor of 100 in comparison with Figure 1. Furthermore, the classical cut-off law is no longer a reliable guide to the range of the plateau in Figure 2. Indeed the spectral density shows strong yields around 5nm, corresponding to the 150th harmonic, not replicated by Figure 1.

The primary reason for these quantal features is that molecular vibration assists the ionization process occurring via dynamic tunnelling ionization³⁾. One could cite this as an extreme example of phonon-assisted tunneling. Another factor is the quantum enhancement of bremsstrahlung due to nuclear wave packet expansion and dispersion increasing the cross section for electron-ion scattering.

Additional quantal effects are visible in the structure of the spectral lines. A closer analysis of the spectrum, see Figure 3 upper diagram, around the 45th harmonic shows that the sidebands of the triplet are prominent and well resolved. This is further evidence of strong continuum coupling. Conversely the fixed nuclei results show sharp central lines with very weak sidebands. We note that the small permanent dipole moment of HD^+ gives even harmonics for all harmonics. Around the 85th harmonic (Figure 3 lower) the even harmonics are present for both species indicating polarization during the pulse rise – a feature of high intensity and short pulse rise time.

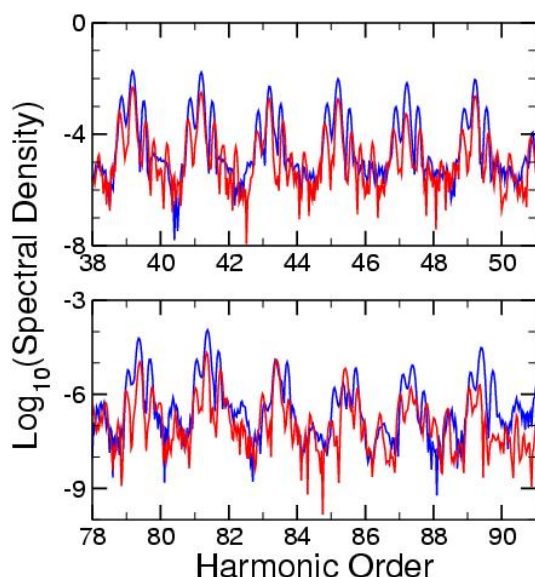


Figure 3. Simulation with quantal vibration. Expanded from Figure 2. The incident pulse is the same as that used for the results in Figure 1.

Quantum spectra for 5 fs pulses

Recent advances have led to the production of IR pulses that contain only a few optical cycles¹⁾. In Figure 4 we show full quantal simulations of few cycle intense IR pulses with molecular systems for $\lambda=750\text{nm}$, and $I=1\times 10^{15}\text{ W cm}^{-2}$.

Although the intensity is slightly higher than before (Figure 2), we do not saturate the process. For this case we find that 15% of the H_2^+ molecules are ionized and 12% of the HD^+ , showing the less important role of inertia in the ionization process. As for harmonic generation, in Figure 4 we note that the classical cut-off reappears – again a feature of the weaker effect of vibration.

The low-order spectral lines are broader than those of Figure 2 due to the bandwidth of the incident pulse and there is some significant blue shifting. In terms of efficiency, the yield around the 100th harmonic is comparable with the longer, lower-intensity pulse (Figure 2). However extreme UV generation is strongly attenuated and limited by I_0 . Another feature of this short pulse is unusual resonance lines at the lower harmonics.

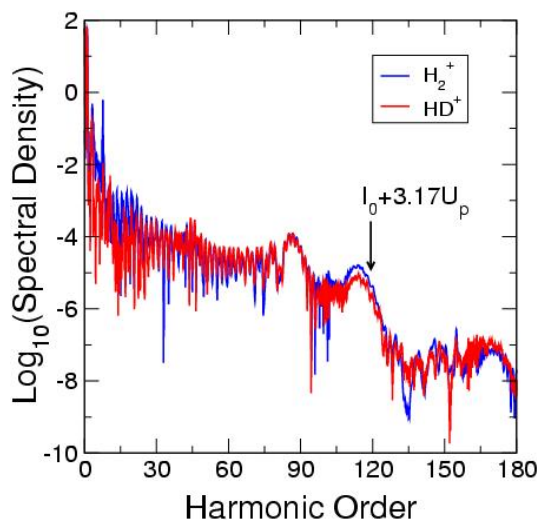


Figure 4. Simulation with quantal vibration as in Figure 2. The incident pulse has a Gaussian envelope FWHM 5fs, $\lambda=750\text{nm}$, with intensity, $I=1\times 10^{15}\text{ W cm}^{-2}$.

Conclusions

The simulations show that quantal vibration enhances the high-harmonic yield from hydrogen and deuterium molecules for intense femtosecond IR pulses. The spectral line shapes, sidebands and intensities of the harmonics show quantum features and can be calculated to high precision for arbitrary IR pulses. This will provide a useful tool for attosecond pulse design. For few-cycle IR pulses the molecular expansion is suppressed and the classical cut-off formula gives a reasonable limit for the harmonic plateau. The yields (intensities) of extreme UV light from these light dimers would be rather low in comparison with heavier multi-electron systems, although the a smaller ionization potential will limit the extent of the plateau. Diatomic molecules such as O_2 and N_2 relax slowly and thus quantal vibration will have a minor role for high harmonic generation using fs pulses. However IR-active molecules such as CO_2 will undoubtedly show quantal rovibration features of the initial state that will be an important factor in the spectrum and hence of interest to future developments in this field.

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Simulations of the production of mono-energetic electron beams from high-intensity laser plasma interactions

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Introduction

Electron plasma waves are highly suitable for accelerating electrons to relativistic energies since they are space charge longitudinal waves which can have relativistic phase velocities. They can support huge electric fields of the order of 100 GV/m and thus can accelerate electrons to large energies in extremely short distances.

Initial work on laser-plasma based accelerators envisioned the injection of pre-accelerated electrons into the wake of a laser pulse. This has many technical difficulties. The temporal duration of the injected bunch must be much shorter than the plasma wavelength or the energy spread of the bunch traveling at speed βc will increase dramatically.

$$\beta_{\text{ctbunch}} \ll \lambda_p$$

The electron bunch must be injected at the proper phase, meaning the timing jitter of the electron beam relative to the plasma wave must be much smaller than a plasma wavelength.

$$\beta_{\text{ctjitter}} \ll \lambda_p$$

These are both difficult to achieve for laser-plasma based accelerators. Simple wakefield generation is most efficient when the laser pulse duration is half the plasma wavelength.

$$\tau_{\text{laser}} = \lambda_p / 2$$

Also the transverse dimension of the electron bunch must be comparable to, or smaller than, the width of the plasma waves. If the bunch is wider than the wave only a fraction of the injected electrons will be accelerated in the forward direction. There will also be an increase in the emittance of the accelerated beam. In laser driven systems the plasma wave width (and hence the width of the electron bunch) is governed by the focal spot diameter, typically $\sim 25 \mu\text{m}$ for a long focal length system.

$$W_{\text{bunch}} \sim W_{\text{focus}}$$

Therefore to achieve optimum wakefield generation and optimum acceleration of an electron bunch with the Astra laser would require the following characteristics:-

$$\begin{aligned} \tau_{\text{laser}} &= 40 \text{ fs} \\ n_e &\sim 2 \times 10^{18} \text{ cm}^{-3} \\ \tau_{\text{bunch}} &\ll 80 \text{ fs} \\ \tau_{\text{jitter}} &\ll 80 \text{ fs} \\ W_{\text{bunch}} &\sim 25 \mu\text{m} \end{aligned}$$

These parameters, in particular the bunch duration and jitter are difficult to achieve using conventional pre-acceleration techniques. It seems likely therefore that the realisation of a laser plasma accelerator will rely on the optical injection of electrons into a wakefield.

The electrons produced by laser-plasma interactions typically originate from the breaking of plasma waves. This is when the plasma wave is driven non-linearly to very large amplitudes and wave energy is then directly transferred to particle energy.

The broken-wave based electron sources measured to date have one major drawback for most applications; the energy spreads are always exceptionally broad ($\Delta E/E \sim 100\%$) and have an exponential spectrum, meaning there are many more low energy electrons than the desired high energy ones.

In theory, wavebreaking is capable of producing narrow energy spread electron energy spectra^{1, 2)}, but the experimental data measured previously has only shown quasi-thermal distributions. Recent results obtained on the Astra laser system^{3, 4)} have shown experimentally that, under the right

conditions, mono-energetic features can be produced by wavebreaking itself.

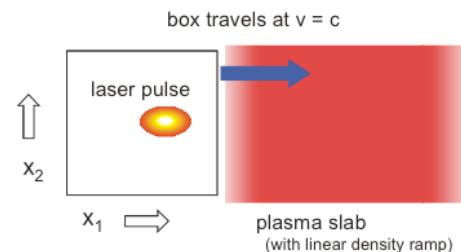


Figure 1. Schematic of the 2D3V PIC simulations performed with OSIRIS.

Set up of simulations

A series of 2D3V PIC simulations using the code OSIRIS has been performed to investigate the acceleration of electrons from the breaking of plasma waves with the Astra laser. The simulations use a 40 fs laser pulse with a normalised vector potential of $a_0 = 1.1$ and a focal waist of $25 \mu\text{m}$ FWHM. The plasma profile used closely matches that of a gas jet target as used in experiments^{5, 3, 6)}.

The simulation space is a 2 dimensional slab which moves at the speed of light along the laser propagation direction, x_1 . The space extends in the transverse direction, x_2 while field and particle momentum quantities are three-dimensional ($p_1, p_2, p_3, E_1, E_2, E_3, B_1, B_2, B_3, j_1, j_2, j_3$). In the simulations presented here, the size of the slab in x_1 - x_2 space was 96×64 laser wavelengths. The simulation space was split into 1536×1024 cells. There were 4 electrons per cell, with a background of immobile ions. The simulations were run on an 8-node Apple G5 cluster at Imperial College.

The plasma waves produced by such laser pulses are far from planar and it is wholly inappropriate to simulate these situations in 1 dimension. Obviously in an ideal situation we would simulate these interactions with a fully 3D code, but this would require large amounts of time on super computers. 2D3V simulations bridge this gap, containing a full description of the electromagnetic fields while reducing the number of grid points and particles needed to simulate these situations with appropriate resolution.

2D3V simulations essentially contain all the physics that occurs in laser plasma interactions, although they do not completely model self-focusing and other phenomena due to the reduced numbers of degrees of freedom. 2D3V codes consistently predict lower electron energies than observed either experimentally or in fully 3D simulations of the same parameters⁷⁾.

The simulations were performed over a range of electron densities, ranging from $0.001 n_c$ to $0.01 n_c$ (n_c is the critical plasma density and, for a 800 nm laser is $1.75 \times 10^{21} \text{ cm}^{-3}$).

Simulation Results

In the simulations the laser pulse drives a plasma wave, which traps and accelerates electrons. Under certain conditions these waves become highly non-linear and wave breaking occurs in such a way as to inject a short, narrow energy spread bunch of

electrons into the wave, which are then further accelerated. If this bunch of electrons continues to interact with the plasma wave it eventually becomes de-phased from the wave (because the electrons travel at a higher velocity than the phase velocity of the wave).

The simulations show that quasi-thermal spectra produced in previous experiments are due either to catastrophic wave breaking (where wave breaking results in the complete loss of coherence of the plasma wave) or because the injected bunches propagate for a significant distance after they are injected, such that they de-phase from the plasma wave, during which time the energy spread of the bunch is significantly increased.

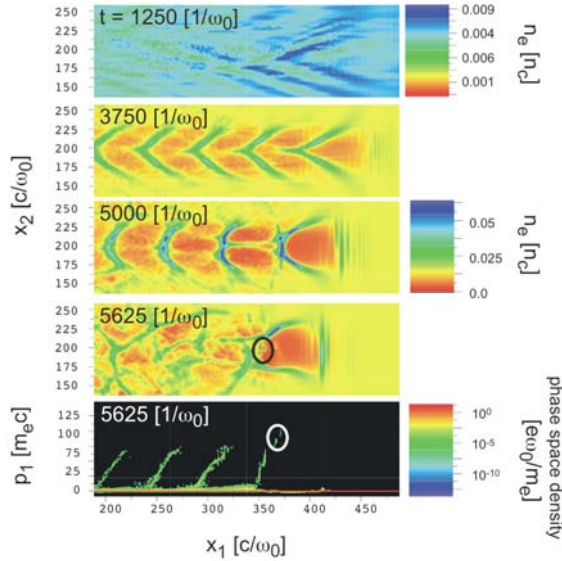


Figure 2. Electron density at various times in a $n = 0.015 n_c$ simulation. The bottom panel shows the p_1 - x_1 phase space at the latest time. The bunches that have been injected into the wave are circled. The simulation window is moving from left to right.

Figure 2 shows the electron density at various times in a typical simulation. When the plasma waves are set up initially they have distinctly 2D shape, forming a series of “<” shaped density perturbations behind the laser pulse. This is due to the multi-dimensional nature of the plasma waves. In the simulations presented here, the ponderomotive force of the laser, which drives the plasma waves has strong longitudinal and transverse components. The ratio of these two is simply given by the ratio of the focal spot diameter to the pulse length, which for the set-up described here means that the longitudinal component is twice the transverse component. As the wave amplitude increases the plasma wave becomes non-linear, introducing a curvature to the wave front.

As the plasma wave amplitude increases further it eventually reaches a point where wavebreaking occurs. The multi-dimensional nature of the plasma wave means that this happens primarily due to transverse effects. When wave breaking occurs it can inject a bunch of electrons into the wakefield. Such a bunch is clearly visible in the $t = 5625 \text{ } 1/\omega_0$ panel of Figure 2.

It can be seen that the curvature of the plasma wave is due to the non-linearity of the plasma wave by examining the frequency spectrum of the plasma wave electric field, E_1 (see Figure 3). At early times the k-spectrum is dominated by the fundamental plasma frequency, where as at later times, when the wave front is curved, higher order harmonics of the plasma wave frequency are visible in the spectrum, as shown in Figure 3. This is characteristic of non-linear waves⁸⁾.

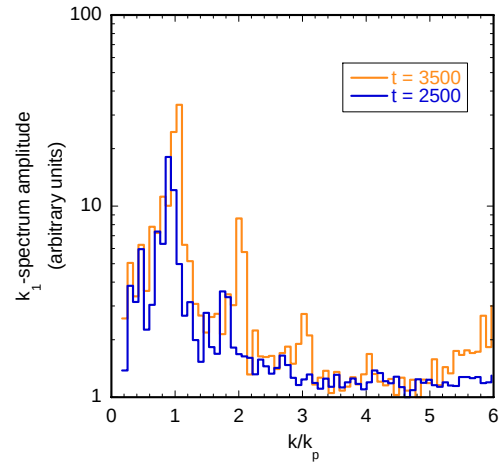


Figure 3. Plasma wave electric field k-spectrum (examining wavelengths in the x_1 direction) in a $n = 0.015 n_c$ simulation at $t = 2500 \text{ } 1/\omega_0$ (blue) and $t = 3500 \text{ } 1/\omega_0$ (orange). The wave-number k_1 has been normalized to the relativistic plasma wave-number $k_p = \omega_p/c$.

The non-linearity is driven in part by focusing of the laser pulse in the plasma wave, which leads to conical shaped laser cone that is more efficient at driving plasma waves. The plasma is capable of focusing the pulse due to the transverse density gradients associated with the wave. Focusing due to a plasma density profile occurs when there is a density minimum on axis, since the laser pulse sits in the plasma wave, the rear of the pulse experiences this focusing effect. Since the rear of the pulse is now focused more tightly it is now more efficient at generating the plasma wave – leading to positive feedback. The focusing of the laser pulse is the primary cause of the increase of the plasma wave amplitude throughout the simulation, without some non-linear effect or inhomogeneity in the plasma density, the plasma wave amplitude would not grow.

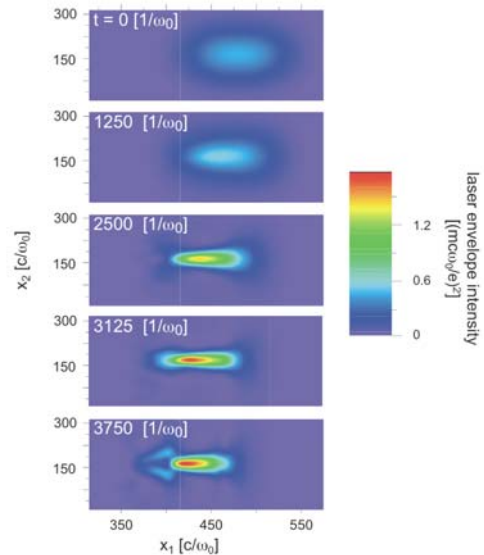


Figure 4. Laser intensity envelope at various times in a $n = 0.015 n_c$ simulation.

As the plasma wave amplitude grows it eventually ‘pinches off’ some of the laser intensity – this results in a reduction in the laser intensity in the region of the plasma wave. This allows the injection of electrons into the wake at points from which they would otherwise be excluded due to the laser’s ponderomotive force. This can be seen in the $t = 3750 \text{ } 1/\omega_0$ panel of Figure 4. This pinching actually seeds the injection of the electrons into the wake. When wavebreaking occurs, it lowers the plasma

wave amplitude – to a point below the wave-breaking threshold, thus “switching off” the injection mechanism and resulting in a short bunch. This bunch is therefore at a particular phase of the plasma wave and hence has a narrow energy spread. At later times the amplitude of the plasma wave can rise to the breaking point once more, either in the first wave period or in subsequent trailing wave periods, resulting in the creation of other electron bunches with different energies. This would result in the observation of multiple spikes in the electron energy spectrum, as seen in experiments^{4, 3)}.

If the plasma or interaction length is sufficiently long then the electron bunches have sufficient time to overtake (or de-phase) from the plasma wave – this leads to an increase in the energy spread of the bunch. The de-phasing length $L_d = 2\pi c \omega_0^2 / \omega_p^3 \propto n^{-3/2}$ decreases with density so shorter interaction lengths are required to transport the mono-energetic features out of higher density simulations. Figure 5 shows the time history of the electron energy spectrum (integrated over the simulation space) as a function of time in a $n = 0.0125n_c$ simulation. Four specific points in time are indicated: (1) the plasma wave becomes non-linear and electrons become trapped in the wave; (2) wave breaking occurs and a narrow energy spread feature emerges and is accelerated; (3) wave periods further down the wave train also reach wave breaking amplitude resulting in further narrow energy spread features and (4) the electrons have outrun the plasma wave, leading to an increased energy spread.

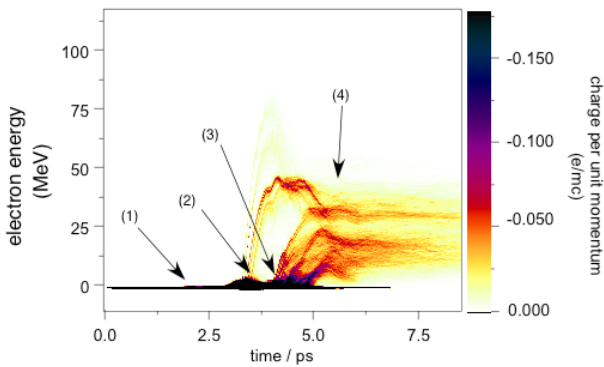


Figure 5. Time history of the electron energy spectrum in a $n = 0.0125n_c$ simulation.

In our simulations of the Astra experiments it has emerged that there are two parameters which determine whether mono-energetic features are produced in the electron spectrum. These are the plasma density and the interaction length. The time at which the plasma waves takes on the curved shape before wavebreaking and the time at which wave breaking itself occurs are both inversely proportional to the plasma density, suggesting that the growth of the plasma wave is linear with time. This is shown in Figure 6, and suggests that it should be possible to choose a density – interaction length combination which produces narrow energy spread electron bunches over a range of plasma densities.

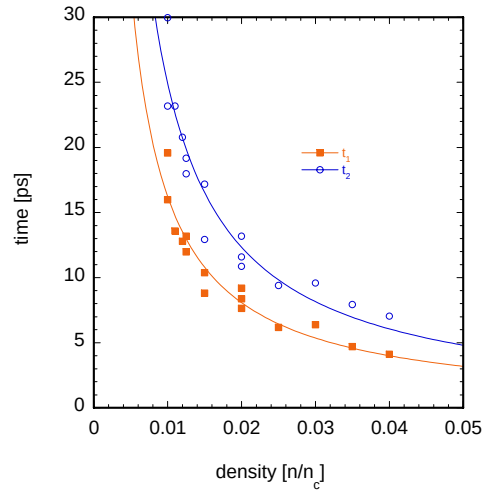


Figure 6. Variation with density of the time when the electron plasma wave becomes non-linear (t_1 , orange squares) and when injection due to wavebreaking occurs (t_2 , blue circles).

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Quasi-linear model of non-local magnetic field generation in laser-plasmas

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Introduction

A new magnetic field generation mechanism in laser-plasmas was recently reported¹⁾. This source, which was first seen in Vlasov-Fokker-Planck simulations using the simulation code IMPACT, works in a semi-collisional regime in contrast to conventional mechanisms such as the $\nabla n \times \nabla T$ source (collisional) or ponderomotive mechanisms (collisionless). In essence it is a non-local analogue of the $\nabla n \times \nabla T$ mechanism but can operate without the need for a density gradient. Analytical models are being developed to further our understanding of how this B-field source works and also to identify the key parameters and their scalings. One model predicts the early time growth (i.e. over the first few collision times) of B-field from arbitrary temperature, density and Z (degree of ionization) profiles. The newest model employs a quasi-linear like approach and is valid for arbitrarily long times. It applies to pairs of temperature perturbations (with ∇n_e and ∇Z uniform) and shows that non-parallel perturbations with *different* wavelengths drive B-field generation. Although this quasi-linear model does not include heating – it is developed in terms of decaying temperature perturbations – we find that it does a very good job at describing B-field growth seen in simulations where the plasma is heated.

Overview

The $\nabla n \times \nabla T$ or thermoelectric mechanism is a well-known source of B-fields in laser-plasmas under collisional conditions²⁾. It is responsible for the B-fields observed in the plasma ablated from the surface of solid targets and foils when illuminated by an intense laser pulse. These fields have been shown to affect expansion of the ablated plasma³⁾. Additionally strong thermoelectric magnetic fields are believed to be responsible for the hot spots measured in the (ionized) gas fill of hohlraums⁴⁾ since they suppress thermal transport. The thermoelectric B-field mechanism originates from the curl of the ambipolar electric field that maintains quasineutrality, i.e. $\mathbf{E} = -\nabla P_e / (en_e)$, where $P_e = n_e T_e$ is the electron pressure. The pressure gradient is one term appearing in Ohm's law, which describes momentum balance of the electron fluid. A detailed discussion of the effect of each term in Ohm's law on B-field dynamics in laser-plasmas can be found in Reference 5.

The local approximation is conventionally made when obtaining the versions of Ohm's law (e.g. Braginskii's version) from the Vlasov-Fokker-Planck (VFP) equation which are then used to derive the $\partial \mathbf{B} / \partial t = -(k_B / en_e) \nabla n_e \times \nabla T_e$ source. In the local approximation, f_0 the isotropic part of the electron distribution function is assumed to be Maxwellian f_M (in the ion rest frame). This is only valid when the characteristic temperature and density scale-lengths are much longer than the electron collisional mean-free-path λ_c . By solving the Vlasov-Fokker-Planck equation directly, and thereby dispensing with the local approximation, we have found new B-field source terms which are non-local analogues of the $\nabla n_e \times \nabla T_e$ mechanism. It is well known that non-local effects play a crucial role in determining heat flow down steep temperature gradients; they explain the severe reduction of heat flow compared to the Spitzer-Harm value (which uses the local approximation) when the temperature scale length approaches λ_c the collisional mean-free-path. This necessitates the use of flux limiters in hydro codes. We find that non-local effects are also relevant to magnetic field generation and in this context they also become important when the characteristic temperature, density and/or Z scale-lengths approach λ_c . Such conditions are found, e.g., in

the gas fill of hohlraums where the high temperature $\sim 5\text{keV}$ plus low density, of the order of 10^{21}cm^{-3} , and Z result in a mean-free-path (for thermal electrons) that is a substantial fraction of the dimensions of the hohlraum container.

VFP simulations

Kinetic simulations of a uniform density plasma undergoing strong heating, carried out using the VFP code IMPACT⁶⁾, have shown that magnetic fields strong enough to seriously affect heat flow out of the heating region can spontaneously grow via the non-local mechanism. IMPACT uses the diffusion approximation and expands the electron distribution function (EDF) as $f = f_0 + (\mathbf{v} \cdot \mathbf{f}_1) / v$ where f_0 essentially describes densities (e.g. number and energy), while $\mathbf{f}_1$ describes fluxes (e.g. current and heat). The part of the EDF that describes anisotropic pressure and electron viscosity, i.e. $\mathbf{f}_2$, is not currently considered (nor the higher order anisotropic components, $\mathbf{f}_3$, $\mathbf{f}_4$, etc.). In one simulation¹⁾ heating with a rippled profile, described by $1 - \tanh[(x - \{x_0 + \Delta \cos(ky)\}) / L]$, was applied at the left edge of a computational domain of size $x_{\text{len}} = 12\lambda_c$ by $y_{\text{len}} = 2\lambda_c$. In another simulation⁷⁾ a larger system with $x_{\text{len}} = 60\lambda_c$ by $y_{\text{len}} = 10\lambda_c$ was simulated. Unlike in Reference 1, it was the degree of ionization Z that was modulated (with a rippled profile) and the heating was planar. In both cases the plasma became magnetized with $\omega_{ge} \tau_c$ reaching values of 10 in places. The absence of anisotropic pressure, rules out mechanisms like Weibel as the cause of the B-fields observed.

The general basis for this non-local B-field source can be understood by obtaining a more general version of Ohm's law that does away with the local approximation. Under the assumptions/simplifications used in the simulations, Ohm's law becomes $e\mathbf{E}/m_e = -\nabla(n_e \langle v^5 \rangle) / (6n_e \langle v^3 \rangle)$ when the current and magnetic field are negligible (as occurs initially). This is valid for arbitrary f_0 and the moments are defined as $n_e \langle v^m \rangle = 4\pi \int f_0 v^{2+m} dv$. The curl of the electric field therefore involves the cross product $\nabla(n_e \langle v^3 \rangle) \times \nabla(n_e \langle v^5 \rangle)$. When $f_0 \rightarrow f_M$ the moments become $\langle v^m \rangle \propto (T_e)^{m/2}$ and the familiar result, $\nabla n_e \times \nabla T_e$, is recovered. But if f_0 is not Maxwellian a B-field can be generated even when $\nabla n_e = 0$ if the gradients in the $\langle v^3 \rangle$ and $\langle v^5 \rangle$ moments are not parallel. Non-local transport, which leads to a non-Maxwellian f_0 , can achieve this.

Early time model

The 'early time model'⁷⁾ describes this distortion of f_0 due to non-local transport of electrons and the subsequent spontaneous generation of B-field. We have developed an analytical expression for the magnetic field that is generated at early times by prescribed, initial, electron temperature, density and Z profiles. When the density and temperature are uniform:-

$$\frac{e\mathbf{B}}{m_e} = -\left(\frac{\lambda_c^4}{\tau_c^3}\right) \frac{\nabla T}{T} \times \left[154 \frac{\nabla(\nabla^2 T)}{T} + 620 \frac{\nabla(|\nabla T|^2)}{T^2} \right] \quad (1)$$

where $\lambda_c \propto T_e^2 / Zn_e$ and $\lambda_c = v_{Te} \tau_c$ as usual and the numerical coefficients are given to 3 significant figures. The model assumes that f_0 starts out as Maxwellian (with the relevant local density and temperature) at $t=0$. Other assumptions are no time dependent ionization, no ion motion, no electron inertia and only e-i collisions. It is valid in the limit when $\mathbf{B}$ and $\mathbf{j}$ are negligibly small. Its range of validity extends over the first few collision times only. Next, adding in spatially varying Z

introduces 4 extra terms involving factors like $(\nabla Z/Z) \times (\nabla T/T)$ [see⁷]. Finally introducing density gradients reveals another 14 terms with factors like, e.g., $(\nabla n/n) \times (\nabla T/T)$ and $(\nabla n/n) \times (\nabla Z/Z)$. Note that a similar expression can be obtained in the local limit but has 9 terms, none of which vary like $(\nabla T/T) \times$ or $(\nabla Z/Z) \times$, and the numerical coefficients are 4–15 times smaller.

Quasi-linear model

The quasi-linear model is based on linearization of the f_0 and f_1 VFP equations for harmonic, decaying temperature-perturbations (but uniform density and Z) with $\delta T_j \propto \cos(\mathbf{k}_j \cdot \mathbf{x}) \exp(-\gamma_j t)$, (see⁶ for the f_0 and f_1 equations.) Electron-electron collisions are included in the evolution equation for f_0 but we use a Krook collision operator, $(\partial_t f_0)_c = -(\mathbf{v}_{ee}/v^p)(f_0 - f_M)$ (where ‘p’ can be changed to specify how collision rates scale with velocity) rather than the full integro-differential operator (involving Rosenbluth coefficients etc.) used in IMPACT. The first order f_0 and f_1 equations are combined and using two appropriate constraints (usually $j=0$ and $\delta n=0$ to first order in δT_j), we are able to obtain a dispersion relation which relates the decay rate γ_j to that perturbation wavenumber $\mathbf{k}_j$. This shows that $k\lambda_{ed}$ is the key parameter where $\lambda_{ed} = \sqrt{(\lambda_{ee}\lambda_{ei})}$ is the electron delocalization length⁸). Proceeding onto the second order f_1 equation it is possible to derive the following expression for non-local B-field growth:-

$$\dot{\omega} = \tau_c^{-2} \psi_{NL} (\mathbf{k}_1 \lambda_c \times \mathbf{k}_2 \lambda_c) \left(\frac{\delta T_1}{T} \right) \left(\frac{\delta T_2}{T} \right) \sin(\mathbf{k}_1 \cdot \mathbf{x}) \sin(\mathbf{k}_2 \cdot \mathbf{x}) \quad (2)$$

where ω is the electron gyro frequency (vector) and ψ_{NL} is a function that essentially encapsulates the degree of non-locality and is a (complicated) function of $k_1 \lambda_{ed}$ and $k_2 \lambda_{ed}$. It turns out that $\psi_{NL} \rightarrow 0$ when $k_1 \lambda_{ed} = k_2 \lambda_{ed}$. Additionally, it is immediately apparent from Equation (2) that the temperature perturbations must not be parallel either.

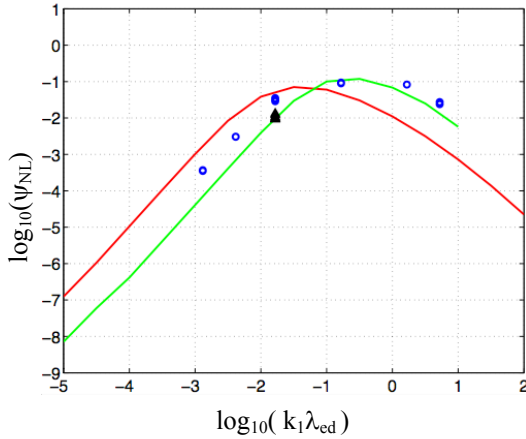


Figure 1. Scaling of the non-locality parameter for B-field generation, $\psi_{NL}(k_1 \lambda_{ed}, k_2 \lambda_{ed})$, with temperature perturbation $k_1 \lambda_{ed}$ (when $k_2 \lambda_{ed} = 2k_1 \lambda_{ed}$). The quasi-linear model with $v_{ee} \propto v^{-3}$ (red curve) and $v_{ee} \propto v^0$ (green), VFP simulations with full e-e collision operator (blue points) and the simplified Krook collision operator with $v_{ee} \propto v^0$ (black points) are compared.

Figure 1 shows how ψ_{NL} varies with $k_1 \lambda_{ed}$ when $k_2 \lambda_{ed} = 2k_1 \lambda_{ed}$. It is apparent that degree of non-locality is within a factor of ~ 3 of the optimum over a wide range, $0.01 < k_1 \lambda_{ed} < 1$ (i.e. $6 < \lambda_1/\lambda_{ed} < 600$). Figure (1) shows that the quasi-linear model (with its simplified treatment of e-e collisions) recovers the essence of the non-local source. Furthermore Figure 2 demonstrates that if heating is applied with a dual $1 + \cos(\mathbf{k} \cdot \mathbf{x})$ spatial dependence (instead of starting with temperature

perturbations and letting them decay), the ψ_{NL} parameter measured in VFP simulations is still in good agreement with the quasi-linear model. Therefore the mechanism is robust. The blue curve on the right figure corresponds to $\lambda_1 = 380 \lambda_{ed}$, $\lambda_2 = \lambda_1/2$, $Z=10$, and heating at a (peak) rate (per mode) that raises T_e by the initial temperature T_0 in 10^4 e-i collision times (τ_{ei}). Time progresses along the curve starting at the lower left. The non-locality rapidly develops (the ‘stem’ of the curve) and then over time the system gradually heats up and $k\lambda_{ed}$ increases (the ‘cap’ of the curve) since $\lambda_{ed} \propto T^2$. The simulation ends after $8500 \tau_{ei}$. The magenta curve corresponds to $\lambda_1 = 200 \lambda_{ed}$, $\lambda_2 = \lambda_1/2$, $Z=1$, $t_{max} = 450 \tau_{ei}$ and heating at T_0 per $180 \tau_{ei}$. For very strong heating rates approaching T_0/τ_{ei} we expect significant departures from the quasi-linear model.

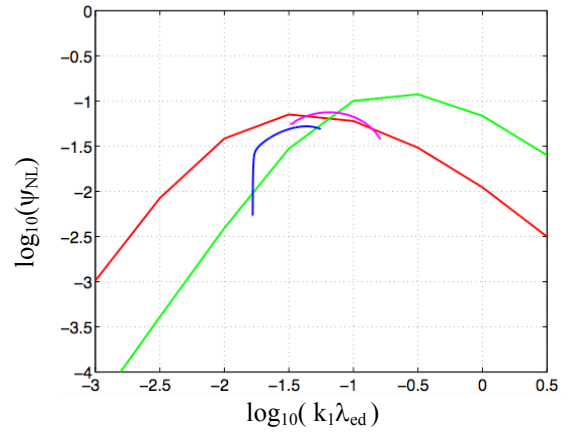


Figure 2. Non-locality parameter for B-field generation measured from two VFP simulations of heated plasma (blue and magenta curves) next to the same ‘quasi-linear model’ curves (red and green) described in figure (1).

Finally, it should be said that simple scaling arguments suggest that non-local B-field generation by dual δT_e modes will exceed the (local version of the) $\nabla n_e \times \nabla T_e$ source when $L_T < L_n \psi_{NL}$ where $L_T = |\nabla T/T|$, etc. Thus for sufficiently compact hot spots where the main Fourier components fall within $0.01 < k\lambda_{ed} < 1$ and for gentle enough density gradients, non-local B-field generation is expected to exceed the conventional $\nabla n_e \times \nabla T_e$ source.

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Highly resolved spectroscopic measurements of aluminium plasma

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Introduction

X-ray spectroscopy provides a powerful tool for accurately diagnosing the hydrodynamic conditions and ionisation balance of a hot dense plasma. Detailed spectral line shape measurements can yield information on population kinetics, opacity, and radiative processes¹⁾. In addition, Baranger and Mozer²⁾ suggested that an oscillating electric field can be diagnosed through the appearance of field induced satellites to allowed and forbidden transitions. Vinogradov³⁾ proposed that the intensity of a laser focusing in to a plasma may be determined from such satellites. Here we describe an experiment suitable for studying so-called laser satellites. The objective is to produce a test-bed plasma with minimal temperature and density gradients, and independently diagnosed using both X-ray and optical methods. This plasma is then suitable for use as a spectroscopic source for highly resolved spectral measurements. Measurements are made in the absence of a perturbing laser field for comparison with future laser-satellite studies. Experiment, high-resolution spectral data and the proposed laser-satellite suitable for study are discussed.

Experimental target requirements

An ideal test-bed plasma for the experiment consists of a one dimensional (1d) expanding column of plasma with an expansion direction normal to the target surface. The plasma should be optically thin and lateral expansion as small as possible. This will ensure that the density gradients are predominantly normal to the target surface and that in a horizontal slice of the expanding plasma, the same conditions of temperature and density will be present throughout. A further target requirement is that the plasma conditions are consistently reproduced on a shot to shot basis. The target design therefore plays a vital role in the formation of the 1d plasma.

A target that meets these requirements consists of a small aluminium dot (100 – 200µm dot or square, 1µm thick) deposited on a mylar (C₁₀H₈O₄) substrate⁴⁾. When the target surface is ablated, the Al plasma is confined by the surrounding lower density mylar plasma to rise in a vertical column.

Experiment arrangement and diagnostics

The experiment was carried out using Target Area West at the Vulcan laser facility. Targets consisted of a 1µm thick, 200µm square aluminium dot mounted on a mylar substrate. These were irradiated by four infra-red (1054nm) beams giving a pulse of 1ns and intensity of 10¹⁴ Wcm⁻² (500µm focal spot diameter), producing the 1 dimensional column of plasma. An intense CPA pulse of 10ps at 527nm was focused into the aluminium plasma. The beam provided the probe for the Raman scattering diagnostic. Introducing the pulse at heights of 100–1000µm above the target surface allowed the CPA pulse to interact with plasma over a range of different temperatures and

densities. The CPA pulse also supplied the electric field needed to allow a possible production of laser-satellites. Figure 1 shows the target and geometry of the laser pulses (the CPA is not shown).

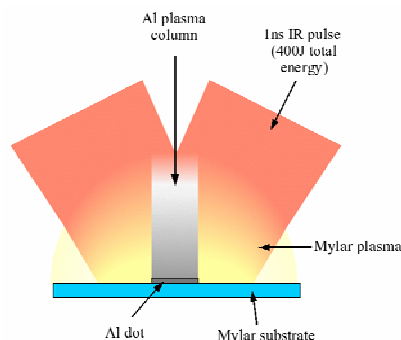


Figure 1. Geometry of target and infra-red heater beams.

To diagnose the plasma, both optical and X-ray diagnostics were used. Thomson and Raman scattering provided information on the electron temperatures and densities. A flat crystal spectrometer coupled to a CCD camera was used to record the hydrogen and helium like series of X-ray K-shell emission. High resolution X-ray spectroscopy was carried out using a vertical-geometry Johann spectrometer⁵⁾ and with a toroidally bent crystal^{6,7)}. These devices employ curved quartz crystals and allow the profiles of individual emission lines to be resolved spectrally and spatially without the use of a slit.

For dot targets, the spectral resolution of the two curved crystal spectrometers was primarily limited by the size of the crystal rocking curve, allowing resolution of line profiles and identification of spectral features to better than milli-Angstrom level. The high-resolution toroidal crystal device gave a spatial resolution of ~5µm. The geometry and luminosity of this diagnostic also enabled time resolved spectra to be recorded using a streak camera. In contrast, the flat crystal spectrometer had a spectral resolution that was dominated by the source size. A slit was used with this device, giving a spatial resolution of ~25µm.

Pinhole cameras with sufficient filtering to remove X rays with energies of less than 1keV were used to image the expanding plasma. These were positioned to look at the plasma from above and from the side, to help determine whether a 1d system had been achieved by examining the extent of the X-ray emission.

Results

A pinhole camera image of an ablated dot target is shown in Figure 2. This indicates that there was very little lateral expansion of the plasma up to 800µm from the target surface and that the expansion can be considered to be 1 dimensional up

to this position. This contrasts strongly with results from foil targets in which plasma expands in a near semi-spherical plume with a substantial optical depth. Large line profile modifications believed to be due to opacity were also observed in the He β emission ($1s^2\ ^1S - 1s3p\ ^1P$) for foil targets close to the target surface. No similar effects were found in spectra from dot targets. This supports the assumption that the plasma from dot targets can be considered to be one-dimensional.

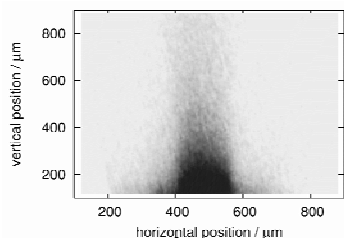


Figure 2. An X-ray pinhole camera image of an ablated dot target. The Al plasma column remains well collimated up to $\sim 800\mu\text{m}$ from the target surface.

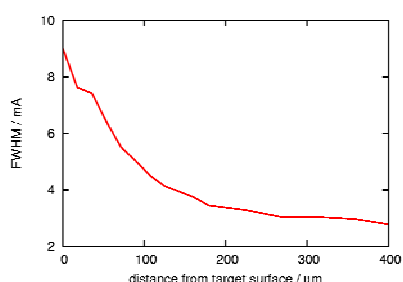


Figure 3. The line width of the He β transition as a function of distance from target surface.

The quality of the high-resolution spectral data (see Figure 4a) was sufficient to allow Stark and Doppler broadened linewidths of He β to be measured from spectral profiles. The linewidths were then used to provide an estimate of density. This was done using the atomic physics code FLY⁸⁾. This is a zero dimensional atomic physics code that can calculate synthetic K-shell spectra produced by a plasma with a specified electron temperature and density. The measured linewidths are shown in Figure 3. By comparing the theoretical with the experimentally measured linewidths, the electron density at different distances from the target surface can be estimated. Results are approximate, but within $20\mu\text{m}$ of the target surface $n_e > 10^{22}\text{cm}^{-3}$, and beyond $100\mu\text{m}$ $n_e \sim 10^{21}\text{cm}^{-3}$. Beyond $\sim 300\mu\text{m}$ Doppler broadening dominates the linewidth. These can be considered to be reasonable estimates of maximum electron density.

Figure 4 shows a high-resolution X-ray spectrum near to the He β line in which satellite emission close to the target surface was recorded. The raw data in Figure 4a shows that good signal strength was achieved, with low levels of background noise and emission clearly observed at distances of more than 1.5mm above the target surface. Cross sections of the raw data are given in Figure 4b. The high spectral resolution allows the intercombination line at $6.645\text{\AA}$ ($1s^2\ ^1S - 1s3p\ ^3P$) and the satellite emission to be well resolved. The spatial resolution shows that unusual satellite emission occurs near to the target surface. Recent simulations have suggested that the satellites are strongly correlated to an excited $1s2l$ state populated by collisional processes close to the target surface⁹⁾.

No effects of the CPA pulse, used for Raman scattering measurements, such as laser-satellites or additional heating, were observed in the X-ray spectra. The CPA pulse was applied 1ns after the peak of the heater pulse at $\sim 300\mu\text{m}$ from the target surface, so some features could be expected to appear at this position in the spectra. As can be seen from Figure 4, no such features are visible. This could be caused by refractive effects in

the mylar plasma leading to a reduced focused intensity at the Al core, or due to low He-like excited state populations.

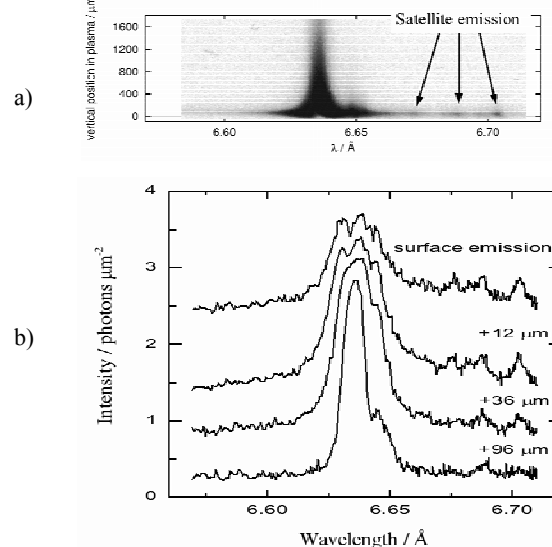


Figure 4. The He β emission line recorded by the high dispersion spectrometer showing unusual satellite emission. a) Raw data, b) Cross sections close to target surface.

This would reduce the intensity of possible satellite emission due to weaker laser electric field. The degree of line profile modification predicted by Peyrusse¹⁰⁾ for large laser fields would also be reduced. Another possible reason for lack of laser-satellites could be an insufficient population of the correct energy levels at the time of the CPA due to overheating of the plasma. Clearly this issue must be resolved to maximise the chance of producing laser-satellites in future experiments.

Had laser-satellites been present, they would have been recorded by the high resolution X-ray diagnostics. The frequencies of laser-satellite emission are given by $\omega_{\text{sat}} = \omega_{ij} \pm \omega_{\text{las}}$, where ω_{ij} and ω_{las} are the forbidden transition and laser photon frequencies respectively. In the experiment, the observed X-ray emission was between $5.5\text{\AA}$ to $7.2\text{\AA}$ and a 532nm laser (the Raman scattering beam) was used. With these conditions laser-satellites to the forbidden $1s3d\ ^3D$ level at 6.628 and $6.645\text{\AA}$ may be produced, separated from the He β resonance line by $\sim 8.3\text{m\AA}$. These wavelength differences are resolved by the high spectral resolution X-ray diagnostics.

Conclusions

The experimental results have shown that a one-dimensional plasma was formed from a dot target, with repeatable plasma conditions from shot to shot. Dielectronic satellites of an unusual origin were produced in the dense region close to the target surface. Strong line profile modification due to opacity and density effects was also found for foil targets. No laser-satellite emission was observed, possibly a result of refractive index effects and overheating of the plasma. Work is currently in progress to diagnose the plasma conditions more thoroughly to gain insight into the population kinetics.

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Ultrafast photochemical dissociation of an equatorial CO ligand from *trans*(X,X)-[Ru(X)₂(CO)₂(bpy)] (X = Cl, I). A picosecond time-resolved infrared spectroscopic and DFT computational study

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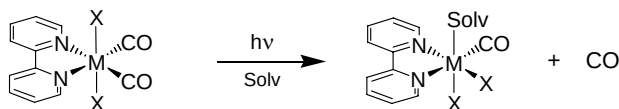
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Introduction

Optical excitation of transition metal carbonyl complexes often results in breaking of a metal-CO bond. The nature of the reactive excited states, excitation-energy dependence, vibrational excitation, stereospecificity, and competition with alternative pathways, is of a considerable importance. Photodissociation of a CO ligand generates highly reactive coordinatively unsaturated species that can even activate C-H bonds in hydrocarbons.

Mechanistically, a very interesting case is posed by carbonyl complexes containing electron-accepting ligands such as [M(CO)₄(α-diimine)]. Photochemical carbonyl dissociation from [M(CO)₄(diimine)] complexes is highly stereospecific, concerning only the axial CO ligand that is coordinated perpendicularly to the M(diimine) plane. Equatorial CO ligands in these complexes are inert towards photodissociation. Nevertheless, equatorial CO dissociation was observed¹⁻⁴ in the complexes *trans*(X,X)-[Ru(X)₂(CO)₂(4,4'-R₂-bpy)] (X = Cl, Br, I, R = H, C(O)OiPr, C(O)OH or Me). Irradiation into the lowest absorption band of the prototype complex *trans*(Cl,Cl)-[Ru(Cl)₂(CO)₂(bpy)] in a CH₃CN or CH₃OH solution produces *cis*(Cl,Cl)-[Ru(Cl)₂(CO)(Solv)(bpy)]¹⁻³. Interestingly, CO substitution is accompanied by shift of one Cl ligand from the axial to the equatorial position^{2,3}.



Scheme 1

Herein, we have chosen the complexes *trans*(X,X)-[Ru(X)₂(CO)₂(bpy)] (X = Cl, I) to investigate the mechanism and dynamics of photochemical dissociation of an equatorial CO from carbonyl-diimine complexes with a low-lying MLCT excited state. Moreover, the associated shift of an axial halide ligand poses further interesting mechanistic questions, namely whether it is concerted with or subsequent to the dissociation of an equatorial CO ligand. These questions are addressed experimentally using picosecond time-resolved IR spectroscopy and theoretically, whereby DFT calculations are employed to reveal the nature of the low-lying excited states and to identify the experimentally observed intermediates.

Calculation of molecular structures and ν(CO) IR spectra

Molecular structures of *trans*(Cl,Cl)-[Ru(Cl)₂(CO)₂(bpy)] and of several photochemical intermediates, were optimized using G03/B3LYP - DFT calculations. The structure of *trans*(I,I)-[Ru(I)₂(CO)₂(bpy)] is very similar to that of the chloro complex and the calculated structures replicate the structures obtained by single crystal X-ray diffraction well.

The lowest absorption band of *trans*(Cl,Cl)-[Ru(Cl)₂(CO)₂(bpy)] at 352 nm (ε = ca. 1560 M⁻¹cm⁻¹) is attributed by TD-DFT predominantly to the a¹A₁→b¹A₁ transition. Its mixed LLCT/MLCT character is obvious from the

calculated changes of electron density distribution, see Figure 1, left. A weaker a¹A₁→b¹B₁ LLCT transition lies at higher energy. The lowest in energy is the forbidden a¹A₁→a¹B₂ transition. It has a mixed LLCT/MLCT character, see Figure 1 right. As was found⁵) for other halide complexes of low-valent metals, TD-DFT calculations underestimate energies of low-lying MLCT/LLCT transitions, although the characters of the transitions are well accounted for.

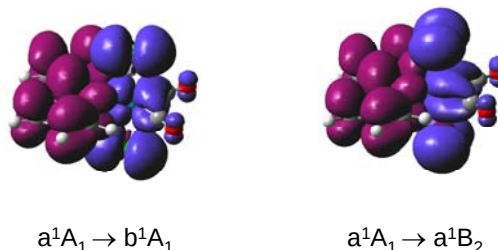


Figure 1. Changes of electron density distribution of the two lowest electronic transitions of *trans*(Cl,Cl)-[Ru(Cl)₂(CO)₂(bpy)]. Blue and violet colors correspond to a decrease and increase of electron density, respectively.

The lowest allowed transition for *trans*(I,I)-[Ru(I)₂(CO)₂(bpy)] was identified as a¹A₁→b¹A₁. It has the same LLCT/MLCT character as was discussed above for *trans*(Cl,Cl)-[Ru(Cl)₂(CO)₂(bpy)], only with a higher LLCT contribution. Very close in energy lies the a¹A₁→b¹B₁ transition of a comparable intensity. It is very different from the corresponding transition of the chloro complex. Qualitatively, the a¹A₁→b¹B₁ transition of *trans*(I,I)-[Ru(I)₂(CO)₂(bpy)] can be viewed as LF-like in character, accompanied by reorientation of electron density at the halide atoms (Figure 2). The relative energies of the a¹A₁→b¹A₁ and a¹A₁→a¹B₁ transitions depend somewhat on the functional used. The actual energy order of these two transitions could depend on the medium, since larger solvatochromism is expected for the MLCT/LLCT transition than for the LF-like a¹A₁→a¹B₁. The next higher transition is a¹A₁→d¹A₁, which can also contribute to the lowest absorption band. It has a σπ* character, that is sigma bond to ligand charge transfer (SBLCT).

Trans(Cl,Cl)-[Ru(Cl)₂(CO)₂(bpy)] has a³B₂ and a³A₁ lowest-lying triplet states. They have the same LLCT/MLCT character as the corresponding singlets, Figure 1. The next higher state is a³A₂, which involves population of the σ* orbital, which lies 0.47 eV above the a³A₁ state. The situation is profoundly different for *trans*(I,I)-[Ru(I)₂(CO)₂(bpy)]. A manifold of very closely spaced four triplet states is present. Two of them, a³B₂ and a³A₁ have the usual LLCT/MLCT character, whereas the a³A₂ and a³B₁ states involve excitation into the σ*(I-Ru-I) orbital, acquiring a LF-like character. The changes in electron density distribution upon population of the a³A₂ and a³B₁ states are shown in Figure 2. The calculated energies of the four lowest triplet states are so close to each other that it is not possible to decide which of them is the lowest. In contrast to

TD-DFT, single-determinant Kohn-Sham optimization yields a^3A_2 as the lowest state.

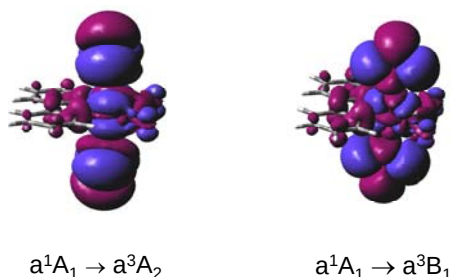


Figure 2. Changes of electron density distribution of the $a^1A_1 \rightarrow a^3A_2$ and $a^1A_1 \rightarrow a^3B_1$ triplet electronic transitions of *trans(I,I)*-[Ru(I)₂(CO)₂(bpy)]. Blue and violet colors correspond to a decrease and increase of electron density, respectively.

TRIR spectroscopy of *trans(Cl,Cl)*-[Ru(Cl)₂(CO)₂(bpy)]

TRIR spectra (Figure 3) of [Ru(Cl)₂(CO)₂(bpy)] consist of four spectral features: (i) Two negative bands (bleaches) due to depleted ground-state absorption at 2004 and 2666 cm⁻¹ (ii) A transient band at 1989 cm⁻¹ that is attributed to a penta-coordinated intermediate *trans(Cl,Cl)*-[Ru(Cl)₂(CO)(bpy)]. The assignment of the 1989 cm⁻¹ transient band to the penta-coordinated *trans(Cl,Cl)*-[Ru(Cl)₂(CO)(bpy)] is based on DFT calculations (iii) Band at 1969 cm⁻¹ band is assigned to the *cis(Cl,Cl)*-[Ru(Cl)₂(CO)(CH₃CN)(bpy)] photoproduct by comparison with the IR spectrum of an authentic sample (iv) A very weak shoulder at 1941 and 1945 cm⁻¹ that belongs either to an unidentified side-product or to a vibrationally excited species.

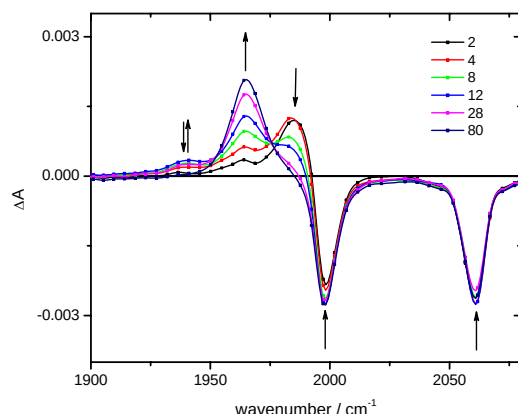


Figure 3. Difference time resolved IR spectra of *trans(Cl,Cl)*-[Ru(Cl)₂(CO)₂(bpy)] measured in CH₃CN, 400 nm excitation.

Temporal evolution of TRIR spectra of *trans(Cl,Cl)*-[Ru(Cl)₂(CO)₂(bpy)] shows (Figure 3) that both bleach bands and the 1989 cm⁻¹ intermediate band (which partly overlaps with the 2004 cm⁻¹ bleach) are formed within the instrument time resolution. These features are well developed already in the spectrum measured at 2 ps after 400 nm excitation. The intensity of the 1989 cm⁻¹ intermediate band rapidly decays with a time constant of 10.0 ± 1.6 ps while the 1969 cm⁻¹ product band grows-in with a similar time constant of 13.7 ± 1.0 ps. The presence of an isosbestic point and similar time-constant values testify to a direct conversion of the *trans(Cl,Cl)*-[Ru(Cl)₂(CO)(bpy)] intermediate into the *cis(Cl,Cl)*-[Ru(Cl)₂(CO)(CH₃CN)(bpy)] product.

TRIR spectroscopy of *trans(I,I)*-[Ru(I)₂(CO)₂(bpy)]

The excited-state behavior of *trans(I,I)*-[Ru(I)₂(CO)₂(bpy)] is very different from the chloro complexes. The TRIR spectra of *trans(I,I)*-[Ru(I)₂(CO)₂(bpy)] exhibit the following four features, Figure 4: (i) Bleached ground-state bands at 2000 and 2059 cm⁻¹. (ii) A photoproduct band at 1967 cm⁻¹ that grows-in.

(iii) Two transient bands at ca. 1981 and 2045 cm⁻¹ whose long-time decay kinetics are the same within the experimental accuracy. This feature belongs to a dicarbonyl species whose ν(CO) bands are down-shifted from the ground-state values. It was assigned by DFT to the LF-like a^3A_2 excited state. The calculated downward shift is in a reasonable agreement with the experimental observation. Initially, the 1981 cm⁻¹ band is more intense than the 2030-2045 cm⁻¹ feature but these two IR features become comparable in intensity after about 10 ps. It appears that the 1981 cm⁻¹ absorption initially contains a second component, which is also responsible for its extensive broadening on the low-energy side. By analogy with the chloro complex, it is attributed to the penta-coordinated *trans(I,I)*-[Ru(I)₂(CO)(bpy)] intermediate. (iv) A weak feature at 1935 cm⁻¹ is due to an unidentified side-product or a vibrationally excited species.

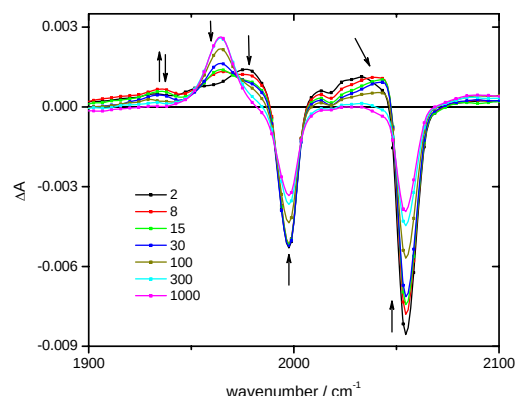


Figure 4. Difference time resolved IR spectra of *trans(I,I)*-[Ru(I)₂(CO)₂(bpy)] in CH₃CN, 400 nm excitation.

Pronounced growth of the product band and decay of the a^3A_2 excited-state features (2045, 1981 cm⁻¹) continue with a common time constant estimated as 100-170 ps. This is accompanied by a partial bleach recovery that occurs with the same kinetics. The 1935 cm⁻¹ feature partially decreases in about 300 ps and then stays approximately constant. No spectral changes occur on a time scale longer than ca. 600 ps.

Discussion

Electronic structures of the complexes *trans(X,X)*-[Re(X)₂(CO)₂(bpy)] (X = Cl, or I) are characterized by highest occupied orbitals with strongly mixed Ru(d_π/X(p_π) character. The lowest unoccupied MOs are almost entirely bpy(π*). Interestingly, an unoccupied Ru-X σ-antibonding orbital occurs at relatively low energies. It originates in an out-of-phase overlap between the symmetric combination of halide p_σ orbitals with Ru(d_σ) orbitals. Population of this σ* MO upon electronic excitation has profound photochemical consequences, as will be discussed below.

TD-DFT analysis and assignment of electronic transitions show that 400 nm laser pulse irradiation of either the chloro or the iodo complex *trans(X,X)*-[Re(X)₂(CO)₂(bpy)] excites predominantly the $a^1A_1 \rightarrow b^1A_1$ LLCT/MLCT electronic transition. Previous studies have shown that the same overall photochemical reaction (Equation 1) occurs for X = Cl, Br, and I, although the quantum yield drops in the order Cl > Br > I^{1,4)}. Nevertheless, the results presented above demonstrate that the excited-state dynamics and photochemical mechanisms are profoundly different for the chloro complexes on one side and the iodo complex on the other.

For *trans(Cl,Cl)*-[Ru(Cl)₂(CO)(bpy)], excitation into the lowest absorption band triggers an ultrafast (<1 ps) dissociation of a Ru-CO bond that yields a penta-coordinated *trans(Cl,Cl)*-[Ru(Cl)₂(CO)(bpy)] intermediate with a coordination vacancy in the equatorial Ru(bpy) plane. Movement of a Cl ligand from

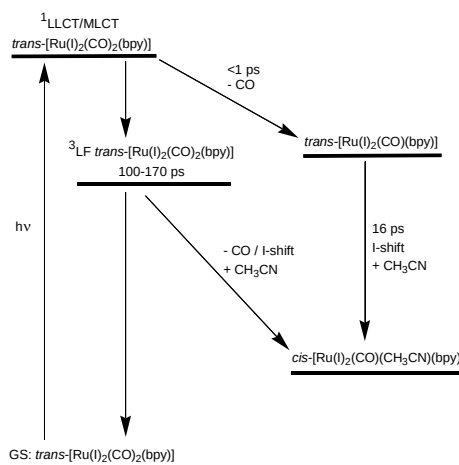
the axial to the vacant equatorial position follows with a time constant of 13 ps, accompanied by coordination of a CH₃CN solvent molecule at the axial position. Importantly, the *trans* geometry of the square-pyramidal intermediate *trans*(Cl,Cl)-[Ru(Cl)₂(CO)(bpy)], identified by comparison between calculated and experimental IR spectra, implies that CO dissociation and Cl-ligand shift are sequential processes.

TRIR experiments show no signs of any LLCT/MLCT excited state of the parent molecule *trans*(Cl,Cl)-[Ru(Cl)₂(CO)₂(bpy)], whose population would precede the CO loss. Unreactive "trapping" spin-triplet LLCT/MLCT states were also not observed. This, together with the femtosecond rate of CO dissociation, implies that potential energy surfaces of the optically excited b¹A₁ and/or the lower-lying a¹B₂ singlet states are completely dissociative. The Ru-CO dissociation is much faster than relaxation (intersystem crossing) to any ³LLCT/MLCT state or internal conversion to the ground state. This conclusion agrees with the near-unity quantum yield¹⁾ of the photochemical CO substitution in *trans*(Cl,Cl)-[Ru(Cl)₂(CO)₂(bpy)].

The LLCT/MLCT character of the b¹A₁ and a¹B₂ (Figure 3) does not warrant a dissociative character, which is presumably acquired by a strongly avoided crossing with higher-lying LF-type state(s) along the reaction coordinate. The same behavior is exhibited by ¹MLCT excited states of [Cr(CO)₄(bpy)] and other metal carbonyls^{6,7)}. The 13 ps rate of the follow-up shift of the Cl ligand to the equatorial position is very fast, indicating that it takes place within vibrational relaxation of the *trans*(Cl,Cl)-[Ru(Cl)₂(CO)(bpy)] intermediate.

Unusually, the ultrafast photochemistry of *trans*(I,I)-[Ru(I)₂(CO)₂(bpy)] involves two distinct CO dissociation pathways, that is the femtosecond dissociation from the optically populated ¹LLCT/MLCT Franck-Condon state followed by the I-shift and a slower Re-CO bond breaking concerted with I-ligand movement from the triplet LF-like excited state ³A₂. The reaction mechanism is shown in Scheme 2. Optical excitation populates a LLCT/MLCT b¹A₁ state which undergoes femtosecond intersystem crossing to the ³A₂ and, possibly, also the ³B₁ LF-like states and a parallel CO dissociation to produce vibrationally excited *trans*(I,I)-[Ru(I)₂(CO)(bpy)] intermediate. Its presence is manifested by the relatively high intensity of the 981 cm⁻¹ band and its broad low-wavenumber shoulder. It undergoes ca. 16 ps conversion into the *cis*(I,I)-[Ru(I)₂(CO)(CH₃CN)(bpy)] intermediate by a shift of an I ligand, and a solvent coordination. The LF-like state, characterized by the 2030-2045 and 981 cm⁻¹ features, is formed vibrationally hot. It undergoes ca. 9 ps vibrational cooling, manifested by the up-shift, narrowing and decay of the excited-state 2030-2045 feature. On a longer time-scale, the triplet LF-like state decays in parallel to the ground state and to the photoproduct with a 100-170 ps time constant.

The mechanism proposed for the *trans*(I,I)-[Ru(I)₂(CO)(bpy)] (Scheme 2) is in agreement with the rather low quantum yield (0.34) measured⁴⁾ for CO photosubstitution in *trans*(I,I)-[Ru(I)₂(CO)₂(4,4'-(COOH)₂-bpy)]. TRIR experiments reveal that the quantum yield is limited by two branching steps: first, the branching of the Frank-Condon LLCT/MLCT a¹A₁ excited-state evolution between CO dissociation and intersystem crossing to the LF-like a³A₂ state and, second, branching of the a³A₂ evolution between CO dissociation and relaxation to the ground state. The presence of a low-lying excited state in the iodo complex is further supported by the observation⁴⁾ of a low-energy (652 nm) emission from *trans*(I,I)-[Ru(I)₂(CO)₂(4,4'-(COOH)₂-bpy)] in low-temperature glasses.



Scheme 2. Proposed mechanism of photochemical CO substitution / isomerization of *trans*(I,I)-[Ru(I)₂(CO)₂(bpy)].

Conclusions

Dynamics and mechanism of dissociation of an equatorial CO ligand from carbonyl-diimine complexes were unraveled using the complexes *trans*(X,X)-[Ru(X)₂(CO)₂(bpy)] (X = Cl, I). For X = Cl optical excitation of the ¹MLCT/LLCT transition triggers femtosecond CO dissociation, that is followed by movement of an axial halide ligand to the vacant equatorial position, accompanied by solvent coordination. For *trans*(I,I)-[Ru(I)₂(CO)₂(bpy)], this reaction pathway competes with intersystem crossing from the optically excited ¹LLCT/MLCT excited state into a LF-like triplet state. The I-Ru-I bonding is labilized in the LF-like state due to population of a σ-antibonding orbital. The LF-like triplet excited state undergoes parallel CO dissociation concerted with an I-ligand shift and a decay to the ground state, with a time-constant of 100 - 170 ps. Excited state dynamics of *trans*(I,I)-[Ru(I)₂(CO)₂(bpy)] thus involves two distinct CO-dissociation steps. The profoundly different excited-state behavior of *trans*(Cl,Cl)-[Ru(Cl)₂(CO)₂(bpy)] and *trans*(I,I)-[Ru(I)₂(CO)₂(bpy)] is explained by different energetic positions of LF-like triplets relative to the ¹LLCT/MLCT states. The ³LF-like states are too high in energy to be populated for the chloride but lie much lower for the iodide. Their population by intersystem crossing from the ¹LLCT/MLCT states is possible energetically, while facilitated by the heavy-atom effect of the iodide ligands. CO dissociation from the LF-like states is rather slow due to their bound character.

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Investigation of intramolecular vibrational energy redistribution in para-fluorotoluene with an imaging photoelectron spectrometer

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Introduction.

In recent years, understanding the process of intramolecular vibrational energy redistribution (IVR) in molecules containing a methyl group has proved a challenge to experimenter and theorist alike. Interest in this area stems from the observation that the presence of the methyl group can accelerate the rate of IVR by up to two orders of magnitude compared to an otherwise identical molecule in which the group is absent ¹⁾, an increase considerably greater than that predicted purely on the basis of the relative densities of ro-vibrational states. In this respect, a 'prototype' molecular pair consists of p-fluorotoluene (pFT) and p-difluorobenzene (pDFB), where the substitution of a fluorine atom with a hindered methyl rotor has been seen to reduce the IVR lifetime in the S_1 state with around 2000 cm^{-1} of vibrational excitation from 150 ps to about 3.5ps ²⁾.

The use of the pump/probe laser photoionisation technique to investigate IVR in excited electronic states has several advantages over the fluorescence-based methods employed previously ³⁾. Foremost amongst these is the ability to precisely control the time delay between the pump and probe events, which allows for more accurate time resolution than the 'chemical quenching' approach used previously ⁴⁾. The use of picosecond laser pulses provides an amicable compromise between frequency and time resolution, allowing vibrationally resolved spectra to be recorded on a timescale comparable to the process under investigation.

Bellm *et al.* ⁵⁾ recently reported the photoelectron spectra of pFT prepared in a series of S_1 states with up to 1230 cm^{-1} of vibrational energy. The study, which employed overlapped nanosecond or picosecond laser pulses and time-of-flight (TOF) photoelectron detection, showed that while the vibrational levels up to 845 cm^{-1} displayed well-resolved nanosecond spectra, the two levels with higher energies showed a marked loss of structure in the nanosecond experiments due to rapid IVR, the structure being fully recovered by a move to the picosecond timescale. This clearly demonstrated the need for a closer examination of the phenomenon as time evolves. This was initiated using the TOF technique ⁶⁾ and has been extended by the use of an imaging spectrometer with automated subtraction of background spectra as described in this report.

Experimental.

The imaging photoelectron spectrometer has been more fully described elsewhere ⁷⁾ and only an overview of the salient features will be presented here. The spectrometer consists of two vacuum chambers, connected co-axially and independently evacuated by diffusion pumps. In the first of these a pulsed supersonic molecular beam is created by passing pFT, seeded in 2 atm of helium, through a solenoid valve (General Valve) with a 0.5 mm aperture and then through a 0.8 mm conical skimmer. The beam is allowed to pass into the second chamber where it is intersected perpendicularly by a pair of co-propagating 1 ps laser pulses ('pump' and 'probe') with a variable time delay between them. Photoelectrons generated by the resonant ionization of the molecules are focused by a three-element (repeller, extractor and ground) electrostatic lens, adjusted to work in a velocity-mapping mode ⁸⁾, along a 40 cm field-free flight tube and onto an imaging detector (Photek) consisting of

a pair of MCP detectors and a phosphor screen. The image on the screen is recorded by a CCD camera (Basler A302f) and passed to a computer where the results of many repetitions of the experiment are accumulated until the signal to noise ratio has reached an acceptable level. During the work reported here the spectrometer was run at a rate of 50 Hz and up to 30,000 repetitions were performed for each image. The residual pressure in the spectrometer was around 3×10^{-8} mbar when the valve was not operating and rose to 3×10^{-6} mbar when it was.

Laser pulses were generated by a 1kHz titanium sapphire regenerative amplifier (Spectra-Physics, Spitfire), configured for the chirped pulse amplification of picosecond pulses. The amplifier output was frequency tripled to give pulses of about 1 ps length at around 262.5 nm. The beam was split into two, one part acting as the 'pump' beam, the other being sent down a computer-controlled delay line and used as the 'probe'. A CCD camera with a microscope objective was used to ensure spatial overlap of the two beams, which were loosely focused down to a beam diameter of around 100 μm . Pulse energies were typically around 2-3 μJ . Typical bandwidth for each pulse was $\sim 10 \text{ cm}^{-1}$ FWHM. Both beams were linearly polarized, with the plane of polarization perpendicular to both the molecular beam axis and the propagation direction of the laser beam.

At each time delay of interest, three photoelectron spectra were recorded; one each for the pump and probe beams in isolation and one for the combination of the two. The final spectrum was derived by subtracting the individual beam spectra from the combination spectrum. During a run 10 seconds worth of the combination spectrum were recorded, followed by 10 seconds of the pump beam and 10 seconds of the probe beam until sufficient repetitions had been achieved. Computer-controlled electro-mechanical shutters (EOPC) were used to block/unblock the beams. The software (Photek) used to collect the data was also used to control the action of the shutters via a user-generated script function.

Results.

Photoionisation from three vibrational levels of the S_1 state was investigated, in each case at several different time delays. The three states of interest were the 7^1 (+1230), 8^1 (+1194) and 11^1 (+803) levels, where the Mulliken ⁹⁾ notation has been employed throughout and the numbers in brackets are the energies (in reciprocal centimeters) relative to the S_1 vibrationless state. The modes are described as; C-F stretch, CH_3 -C stretch and ring breathing vibrations respectively.

Figure 1 shows a typical 2D photoelectron image for each mode, along with the associated reconstruction of the 3D velocity distribution extracted by the use of the Abel inversion method ¹⁰⁾. The marked lack of anisotropy in all three images will be noted, a distinctive feature of pFT and a contrast to its pDFB analogue when considering S_1 levels with the same amount of vibrational excitation ¹¹⁾. Also of note is the 'noise' generated along the vertical axis of the reconstructed image, a distinctive side-effect of the Abel inversion. The electrode voltages were the same for all three modes, so all the images are to the same scale.

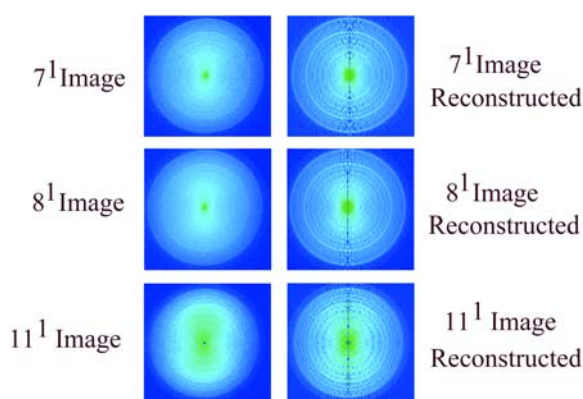


Figure 1: Example images for all three of the S_1 vibrational levels studied.

The range of values of the time delay recorded for each mode, depended on the IVR lifetime it exhibited. Details of the delays measured are given in Table 1.

Mode	S_1 Excess Energy / cm^{-1}	Approximate IVR Lifetime ^(a)	Range of Time Delays ^(b)
7^1	1230	100 ps	0-640 ps (17)
8^1	1194	50 ps	0-80 ps (13)
11^1	803	200 ps	0-320 ps (12)

^(a)The lifetime is the approximate point at which the X^1 , X^11^1 and X^113^1 peaks are no longer all distinguishable. ($X = 7, 8$ or 11)

^(b)The number in parentheses is the number of delays recorded.

Table 1. Approximate IVR lifetimes for the three modes.

Figure 2 shows a series of representative photoelectron spectra, at increasing time delay, for each of the three vibrational modes. The photoelectron spectra were extracted from the reconstructed photoelectron images by taking a plot of the radial intensity (which gave a velocity distribution) and then converting to a kinetic energy scale. Ion internal energies were then calculated, based on a knowledge of the laser wavelength employed and the ionization potential of pFT (70940 cm^{-1}). The difference in timescale of IVR in the three levels is apparent from this diagram. The assignments of the peaks are identical to those of Bellm *et al.*⁵⁾, and for all modes correspond to the following states of the ion (in increasing order of energy): X^1 , X^113^1 , X^111^1 , X^19^1 , X^14^1 , $X^14^113^1$, $X^14^111^1$, $X^14^19^1$, X^14^2 , ($X = 7, 8$ or 11).

Discussion.

The intuitive expectation that greater vibrational excitation promotes faster IVR, seems not to be fulfilled. Comparing the 7^1 and 8^1 modes, the latter is a vibration intimately associated with the methyl group, and as such might be expected to display faster IVR than 7^1 , which is a motion largely confined to the other end of the molecule. This is seen to be the case and it appears that the effects of the methyl group are most strongly felt in its immediate vicinity. Thus, any analysis of the IVR process may not have to consider the whole molecule, merely a sub-set of its vibrations¹²⁾.

Secondly, the appearance of the effects of IVR in the 11^1 mode is unexpected. The nanosecond spectrum⁵⁾ of this state shows a well-resolved set of vibrational peaks, yet at the picosecond timescale the majority of the structure has gone from the spectrum by 160 ps. The obvious explanation is that the greater bandwidth of the picosecond pulse (10 cm^{-1} vs. 0.1 cm^{-1}) allows access to a larger number of intermediate states and hence the number of possible IVR pathways is also increased.

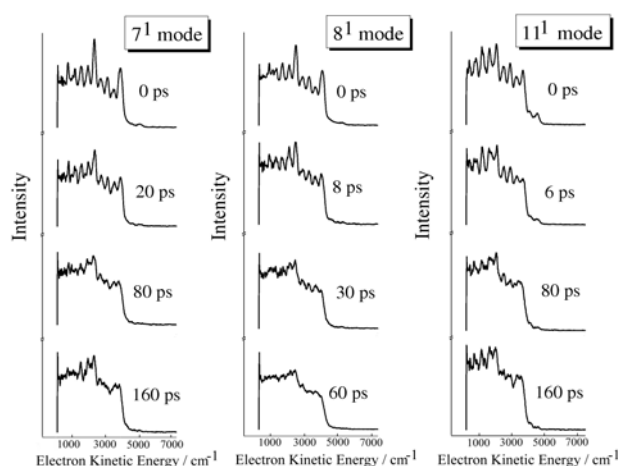


Figure 2: Time evolution of the photoelectron spectra for the three modes of S_1 pFT.

Finally, in both the 7^1 and 8^1 spectra, the time evolution apparently consists of an initial growth of the X^113^1 , X^111^1 and X^19^1 peaks at the expense of the X^1 peak ($X = 7$ or 8), followed by a general broadening of all peaks into an unstructured final state. In 11^1 the process seems different, as the 11^2 and 11^9^1 peaks seem to shrink as the 11^113^1 peak grows. The later general broadening is maintained.

Conclusions.

We have observed IVR in three modes of S_1 pFT. For two of these modes, this is the first study of the phenomenon on the picosecond timescale. The rate of IVR varied between the three levels, and was apparently not dependent simply on the proximity of the vibrational mode to the methyl group. Quantitative analysis is in progress.

Acknowledgements.

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Kerr gated Resonance Raman Spectroscopy in light fastness studies of ink jet prints

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Introduction

Ink jet printing is one of the major imaging technologies because of its versatility. Manifold criteria are generally set for the ink jet print quality, eligible features typically including large colour gamut and long-term fastness of the printed image towards light and moisture. These characteristics are highly dependent on the properties of both papers and inks and their chemical and physical interactions.¹⁾

Vibrational spectroscopy offers several advantages in print studies over many other analytical techniques. The most remarkable benefit is the possibility to directly investigate the printed sample, and thereby obtain information about the actual paper-ink-interactions. Earlier studies²⁻⁵⁾ have shown that Raman spectroscopic methods are applicable to the analyses of ink jet prints, for they enable the detection of even minor amounts of the colorants on the paper surfaces and analysis of ageing, e.g. light-induced changes. However, Raman spectroscopy often suffers from obtrusive sample-related fluorescence, originating from various ink jet colorants and certain paper coating components.³⁻⁵⁾ Several solutions to eliminating the fluorescence in print studies have been suggested. In analyses of colorants, the use of near-infrared excitation and surface-enhanced resonance Raman scattering has been one strategy as a means to avoid or attenuate the sample-related fluorescence.^{2,6)} The fluorescence problem has also been alleviated to some extent by using an immersion objective in the NIR-Raman measurements of the prints, and by collecting the spectra using laser wavelengths in the UV region.^{3,7)}

The objective of this study is to evaluate the applicability of resonance Raman spectroscopy equipped with an optical Kerr gate for investigating the light fastness of ink jet prints. The work has been performed on a set of experimental coatings and inks of known compositions. The results are presented at length elsewhere⁸⁾.

Experimental

Twelve model coatings and three experimental ink jet inks were used to prepare the printed samples⁹⁾, which were exposed to artificial sunlight for 100 hours⁴⁾. The laser equipment of the present measurement set-up provided 800 nm, 1 ps, 2–3 mJ fundamental pulses at 1 kHz repetition rate. The fundamental laser output was split in two such that one part was taken for the gating pulse to drive the Kerr gate, and the remaining part was used as a probe beam yielding at the sample $\sim 1 \mu\text{J}$, i.e. 1 mW. The probe beam was weakly focused down onto sample to around 0.3 mm diameter spot, and the scattered Raman light was collected at 90° angle with respect to the incident beam. Carbon disulfide (CS_2) was used as a Kerr gate material, and 470 nm was chosen as a probe wavelength. The printed paper samples were mounted on to the sample stage at 45° angle to the probe beam, and rotated during the measurement in order to prevent burning. The liquid inks were measured in an 0.5 mm diameter ink stream in an open flow perpendicular to the probe beam. Detailed description of the equipment and the experimental subtleties are given elsewhere.¹⁰⁻¹²⁾

Results and discussion

Preliminary measurements of the resonance Raman spectra of printed samples were accomplished with 400 nm excitation wavelength, for all the studied colorants absorb light strongly at this wavelength region. However, despite the use of Kerr gate, the resulting spectra were found to contain an extremely high amount of fluorescence. This can be attributed to the optical brightener included in the base paper below the coating layer. Consequently, as the absorption region of the studied colorants extends to the higher wavelengths, the following experiments were performed using the excitation wavelength 470 nm to exclude the contribution from the optical brightener.

Figure 1 illustrates the effect of Kerr gate rejection on the quality of the resonance Raman spectra of yellow dye-based ink jet prints at 470 nm excitation wavelength. The uppermost curve is the resonance Raman spectrum of an unexposed ink jet print measured without the Kerr gate. It is evident that the strong background fluorescence almost completely obscures the Raman bands originating from the sample. In contrast, in the corresponding spectrum measured with the Kerr gate (middle curve), the Raman bands are clearly visible. Thus, the Kerr gate system effectively suppresses the fluorescence originating from the sample. Moreover, Figure 1 also illustrates that the resonance Raman bands of the printed sample originate primarily from the colorant used in printing. Thus, the selected laser wavelength is capable of enhancing the chromophore bands even when the ink is printed onto the paper. The baselines of the spectra are somewhat tilted, because the remaining fluorescence has not been removed by baseline subtraction.

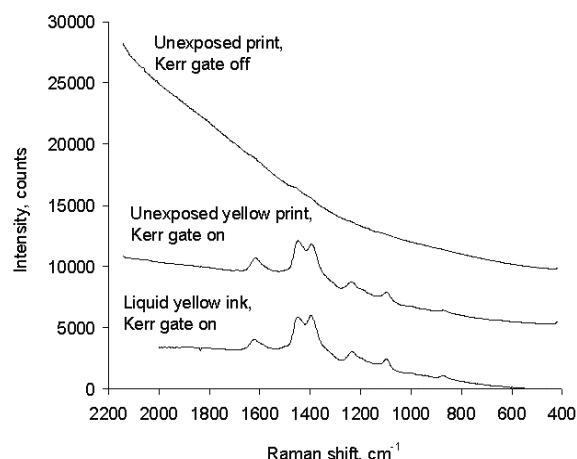


Figure 1. Effect of usage of Kerr gate on resonance Raman spectra of ink jet prints. The spectra are vertically offset for clarity and scaled to fit into the same figure.

Preliminary tests of the Kerr gate rejection system were also accomplished for coatings printed with other types of ink jet colorants, namely a magenta modified direct dye, and a yellow pigment dispersion. The coating containing SA latex – starch polymer system and kaolin as a sole pigment was selected as a substrate. Both of these colorants and the kaolin pigment have

proven to cause fluorescence problems in earlier Raman experiments.^{3,9)} Figure 2 presents the resonance Raman spectra of the magenta dye-based colorant in liquid state, and as printed on the SA latex-starch-kaolin coating before and after light exposure. Figure 3 presents the corresponding spectra for the yellow pigment dispersion.

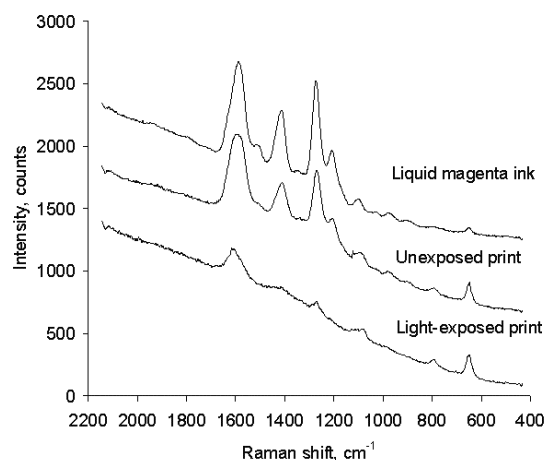


Figure 2. Kerr gated resonance Raman spectra of liquid magenta ink, and corresponding ink jet prints with different light exposure conditions. The spectra are vertically offset for clarity.

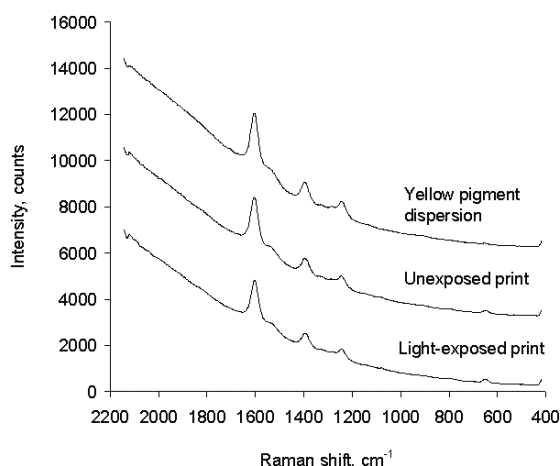


Figure 3. Kerr gated resonance Raman spectra of yellow pigment dispersion, and corresponding ink jet prints with different light exposure conditions. The spectra are vertically offset for clarity.

Figure 2 and 3 clearly illustrate that the Kerr gate fluorescence rejection functions effectively in both cases, for the resonance Raman bands of the colorants stand clearly out. Furthermore, the Raman bands of the printed samples again appear to originate mainly from the colorants, so the selected excitation wavelength seems to be appropriate for the studies of the chemical paper-ink interactions. Furthermore, as a result of light exposure, the bands of dye-based magenta ink decrease clearly in intensity, whereas the bands of the pigmented yellow ink remain relatively unchanged. This is an expected result, because the light fastness of the pigmented ink generally surpasses that of dye-based inks¹⁾. It should be noted that in the case of the dye-based magenta ink the laser power had to be lowered because of the sensitivity of the printed samples to degradation. Despite this, and the sample spinning during the measurement, the printed samples tended to burn somewhat. Consequently, it is possible that there is some uncontrollable variation in the results rendering absolute Raman intensities to be less reliably

observed. However, rather than detecting absolute overall Raman intensities the technique is suited to detecting relative intensity changes within Raman spectra that can result, for example, from the appearance or disappearance of species or conformers in the sample. Nevertheless, these preliminary measurements illustrate that resonance Raman spectroscopy combined with the Kerr gate fluorescence rejection system has a great potential in analyses of paper-ink interactions and light fastness studies of ink jet prints.

Conclusions

The results illustrate that resonance Raman spectroscopy equipped with the Kerr gate fluorescence rejection method is well suited to photo-degradation studies of ink jet prints, owing to the effective damping of the sample-related fluorescence, and the ability to obtain resonance enhancement of the desired chemical groups of a colorant. The first feature makes studies of even highly fluorescent samples possible whereas the latter enables investigations of specific chromophore structures to be interrogated, even directly from the printed sample. Sample degradation by the pulsed laser does not restrict the method. Furthermore, the method is capable of detecting light-induced changes in the chemical structure of the sample. This would enable elaborate studies of chemical paper-ink interactions, which generally play a decisive role in light fastness of an ink jet print.

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Picosecond energy and electron transfer in organometallic porphyrin assemblies: building blocks for novel photonic devices

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Introduction

Interest in the use of porphyrins as components of light harvesting devices has grown considerably in recent years¹⁾. As a result of these studies it is clear that porphyrins present excellent possibilities for the construction of novel molecular components for the development of new materials, and molecular devices.

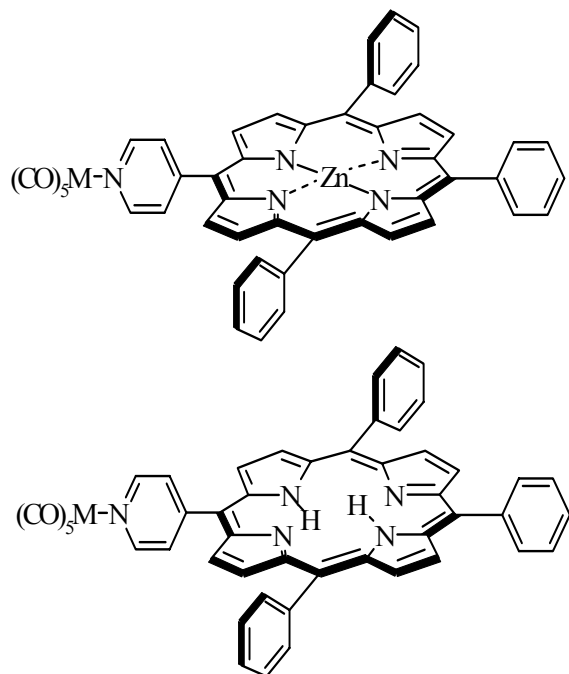


Figure 1. Porphyrin Structures.

The ability of porphyrins to absorb photons and transfer either electrons or energy to the reaction centre forms the basis of this study, involving time-correlated single photon counting (TCSPC) measurements. The reaction centres are metal carbonyl fragments, which have the dual benefit of providing excellent spectroscopic properties and high quantum efficiencies for photochemical reactions. The triplet state of these complexes has previously been investigated in our laboratories, using laser flash photolysis with UV-vis detection. In this study, we investigated the singlet state photophysics of both the free base and metalloporphyrins when co-ordinated to metal carbonyl fragments (Cr(CO)₅ or W(CO)₅) through a pyridyl link (Figure 1). In addition some novel thienyl porphyrins were also investigated

For the free base and the zinc metallated metal carbonyl compounds, emission was observed from the ¹(π - π^*) excited state for all complexes. The free base mono pyridyl triphenyl porphyrin pentacarbonyl complexes (MPyTPPCr(CO)₅ and MPyTPPW(CO)₅) emit between 600 and 750 nm, whereas the zinc metallated porphyrin complexes (ZnMPyTPPCr(CO)₅ and

ZnMPyTPPW(CO)₅) emit at shorter wavelengths *i.e.* between 550 and 700 nm.

The lifetimes of these singlet states were measured in a number of solvents (Table 1). From these results it would appear that solvent does not affect the singlet state lifetimes. For instance the lifetime for the ¹(π - π^*) excited state of MPyTPPCr(CO)₅ is 5.4 and 5.9 ns in dichloromethane and ethanol respectively. These values correspond closely to those previously reported in the literature for free base aryl porphyrins²⁾.

Solvent	ZnMPyTPPCr(CO) ₅ ¹ τ (ns)	ZnMPyTPPW(CO) ₅ ¹ τ (ns)
CH ₂ Cl ₂	1.4	1.4
Ethanol	1.9	1.8
Toluene	1.7	1.7
Pentane	1.7	1.7
	MPyTPPCr(CO) ₅ ¹ τ (ns)	MPyTPPW(CO) ₅ ¹ τ (ns)
CH ₂ Cl ₂	5.4	6.7
Ethanol	5.9	7.4
Toluene	5.5	7.0

Table 1. Singlet state lifetimes monitored at 605 nm following excitation at 435 nm.

When zinc is inserted into the porphyrin macrocycle, the ¹(π - π^*) excited state lifetime is reduced for both systems studied. Again these values are similar to those previously reported for metallated aryl porphyrins which exhibit lifetimes of ~ 2 ns, and compare well with values between 1.4 -1.9 ns obtained in this study²⁾. A typical emission trace obtained following excitation of ZnMPyTPPW(CO)₅ at 435 nm and monitored at 605 nm is shown in Figure 2. This decrease in lifetime for the metallated porphyrins is attributed to the internal heavy atom effect, of the central zinc atom. What is surprising in this study is that the presence of the chromium or tungsten penatcarbonyl moiety has no apparent affect on the lifetimes observed, when compared to zinc mono pyridyltriphenyl porphyrin where a lifetime of 1.5 ns was obtained. In a previous study, Perutz et al used nicotinanilide to

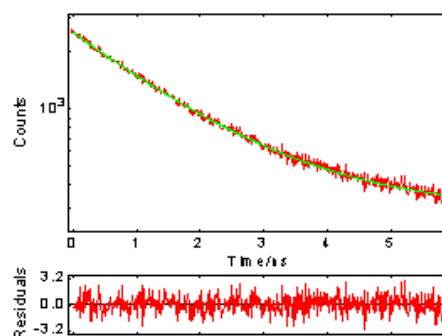


Figure 2. Luminescent trace obtained at 605 nm following excitation (λ_{exc} = 435 nm) of MPyTPPW(CO)₅ at 293 K in dichloromethane.

tether $W(CO)_5$ units to both the free base and zinc porphyrin macrocycle³⁾. As was observed in this study the presence of the organometallic fragment did not appear to influence the singlet state lifetimes.

In addition to the pentacarbonyl porphyrins, lifetimes were also measured for a series of thienyl porphyrins (Table 2).

Porphyrin	$^1\tau(ns)$
Zn-TPP	2.0
Zn-TThP	1.4
Zn-TBrThP	0.5
Zn-mTMSEtThP	1.9
Zn-mEtThP	1.9
Zn-diTMSEtThP	1.5
Zn-diEtThP	1.6
Zn-triTMSEtThP	1.1
Zn-triEtThP	1.1
Zn-tetraTMSEtThP	0.8

Table 2. All singlet state lifetimes were monitored between 660 - 670 nm following excitation at 435 nm in aerated toluene.

In the last few years interest in thienyl porphyrins has grown because of their relative ease in synthesis and suitability as model compounds in energy transfer reactions⁴⁾. Upon substitution of each phenyl group at the *meso* position in the zinc porphyrin macrocycle with either thiophene or a thiophene derivative, the singlet state lifetime reduces.

For instance the singlet state lifetime for 5,10,15,20-tetrakis(2-thienyl) porphyrin zinc(II) [Zn-TThP] is 1.4 ns, as opposed to 2 ns for 5,10,15,20-(tetra phenyl) porphyrin zinc(II) [Zn-TPP]. Upon replacing each thiophene with 2-ethynyl thiophene [Zn-tetraEtThP] or trimethyl-thiophen-2-ylethynyl silane [Zn-tetraEtThP] the singlet state lifetimes are further reduced to ~ 0.8 ns.

Lifetimes were also obtained for macrocycles where one, two or three thiophenes were substituted with either 2-ethynyl thiophene or trimethyl-thiophen-2-ylethynyl silane. The most notable reduction in lifetime was observed for the 5,10,15,20-tetra (2-bromothiophene) porphyrin zinc(II) [Zn-TBrThP], where a life time of 0.5 ns was measured. Presumably this reduction in lifetime is due to the heavy atom effect of bromine.

Metal carbonyls are particularly suitable for infrared spectroscopic studies because of their characteristic absorptions. A better understanding of the photochemistry of the metal carbonyl tethered porphyrins discussed in this study must await future time-resolved infrared studies.

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Laser-pulse induced temperature jumps for investigating fast processes of α -Helix folding – comparison of direct and indirect heating of water

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Introduction

The question of how proteins fold to their unique and highly organised three-dimensional structure is one of the most challenging questions currently investigated in biological research. Given the right conditions, an unfolded polypeptide with a specific primary sequence of amino acids rapidly folds into a well-defined structure, which is the basis of the biological function of the protein. The investigation of *dynamic* aspects of this folding process is important for elucidating the mechanism by which protein folding proceeds. However, it also is of high relevance in the context of predicting the final structure of engineered peptides. Natural proteins as well as designed peptides will only adopt the anticipated (lowest free-energy) functional structure on a reasonable time scale, if there is an efficient folding pathway for the polypeptide which avoids the accumulation of metastable non-functional folds.

The first phase of protein folding is generally believed to be the formation of secondary structures, such as α -helices, β -sheets or turns, which then may act as nucleation sites for the folding to the native structure. Thus, the dynamics of secondary structure formation is of utmost importance for protein folding. However, formation of secondary structural elements occurs on the time scale of milliseconds, which is too fast for most of the experimental investigations performed to date. Specialised techniques had to be developed for initiating and observing the fastest processes of secondary structure formation.¹⁻³⁾

The folding dynamics of α -helical peptides, which occurs on the 100 ns-time scale²⁻⁴⁾, can be observed experimentally using a nanosecond temperature jump, induced by a short laser pulse. The rise in temperature disturbs the helix-coil equilibrium of the peptide, and the ensuing helix-coil relaxation can be observed by a suitable technique, such as nanosecond time-resolved IR-spectroscopy of the amide I-band near 1650 cm^{-1} , which is highly sensitive to secondary structure^{2,5)}.

Two methods have been used to induce fast temperature jumps in aqueous solution: (i) UV/vis laser pulses, which necessitate the use of a heat-transducing dye^{4,6)}, or (ii) direct heating of water, which can be achieved with IR laser pulses, necessitating more complex laser systems^{2,3)}. Here, we describe a comparative study of these two methods. We conclude that direct heating greatly improves the quality, reliability and speed of such experiments; on the other hand, the results also show that the heat-transducing dye does not affect the folding dynamics of a standard alanine-based α -helical model peptide.

Experimental

Our setup for observing folding/unfolding dynamics of α -helical peptides has been described previously.⁴⁾ It is based on a nanosecond pump laser, either (i) an excimer/dye laser (Lumonics TE-861T and Lambda Physik FL2001, 5 ns, 540 nm, 1 mJ), or (ii) CLF laser loan pool system NSL4 (Nd:YAG/dye laser with IR difference frequency generation, 7 ns, 1970 nm, 4 mJ). By focussing the laser pulses into aqueous solution, we can induce nanosecond temperature jumps of up to 10°C . Using a tunable IR-laser diode and a fast IR-detector, we are able to observe the resulting changes of the IR absorbance of aqueous peptide solutions with a time resolution of 12-14 ns.

The peptide used here is the α -helical peptide Ac-AAAAA-(AAARA)₄A-NH₂ (Pepsyn Ltd.), dissolved at a concentration of 10 mg/ml in D₂O or in a solution of 0.5 mM basic fuchsin in

D₂O. The pH* of the sample (ignoring the different electrode sensitivity to H⁺ and D⁺) was adjusted by addition of NaOD.

Results Obtained with Pump Pulses at 540 nm

When using the excimer/dye laser system (i), a heat-transducing dye needs to be added to the solution for absorbing a sufficient amount of the laser pulse energy. Typically, triphenylmethane dyes, such as crystal violet or basic fuchsin are used, which undergo rapid internal conversion on the sub-ps time scale. The presence of the dye results in several complications:

(I) Due to dye photobleaching, the amount of laser energy absorbed and thus the temperature jump amplitude decreases if the sample volume is not exchanged regularly. We observed that under our conditions basic fuchsin allows the collection of several hundred single measurements before significant bleaching occurs, whereas crystal violet bleaches more rapidly and thus requires continuous sample flowing. This necessitates sample volumes of more than 1 ml and thus relatively large amounts of peptide (>10 mg), which often are not available.

(II) A problem often encountered in temperature jump experiments are artefacts arising from photoacoustic cavitation.⁷⁾ Pressure waves generated by the sudden increase of temperature in a small sample volume lead to the formation of bubbles which deflect the IR probe beam. Figure 1 (A) shows the time-dependent IR probe intensity observed upon temperature jumps induced by laser pulses at 540 nm in a freshly prepared solution of crystal violet in D₂O. Upon increasing the temperature, the absorbance of D₂O at 1632 cm^{-1} decreases, which leads to the observed rapid increase of transmission. However, after 100 ns there is a sudden decrease of transmission, resulting from the

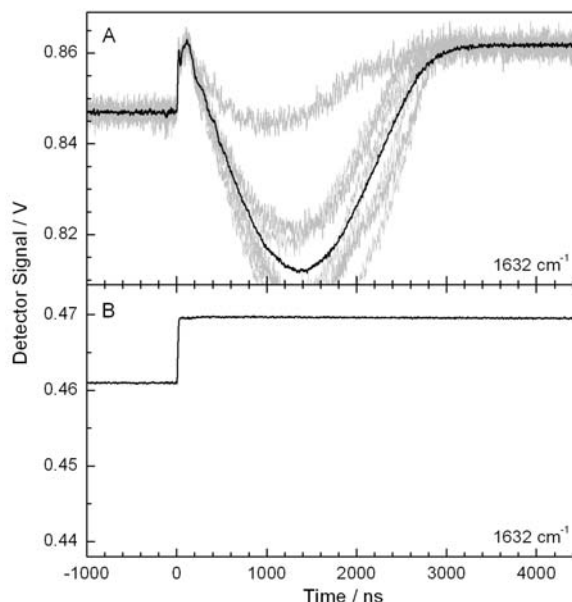


Figure 1. Time-dependent IR probe beam intensities observed after temperature jumps from 20°C to 24°C , induced by 5 ns laser pulses at 540 nm, in (A) a fresh solution of 0.5 mM crystal violet/D₂O, flowed through the cell during the measurement, and (B) a solution of 0.5 mM basic fuchsin/D₂O which had been stirred for 24 hours and was not flowed during measurements. The grey lines in (A) are single measurements, whereas the black line is the average of 64 single measurements; the black line in (B) is the average of 512 single measurements.

formation of bubbles which remain for several microseconds. Cavitation is not present for each temperature jump, and its effect varies from measurement to measurement, as shown in Figure 1 (A), but it does significantly impede measurements which require the averaging of several thousand single events. We observed that cavitation can be completely removed by (i) stirring the dye solution for several days or by (ii) stopping sample flow, compare Figure 1 (B), suggesting that cavitation is induced by particles of aggregated dye molecules acting as nucleation sites for cavitation. Extended stirring reduces the amount of dye aggregates, whereas with stopped sample flow no such particles are flowed through the laser focus. However, for most of the peptide samples studied so far, method (i), which works well in the absence of peptide, did not achieve a sufficient reduction of cavitation events. In these samples, additional counter ions seem to induce increased aggregation of the (ionic) dye. Method (ii), on the other hand, worked for all peptide samples, but leads to a rapid decrease of the size of the temperature jump due to dye photobleaching, necessitating frequent disruption of the measurement for replacing the active sample volume and resulting in less well defined conditions.

(III) Under our experimental conditions (dye concentration 0.5 mM, amino acid residue concentration > 50 mM), the peptide backbone is not expected to significantly interact with dye molecules; however, peptide folding dynamics observed in the presence of the (ionic) dye will remain open to criticism.

Results Obtained with Pump Pulses at 1970 nm

The use of the IR-laser system (ii) allows direct absorption of the laser energy by the weak overtone band of D₂O at 1970 nm, and thus removes the need for using a heat-transducing dye. Thus, all of the complications described above can be avoided:

(I) Obviously, no photobleaching will occur and we have observed constant temperature jumps over more than ten hours.

(II) As long as only moderate temperature jumps (up to 8°C) are induced, and the sample temperature is kept low enough, so that the expansion coefficient is not too high (below approx. 50°C), we do not observe any cavitation. Figure 2 shows the absorbance changes for Ac-AAAAA-(AAARA)₄-NH₂ in D₂O for a temperature jump from 20°C to 24°C. At 1582 cm⁻¹, where only D₂O has significant absorbance, the absorbance decreases, due to the shift of the D₂O absorption band with temperature. This absorbance change appears instantaneously within the time resolution of our setup and then remains constant up to the millisecond time scale (data not shown), when the sample cools due to heat diffusion. Using the known temperature dependence of the D₂O IR spectrum, this absorbance change allows calibration of the temperature jump. At 1632 cm⁻¹, D₂O and peptide contribute; the additional dynamic component on the 100 ns-time scale arises from α -helix relaxation. Even in the presence of basic fuchsin, no cavitation occurs, most likely because there is no need for flowing the sample, so no dye aggregates will be flushed into the laser focus. When moving the sample, cavitation is observed at some positions, presumably those where dye aggregates are found in the laser focus.

(III) The ability to directly heat the solvent allows us to compare α -helix dynamics in the absence and presence of heat-transducing dye. The inset of Figure 2 shows a comparison of α -helix relaxation under different conditions, i.e. absence or presence of basic fuchsin (0.5 mM, BF) and at different pH. The dynamic traces have been scaled to the same amplitude and a logarithmic time scale is used to allow better comparability. All traces can be well fitted to a single exponential, yielding time constants of 173 ns (absence of BF, pH* 1.3), 166 ns (BF, pH* 1.5) and 149 ns (BF, pH* 4.7), respectively. These results show that 0.5 mM BF does not significantly affect the helix dynamics of this peptide, which is very similar to alanine-based peptides investigated previously^{2,3}, whereas adjusting the pH to higher values leads to a measurable acceleration. Since the peptide

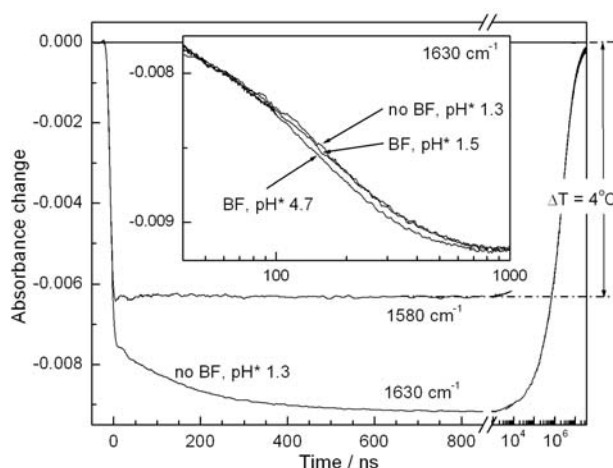


Figure 2. Absorbance changes for Ac-AAAAA-(AAARA)₄-NH₂ in D₂O for a temperature jump from 20°C to 24°C, induced by a 7 ns laser pulse at 1970 nm. Inset: Comparison of helix relaxation following temperature jumps from 20°C to 24°C under different conditions, i.e. absence or presence of basic fuchsin (0.5 mM, BF) and at different pH.

does not contain groups which are titratable in the pH range used here, it is more likely that this results from increasing the ionic strength of the solution than being a direct pH-induced effect. This question is currently under investigation.

Conclusions

Our results show that the presence of the heat-transducing dye basic fuchsin does not significantly affect the helix dynamics of a typical alanine-based α -helical peptide. Therefore, for such peptides the results from experiments using visible pump laser pulses for inducing fast temperature jumps are expected to be as valid as results using direct heating of water by IR laser pulses.

However, the use of IR laser pulses removes the need for flowing the sample. This makes it possible to perform measurements on samples with a volume of 100 μ l (requiring only 1 mg of peptide), reduces the incidence of cavitation events and permits one to average over a large number of measurements, which results in dynamic scans with significantly enhanced signal-to-noise. Therefore, direct heating by IR laser pulses is the preferred method for such measurements.

Acknowledgements

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Anti-viral agents and immuno-suppressive drugs: gas phase conformational studies of the Frentizole analogues Phenylurea and Diphenylurea

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Introduction.

Urea, one of Nature's simplest 'biomolecular' species with just eight atoms and two amide bonds, provided the first link between chemistry and chemical biology. It is a powerful protein denaturing agent and is also an anti-viral agent, as are many of its derivatives (see Figure 1).

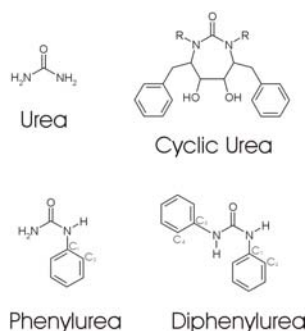


Figure 1. Structures of a number of urea derivatives.

In its crystalline state intermolecular hydrogen bonding enforces a fully planar molecular structure; in the gas-phase, rotational and dipole bound anion spectroscopy^{1,2)} together with *ab initio* computation, indicate a non-planar structure, though the distinction is rendered academic by large-amplitude motion of the NH_2 groups²⁾. Computational and dipole bound anion studies of the substituted, 1,1- and 1,3-dimethyl ureas indicate the possible population of structures with both *trans* and *cis* arrangements about the amide bond(s)²⁾, although no direct gas phase studies appear to have been reported. The same is true for phenyl- and 1,3-diphenyl urea where the influence of intermolecular hydrogen bonding favours a *trans* configuration; their structures, computed *ab initio*³⁾, are shown in Figure 2.

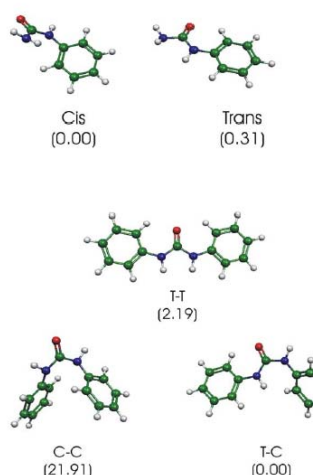


Figure 2. Structures of phenyl- and 1,3-diphenyl urea computed *ab initio*, (relative energies (kJ mol^{-1}) from MP2/6-311++G** single-point calculations on the B3LYP/6-31+G* optimized geometries).

In view of the anti-viral nature of urea and of its pharmaceutical derivatives, and the effectiveness of a number of protease enzyme inhibitors of the HIV virus based upon a cyclic urea template, it was appropriate to widen the gas-phase studies of

the family to include a conformational exploration of the simpler model species, phenylurea and 1,3-diphenylurea, in the absence of the intermolecular constraints introduced in a crystalline environment.

1. Phenylurea.

The UV resonant two photon ionisation (R2PI) and associated UV 'hole-burning' spectra shown in Figure 3, establish the presence of two distinct conformers. A comparison of their experimental mid IR spectra, with those computed for the *cis* and *trans* amide conformations, also shown in Figure 2, establish their assignments, as A(*cis*) and B(*trans*). The *trans* conformer adopts a co-planar geometry, supported by a weak interaction between the *ortho* CH and the neighbouring carbonyl groups. The *cis* conformer in contrast, adopts a twisted geometry with an amide-ring dihedral angle *ca.* 42° .

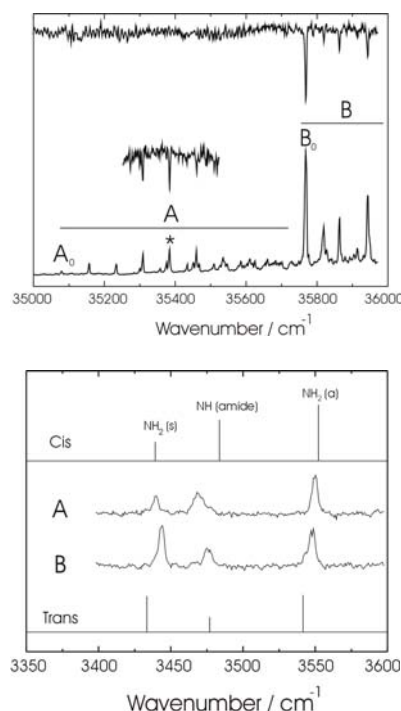


Figure 3. UV R2PI, UV hole-burn (upper panel) and IR ion-dip spectra (lower panel) of jet-cooled phenyl urea: computed IR spectra (B3LYP/6-31+G* with a scaling factor of 0.956) for the *cis* and *trans* conformers are presented as 'stick' diagrams.

2. 1,3-Diphenylurea.

The relative energies associated with the *ab-initio* structures shown in Figure 2 favour the population of the all *trans* (T-T) and partially *trans* (T-C) conformers. As with phenyl urea, the UV R2PI and UV 'hole-burn' spectra, shown in Figure 4, again indicate the population of two distinct structures and a comparison of their mid IR ion-dip spectra with those computed for the T-C and T-T structures establishes the assignment of the (weaker) UV system A to the all *trans* structure, T-T and the principal UV band system B to the calculated global minimum *trans-cis* structure, T-C. The 'weak-strong' infrared intensity pattern displayed by the T-T structure reflects the symmetric

and asymmetric stretch character of its two, equivalent NH bonds.

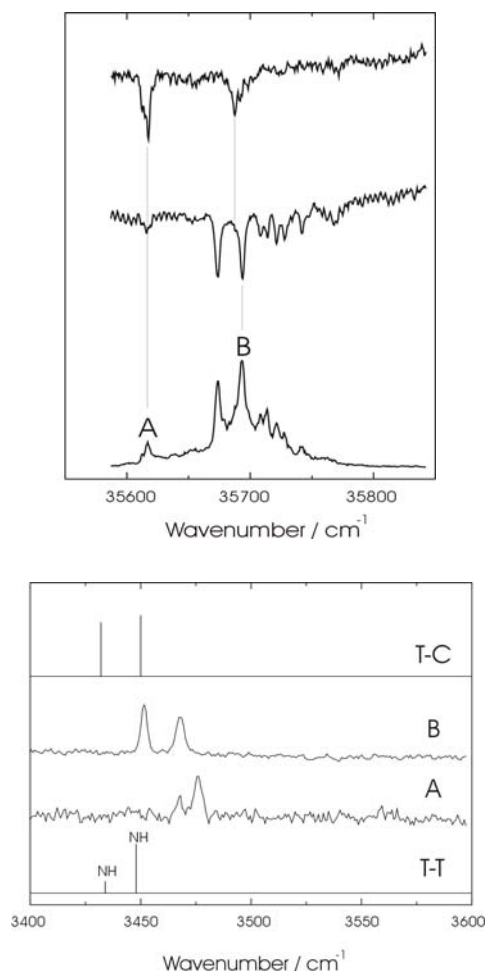


Figure 4. UV R2PI, UV 'hole-burn' (upper panel) and IR ion-dip spectra (lower panel) of 1,3-diphenylurea. Computed spectra (B3LYP/6-31+G* with a scaling factor of 0.956) are shown as 'stick' spectra.

Conclusions.

The conformational landscapes of the related series of molecules, N-phenyl formamide (formanilide), phenyl urea and N-phenyl acetamide (acetanilide) are strongly influenced by their terminal groups, respectively H, NH₂ and CH₃. In formanilide and phenyl urea, the *cis* and *trans* conformers have similar relative energies and both conformations are populated in a free jet expansion. Their *trans* conformers all adopt a planar geometry, stabilised by H-bonding between the C=O group and the *ortho* H atom on the phenyl ring, an interaction that is common in peptides and proteins. The *cis* conformers all adopt twisted geometries about the N-phenyl bond in the ground electronic state, S₀, with C₂C₁-CN dihedral angles ≥40°. Steric repulsion between the terminal amino group and the *ortho* H atom, aided by weak NH→π hydrogen-bonding with the aromatic ring, *cf.* the isoelectronic molecule, 2-phenyl acetamide where the dihedral angle is ~90°, both act in favour of a non-planar geometry. In acetanilide, where the replacement of the amino group by a methyl group enhances the steric repulsion and removes the hydrogen bonding, the *cis* configuration lies at too high a relative energy to allow its population in a free jet expansion. Weak NH→π hydrogen bonding in the folded (global minimum) T-C structure of 1,3-diphenylurea also favours its stability over the planar, all *trans* conformer.

Anti-viral pharmaceuticals such as 'frentizole', which are based upon the 'open' 1,3-diphenylurea template, have proved to be less successful than those with more rigid, cyclic geometries. 1,3-diphenylurea shares many of the structural features of the cyclic urea anti-viral compounds but the incorporation of the urea sub-unit into a fully cyclic structure necessarily locks the two amide bonds into an all *cis* configuration, see Figure 1, implicating this structure as an important pharmacophore. Since the corresponding structure (C-C) in the generic 1,3-diphenylurea molecule lacks both the NH → π and CH→O=C hydrogen bonds of its counterparts (T-T and T-C) and hence is some 20 kJ mol⁻¹ less stable than the other configurations, this too implies a clear structure-activity relationship.

Acknowledgements.

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Neurotransmitters in the gas phase: infrared spectroscopy and structure of protonated Ethanolamines

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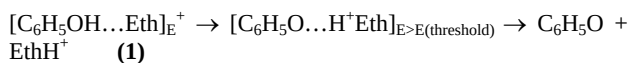
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Introduction.

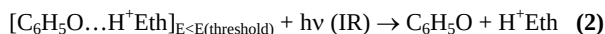
When a catecholamine neurotransmitter such as noradrenaline, binds to a protein receptor site, such as the β -adrenergic receptor on a trans-membrane protein, it is generally assumed to be protonated, its prevailing state in the aqueous physiological environment at the cell (pH, 7.4). Indeed, under these conditions, at least 90% of the ligands containing basic amino groups, *e.g.* amine neurotransmitters, such as histamine or dopamine; amino acid neurotransmitters such as γ -amino butyric acid (GABA); peptide neurotransmitters such as the penta-peptide, met-enkephalin; or neurotransmitters based on the ethanolamine template, such as noradrenaline or the ephedra, will be protonated. In each case their preferred conformations, whether in solution or at the receptor, may differ markedly from those of their neutral, or *zwitter*-ionic counterparts. They may also carry explicitly bound water molecules, though whether these are still retained at receptor binding sites remains an open question. So too, does the conformational structure of both the solvated and the bound, protonated ligand.

The principal approaches to addressing these questions in larger systems have been based on computational modelling or on mass spectrometry using electrospray ionisation to transfer the protonated and hydrated species into the gas phase. All experimentally based investigations of ethanolamine neurotransmitters conducted to date have been directed to studies of molecular conformation and structure of the *neutral* ligands and their solvated complexes. This has been due, principally, to difficulties in generating protonated and solvated molecules in sufficient number densities and at low enough temperatures in the gas phase to allow their spectroscopic interrogation and analysis, although there have been a number of encouragingly successful infrared photo-dissociation studies of protonated, solvated or clustered 'non-biological' molecules, generated in free jet expansions either through electron impact or pulsed corona discharges in hydrogen.

An alternative approach to the spectroscopic detection and structural assignment of protonated molecules in general, and neurotransmitters in particular, generated in high concentration in the gas phase was recently proposed¹, based upon the two photon ionisation of [phenol-proton acceptor] complexes. The time of flight mass spectrum generated by resonant two-photon ionisation of the phenol chromophore in jet-cooled [phenol-ethanolamine] complexes for example, did indeed include free protonated ethanolamine (and protonated ethanolamine dimers) as well as the (more intense) [phenol-ethanolamine]⁺ cation¹. Supporting *ab initio* and thermochemical calculations indicated a mechanism in which the protonated ions were generated spontaneously, through a predissociation pathway following an initial *proton* transfer within the *cationic* complex, [phenol-ethanolamine]⁺, favoured by the high proton affinity of the substituted amine.



This discovery laid the foundation for a versatile alternative structural strategy, which exploits the well-established method of infrared induced photo-dissociation spectroscopy to enhance the yield of the free protonated ion from its phenoxy complex,



and generate an infrared spectrum of the protonated ion complexed with, but not greatly perturbed by its phenoxy radical partner.

1. Phenol-ethanolamine and protonated ethanolamine clusters.

The resonant 2-photon ionisation spectra of phenol complexed with ethanolamine, in the $S_1 \leftarrow S_0$ ($\pi \rightarrow \pi^*$) origin band region, are reproduced in Figure 1. Previous UV-UV hole-burning experiments¹ resolved the overlapping spectra into three interleaved band systems, based on the origin bands labelled as A, B and C, associated with three distinct [phenol-ethanolamine] complexes (their structures are also shown in Figure 1). Analysis of their infra-red ion-dip spectra in combination with *ab initio* computation, allowed the three band systems to be assigned to a pair of 'O-addition type' clusters (bands B and C) and an 'insertion' structure (band A), in which phenol provided a hydrogen-bonded bridge linking the terminal OH and NH_2 groups in the ethanolamine molecule.

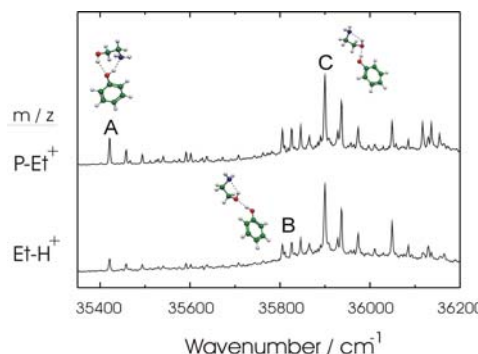


Figure 1. R2PI spectra of the origin band region of the $S_1 \leftarrow S_0$ transitions of phenol complexed with ethanolamine together with their associated structures.

The infrared photo-dissociation spectrum of the phenol-ethanolamine cation, recorded by monitoring the appearance of the protonated fragment ion, ethanolamineH⁺, is shown in Figure 2. (The same spectrum could also be recorded by monitoring the depletion of the parent ion). The UV laser was tuned to the origin band of complex A (see Figure 1) but similar spectra were also recorded based upon the bands, B and C. The IR spectrum displays four principal features: a relatively sharp band at 3670 cm^{-1} (contaminated by sharp water absorption bands absorbing in the same spectral region), a further pair of relatively narrow bands centred at 3365 cm^{-1} and 3275 cm^{-1} and a very broad band extending from 3100 cm^{-1} down to the limit of the infrared laser range, 2800 cm^{-1} . The similarities between the experimental spectrum and those of protonated ethanolamine, whether bare or complexed, are striking. Apart from the very broad band at low wavenumbers, which is assigned to the hydrogen-bonded N-H mode linking the protonated amine and phenoxy partners, the experimental spectrum is almost identical to that of bare protonated ethanolamine. The same is true of their structures, which are also displayed in Figure 2. The two dihedral angles, O-C-C-N and H-O-C-C, and the lengths and angles of the internal $\text{NH}^+ \rightarrow \text{O}$ hydrogen bond in free protonated ethanolamine are virtually identical to those in its complex with the phenoxy

ligand, $[\text{PhO}\dots\text{EtH}^+]$. Addition of the phenoxy radical, which is oriented *away* from the protonated ion, has very little effect on the geometry of the protonated ethanolamine and its infrared spectrum is only affected at the addition site. Neutral ethanolamine, in contrast displays a markedly different geometry, and vibrational spectrum, to that of the protonated species; its backbone still adopts a *gauche* configuration about the OC-CN dihedral angle but the direction of the internal hydrogen bonding is reversed (see Figure 2)²⁾.

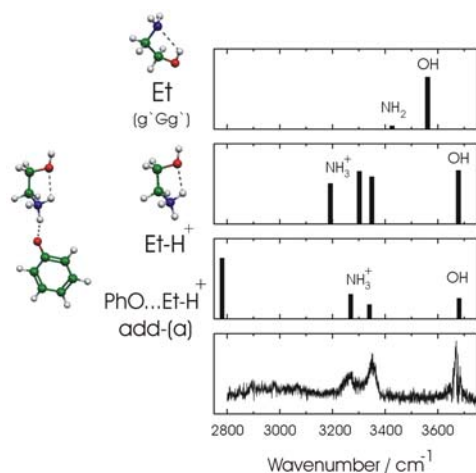


Figure 2. Experimental and computed spectra of protonated ethanolamine complexed with the phenoxy radical and as a free molecular ion. Also shown is the computed spectrum of neutral ethanolamine.

2. Protonated 2-phenyl ethanolamine clusters.

2-phenyl ethanolamine is a very close relative of noradrenaline, the only difference being the link to a phenyl rather than a catechol ring. The IR photodissociation spectrum of its two-photon ionised complex with phenol is shown in Figure 3, where the parallels with the corresponding spectrum of the phenol-ethanolamine cation are clearly displayed. Again the 'free' OH band can be seen (contaminated by water vapour absorption lines) at 3660 cm^{-1} and a pair of unperturbed N-H bands associated with the protonated amino group are located at 3250 and 3350 cm^{-1} . The third N-H band will, as before, be shifted to much lower wavenumbers through H-bonding to the attached phenoxy radical. Although the spacing of the two N-H bands favours an assignment to the extended (AG) side chain structure the folded (GG) conformer is calculated to lie very close in energy and it is possible that the broad IR features reflect contributions from both.

Future Prospects.

The new technique employed should be readily adaptable to a broad range of biomolecular proton acceptors. The proton donor need not always be phenol: indeed, where the ultra-violet absorption of the acceptor overlaps that of the donor, as would be the case, for example, in complexes incorporating phenol and catecholamines such as dopamine or adrenaline, replacement of phenol by naphthol would remove the problem.

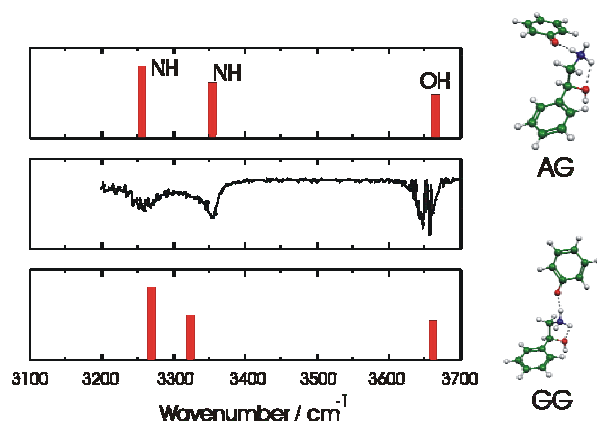


Figure 3. Infra-red photodissociation spectrum of $[\text{Phenol}\dots 2\text{-phenyl ethanolamine}]^+$ and computed structures/vibrational spectra of the extended (AG) and folded (GG) conformers of the protonated ethanolamine-phenoxy complex.

The infrared spectral range need not be restricted to the mid-infrared region, *ca.* $3000\text{--}4000\text{ cm}^{-1}$, with the availability of more broadly tunable infrared laser systems, particularly free electron lasers (e.g. the FELIX system at FOM, Rijnhuizen) which can provide intense radiation across the full spectral range^{3,4)}, extending through the 'fingerprint' region down to THz frequencies. The decrease in photon energy, which militates against single photon photodissociation, will be compensated both by the internal energy present in the absorbing complexes $\{\text{MH}^+\dots\text{OR}\}$ and by the high intensity of the radiation provided by free electron lasers – which will certainly be sufficient to promote multi-photon infrared absorption^{3,4)} and hopefully, dissociation.

Finally, the production of protonated ethanolamine both from complexes in which the proton-donating group is *not* directly attached to the amino group, e.g. from the structures labelled, 'B' and 'C' in Figure 1, as well as the complex 'A' in which there is a direct link, indicates facile proton migration following their two photon ionisation. The strategy that has been implemented promises to provide a much needed bridge, linking the 'ionic' world of mass spectrometry, to the 'structural' worlds of optical spectroscopy and molecular biology.

Acknowledgements.

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Depth profiling of composite polymer nanoparticles using laser vaporisation/mass spectrometric methods

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Introduction

Particulate material of one form or another (between 10nm and a few μm in diameter) has a significant influence on the quality of everyday life. Established industrial processes use or produce finely dispersed materials in the form of ceramics, paints, polymers, pigments etc. all of which enhance our ability to perform particular tasks. In addition, new technologies are developing electronic devices that exploit nano-scale materials, and similar particle sizes are being considered for catalytic systems. There are also many particulate materials that are not beneficial, and these include automobile combustion products, diesel fumes, cigarette smoke, incinerator products, and atmospheric aerosols (smog). Finally, there are particulate materials that need to be characterised if we are to have a better understanding of the physical processes they promote. This latter category includes atmospheric aerosols within which chemical processes involving hydrocarbons, acids, and NO_x compounds may participate.

Although a number of techniques have been developed to establish the characteristics of small particles, e.g. size distribution, structure, electrical properties etc., because of technical difficulties, no method offers the ability to perform systematic physical and chemical measurements on single particles. A particular problem is that many techniques require particles to be supported before they can be interrogated. Reported below are the first results from an experiment that has been designed to use laser ablation as a method for characterizing free particles in the gas phase. To facilitate delivery of the particles into a vacuum chamber the ablation technique has been coupled to an aerodynamic lens. The technique has been tested on latex particles that have a mixed composition, such that they consist of a polystyrene latex core (PSL) that has been stabilized with a thin coating of poly(ethylene glycol) monomethacrylate macromonomer (PEG). The particles are 130 nm in diameter and the coating is approximately 5 nm thick. A typical cross section is shown in Figure 1.

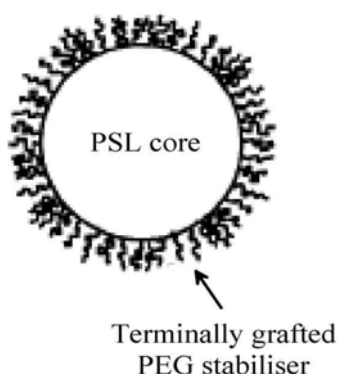


Figure 1. Cross-section of a PEG-PSL particle.

Experiment

An aerosol from particles dispersed in a solvent was generated using an aerosol generator and contained within a stream of nitrogen gas. After passing through a pressure-reducing critical orifice, 150 μm in diameter, the particles entered an aerodynamic lens consisting of a stainless steel tube that housed

a series of thin plate orifices arranged in decreasing diameters downwards from the aerosol inlet. The orifices were typically 1250, 1000, 750, 600 and 400 μm in diameter and separated by spacers ranging from 6 to 30 mm apart. A schematic diagram of the lens is shown below.

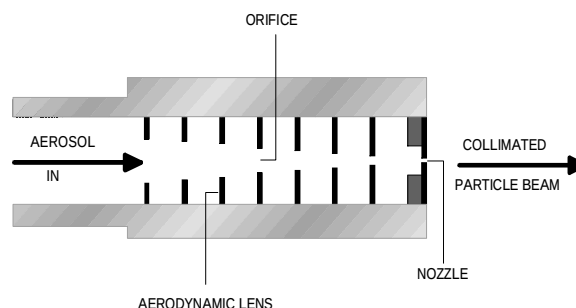


Figure 2. Aerodynamic Lens.

The lens was contained within a differentially pumped chamber comprising of three compartments separated by skimmers. The final skimmer transmitted the particle beam into the ablation/ionisation region where the vacuum was maintained at an operating pressure of approximately 1.0×10^{-7} mbar. A HeNe laser was used to align the skimmers with the aerodynamic lens and, where relevant, was also used to detect the particle beam by light scattering. The aerodynamic lens was able to produce a focused nanoparticle beam with a diameter of ~ 1 mm. Laser ablation was achieved using a Nd:YAG laser focused on to the collimated particle beam using a fused silica planoconvex lens (focal length 63mm). A time-of-flight mass spectrometer was mounted orthogonal to the particle beam, and ions were pushed out from the ablation region with +2 kV potential on a repeller grid and focused into a 1.5 m flight tube.

Previous studies of microparticles using laser ablation in conjunction with linear TOF systems have reported poor resolution. This was largely attributed to uncertainty in the position of the particle in the desorption/ablation beam. However, temporal and spatial variations can also be linked to the amount of energy a particle absorbs from the laser. Particles located in the centre of the focused laser beam, where the irradiance is highest, will absorb more energy than those at the edge where the irradiance is much lower. In the experiments reported here, the laser beam was focused to a spot ≈ 250 μm in diameter; however, as the particles under investigation have diameters of ~ 0.1 μm we expected, and indeed observed, variations in ion flight times as a result of an ill-defined point of ionisation and/or a spread of ion energies.

Results

Preliminary results are presented of mass spectra recorded at two wavelengths, 532 and 266 nm. Figure 3 shows a time-of-flight mass spectrum recorded following the laser ablation of PEG-PSL particles at 532 nm. As can be seen, the largest ion recorded has an m/z value of 41. In contrast, Figure 4 shows a mass spectrum recorded at a wavelength of 266 nm, where it can be seen that ions are generated with much higher m/z values than those seen in Figure 3. An inspection of the basic polymer repeat units that go to make up the composite particles Figure 5, shows that all of the ions generated at 532 nm can be derived

from the surface coating. For example, m/z 26 represents $C_2H_4^+$ and m/z 45 is $C_2H_5O^+$.

In contrast, mass spectra recorded at 266 nm include these ions together with many that are derived from the polystyrene core.

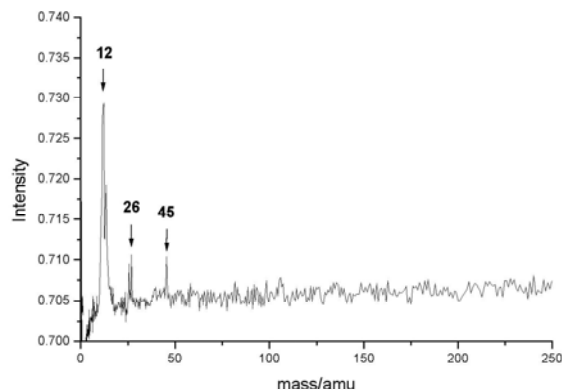


Figure 3. Time-of-flight mass spectrum recorded following the laser ablation of 130 nm diameter PEG-PSL particles at 532 nm and with a laser power of 50 mW.

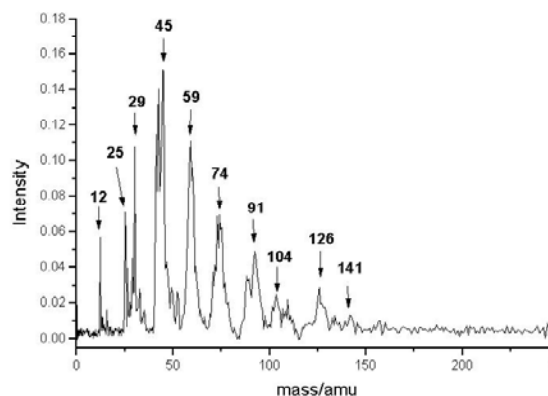


Figure 4. Time-of-flight mass spectrum recorded following the laser ablation of 130 nm diameter PEG-PSL particles at 266 nm and with a laser power of 20 mW.

For example, m/z 91 could be the very stable tropylium ion ($C_7H_7^+$), and ions seen at higher mass have been seen previously in mass spectra recorded from polystyrene films.

Separate power-dependence studies suggest that different ablation mechanisms are operating at the different wavelengths. At 532 nm there appears to be a strong thermal decomposition mechanism that, at high laser powers, reduces all the fragments to C^+ (m/z 12, as seen in Figure 3). In contrast, at 266 nm the photon energy is high enough to penetrate the particles and release high mass ions, which remain intact. However, the C^+ intensity is seen to increase with laser power, and this behaviour is attributed to photochemical processes induced by photons in the trailing edge of the ablation pulse.

These preliminary results show evidence of preferential ablation of material from either the surface or the core of a composite nanoparticle. Further experiments are in progress to explore the potential of the combined aerodynamic lens – TOF mass spectrometer as a technique for studying particles of composite materials composed of a wide range of liquids and solids.

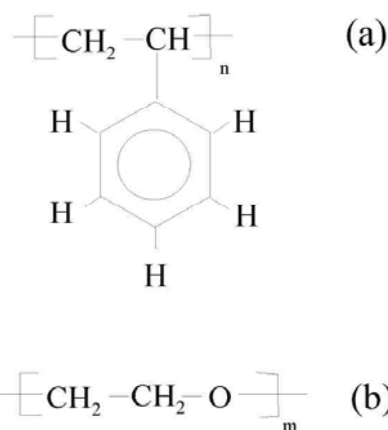


Figure 5. Chemical structure of the repeat units present in the composite nanoparticles: (a) the polystyrene core and (b) the polyethylene glycol surface coating.

Acknowledgements

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Trapping and probing the forces between colloidal particles

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Introduction

The properties of colloidal systems are normally probed using bulk techniques, such as dynamic light scattering. However, to get a clear picture of how individual colloidal particles interact different approaches are required.

Here we have used the optical tweezers apparatus in the Lasers for Science Facility to study the interactions between two trapped polystyrene particles. In addition to measuring the dc displacement in the particle positions as the two traps are brought together, we have oscillated the traps and studied the dependence of the amplitude and phase of the particle motion on separation.

Optical tweezers were invented in 1986 by Arthur Ashkin and co-workers at Bell Labs¹⁾, when they found that a laser beam focussed to a diffraction limited spot could trap high refractive index colloidal particles in the focus of the laser. If the trap is displaced, then there is a restoring force on the particle driving it back towards the minimum of the trapping potential well. There is a lag between the motion of the particle and the trap that depends on the force constant of the trap, k , viscous drag and the interaction potential with other particles. For an oscillatory motion, this lag manifests itself as a phase shift, ϕ , between the motions of the trap and the particle.

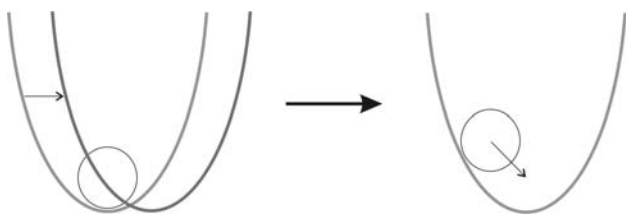


Figure 1. The laser movement changes the position of the potential well with respect to the particle and so induces the particle to move with the laser.

Theory

For the case of an isolated trapped particle, the amplitude of the oscillation (b) of the trapped particle is related to the amplitude of oscillation (δ) of the trap by:-

$$b = \delta \cos \phi \quad \text{and} \quad \tan \phi = \frac{6\pi a \eta \omega}{k} = \frac{\omega}{\omega_0}$$

where a is the particle radius, η is the viscosity of the surrounding medium, ω is the angular frequency of oscillation and $\omega_0 = k / 6\pi\eta a$ is a characteristic frequency.

The expression for $\tan \phi$ allows us to measure the trapping constant k by simply varying the frequency of oscillation and measuring ϕ from the cross-correlation of the laser motion and the particle motion.

For the case of two particles, the motion can be broken down into four orthogonal modes. Two modes involve motion along the particle axis, with the displacement of the second particle being the same as (synchronous) or opposite to (asynchronous) the first. The solution to the equations of motion in the synchronous case is given below.

$$\tan \phi = \left(\frac{\omega}{\omega_0} \right) \frac{1}{(A_{11} + A_{12})}$$

$$b = \delta \cos \phi = \left(\frac{\delta [A_{11} + A_{12}]}{\left\{ \left(\frac{\omega}{\omega_0} \right)^2 + (A_{11} + A_{12})^2 \right\}^{1/2}} \right)$$

where A_{11} and A_{12} are mobility coefficients that describe the hydrodynamic interactions between the particles.

For the asynchronous case an additional term arises from the second derivative of the interaction potential, U'' , which has the effect of modifying the apparent force constant of the trap.

$$\tan \phi = \left(\frac{\omega}{\omega_0 + \omega_i} \right) \frac{1}{(A_{11} - A_{12})}$$

$$b = \left(\frac{\omega_0}{\omega_0 + \omega_i} \right) \delta \cos \phi$$

$$= \left(\frac{\omega_0}{\omega_0 + \omega_i} \right) \left(\frac{\delta [A_{11} - A_{12}]}{\left\{ \left(\frac{\omega}{\omega_0 + \omega_i} \right)^2 + (A_{11} - A_{12})^2 \right\}^{1/2}} \right)$$

where $\omega_i = 2U'' / 6\pi\eta a$.

Sample Preparation

A standard polystyrene latex solution (Bang Labs, 1% vol., 2.7 μm diameter particles) was diluted by 100:1. 1 μL of this solution was injected from a microsyringe onto the surface of a coverslip immersed in pure water. The resulting sample had a small area about 30 μm across where polystyrene spheres could be found. Two particles were trapped and moved away from the remaining particles to avoid interference with the experiments.

Experimental

The standard optical tweezers rig at the LSF was used with a few modifications. A spatial filter was added to improve the laser beam quality. A higher order reflection from the acousto-optic modulators was directed onto a split photodiode to permit measurement of the phase difference between the motion of the laser beam and that of the trapped particle. The brightfield image of the trapped particle was projected onto a split photodiode, which could be scanned across the image. Rather than using the point of maximum sensitivity, we positioned the photodiode on the side of a subsidiary peak to minimise interference from the image of the second trapped particle. A new Lab View program was written to allow us to calibrate the system and to record all the amplitude and phase data simultaneously into an Excel spreadsheet.

The trapped particles were arranged so that the applied oscillations were along the particle axis and then the particle separation was reduced. The power spectrum signal at 30 Hz

(the applied frequency), the phase lag between the particle and laser motion and the cross-power spectrum signal at 30 Hz were recorded by the Lab View software, along with relevant information, such as the particle separation.

As the particles were brought to small separations the repulsive electrostatic interaction between the particles displaces them from the centre of their traps slightly. This displacement can be measured by monitoring the dc signal from the photodiode monitoring the particles motion. The position of both particles was then offset to return the dc signal to its initial value, in order to preserve the linearity of the response of the experiment. This offset is linearly proportional to the interaction force between the particles at a given separation.

Results

Data was recorded for both synchronous and asynchronous motion of the particles along the particle axis and the results together with theoretical fits are shown below. The theoretical model assumes that the hydrodynamics obey the continuum description of Batchelor²⁾ and that the pair potential is a decaying exponential.

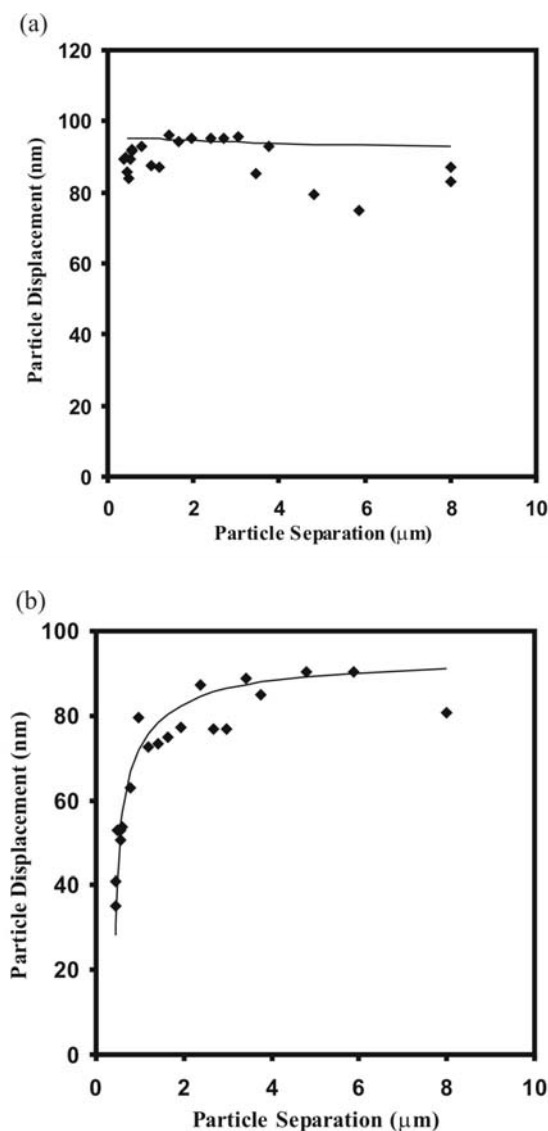


Figure 2. Plot showing how the particle amplitude of oscillation varies with particle separation for a constant applied oscillation of 100 nm for (a) synchronous and (b) asynchronous oscillations. (b) shows strong damping at small particle separations.

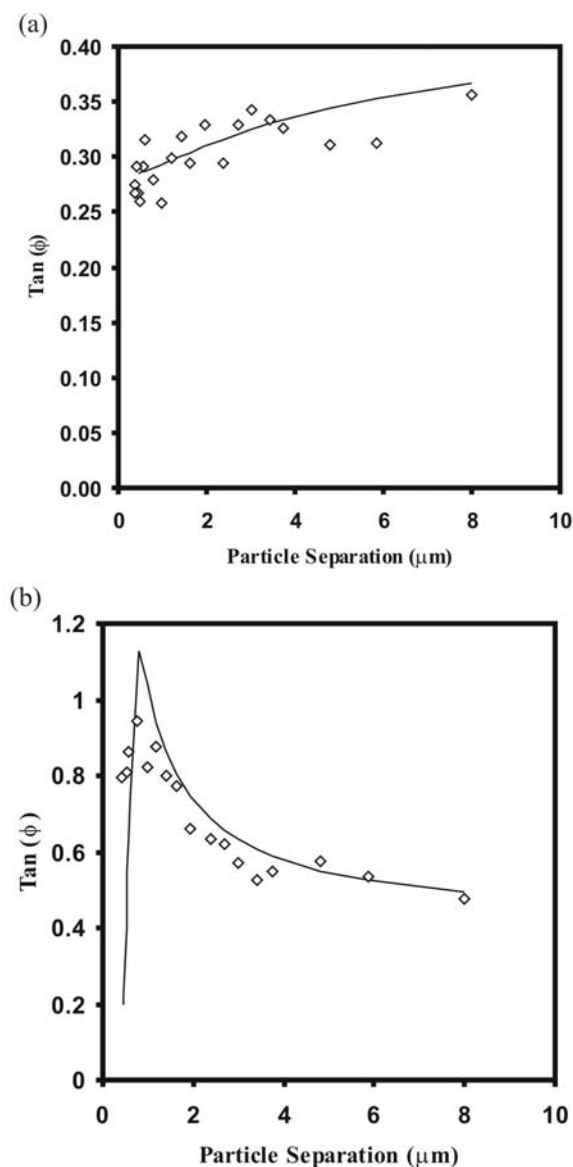


Figure 3. Plot showing how the tangent of the phase varies with particle separation for a constant applied oscillation of 100 nm for (a) synchronous and (b) asynchronous oscillations. (b) shows the change from hydrodynamic to electrostatic potential at separations of $\sim 1 \mu\text{m}$.

Conclusions

We have been able to model successfully the potential between two colloidal particles, based on Batchelor's theory of hydrodynamic motion, and our data shows good agreement for both the synchronous and asynchronous oscillation modes along the particle axis. The asynchronous case shows the presence of an electrostatic potential between the particles, represented by the sharp turning point in Figure 3 (b) at about 1 μm particle separation.

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Ultraviolet resonance Raman (UVR) studies of adsorbates on metal surfaces

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Introduction

During the last two decades, technical developments such as photon detection with charge-coupled devices (CCD) have overcome the major problem of weak Raman signal intensity. Today, Raman spectroscopy has the potential to become a powerful tool for studying the vibrations of molecules at surfaces¹. Like Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy benefits from a high spectral resolution and also low frequency sensitivity. With different selection rules, Raman spectroscopy provides additional complementary information on fundamental spectral vibrations (fingerprinting). Thus, the development of the surface-enhanced Raman scattering (SERS) technique has allowed the observations of Raman scattering from monolayer and single molecules on surfaces². SERS greatly enhances (10^8 - 10^{14} times) the Raman signal from molecules adsorbed on specially prepared metal surfaces³. The main enhancement effect (10^4 - 10^6 times), "electromagnetic" enhancement, is dependent on the presence of a metal roughness feature. The second and independent mechanism, "chemical" enhancement (10 - 10^2 times), has been attributed to the change of the adsorbate electronic states due to the chemisorption process. The new electronic states, which arise from chemisorption, serve as resonant intermediate states in Raman scattering. These states may be related to charge transfer absorption bands associated with the metal-adsorbate complex⁴. Thus, combined studies of SERS and Electron Energy Loss Spectroscopy (EELS), shows a direct relationship between the electronic excitation bands and Resonance Raman excitation profiles⁵.

In this work, UV Raman spectroscopy has been carried out in the 250 nm (5 eV) range to access directly the charge transfer bands known to exist for adsorbed molecules and atoms on flat single crystal metal surfaces⁶. This will extend, for the first time, resonance-enhanced Raman spectroscopy to a wide range of well-defined adsorption systems from small to large molecules, without the need for the surface roughening. These studies, aiming to observe Raman scattering from a "flat" surface, are a challenging experiment but potentially a very promising step forward. Therefore, Resonance Raman spectroscopy (RR) on single crystals will complement and enhance the IR techniques in Surface Science particularly for vibrational modes in the 100-700 cm^{-1} regions where sufficient sensitivity is rarely achieved with IR spectroscopy.

Many Raman and resonance Raman studies have used nitrobenzene for its strong adsorption around 250 nm. In addition, Campion et al. have reported good quality non-resonant spectra of nitrobenzene adsorbed on Ni(111) single crystal surface⁷. Thus, the choice of nitrobenzene as adsorbate became ideal to compare the sensitivity of the surface Raman system designed. However, at about 5 eV, intramolecular charge transfer (CT) from the benzene ring towards the NO_2 group in nitrobenzene results in dissociation in the excited state of the molecule⁸. In order to avoid such photodissociation processes along resonant excitations, benzene was also dosed. With a work function of 5.93 eV, the Pt(111) single crystal surface, was chosen to carry out the resonance Raman experiments.

The visible frequency-doubled Nd:YAG laser (532 nm) was first used in order to optimize the optical set-up. Once,

multilayers of adsorbates were detected, the continuous wave (CW) frequency doubled (coherent FreD) argon ion laser optimized at 244 nm, was used in order to obtain enhanced Raman signals on flat metal surfaces.

Experimental

A diffusion pumped UHV chamber was brought to the Central Laser Facility (CLF) at Rutherford Appleton Laboratory (RAL) in order to perform the UVR measurements. The UHV rig developed at the Surface Science Laboratory at Nottingham University comprises a quadrupole mass spectrometer Q.M.S (Stanford, RGA 200) for gas analysis, a sputter gun (VG) for sample cleaning and fused silica port windows for the laser beam to impinge at 45° to the sample surface normal. Figure 1 shows a schematic diagram of the UVR system designed.

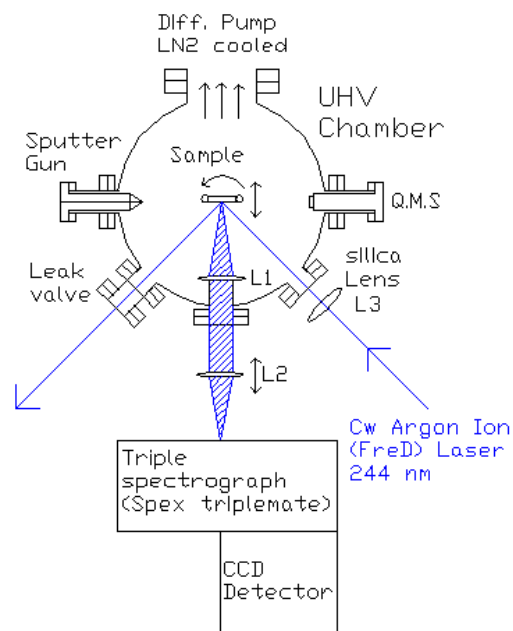


Figure 1. Ultra High Vacuum (UHV) - UVR system.

A fused silica lens L1 (50 mm focal length) was attached to the UHV port window into the vacuum chamber, as shown in Figure 1. Light scattering from the sample, was collimated towards the Raman spectrometer. A second lens, L2 (300mm focal length), focused the scattered beam on the spectrometer entrance slit. The laser beam was directed at 45° from the surface normal, by a set of quartz prisms. The laser beam, with a polarisation parallel to the plane of incidence (p-polarisation), was focused by a lens L3 of focal length 150 mm. The focus was slightly off at the sample surface in order to limit the power density. The laser irradiated a surface area around 1 mm^2 , resulting in a power density of 1 W cm^{-2} . Since the index of refraction of the optics is dependent on wavelength, the sample has to be translated when changing from visible to UV excitation. Thus, the change of focal length could be compensated and the Raman scattering beam collimated.

The base pressure in the UHV chamber was below 5×10^{-10} mbar. Initial cleaning of the Pt(111) crystal was achieved by ion bombardment (12 μA) followed by annealing at

1300°C for two minutes. Once the contamination has been reduced, a second cleaning procedure consisting of oxidation and annealing. The crystal could be cooled below 110 K and heated to 800°C. The temperature was monitored by a K-Type thermocouple spot-welded to the edge of the platinum crystal. Nitrobenzene and benzene were purified by freeze-pump-thaw cycles prior to dosing.

Adsorption of Nitrobenzene on Pt(111)

Preliminary experiments were carried out using a frequency-doubled Nd:YAG (532 nm, CrystaLaser GCL-050-S) to irradiate a film of nitrobenzene adsorbed on clean Pt(111) held at 120 K. Figure 2 displays the Raman spectrum recorded after the nitrobenzene film was condensed on the Pt(111) surface using a dynamic pressure of 5×10^{-6} mbar. The spectrum was averaged for 20 minutes acquisition (60 x 20 seconds) and calibrated.

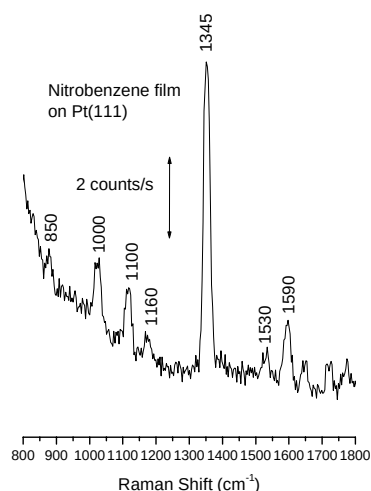


Figure 2. Raman spectrum of nitrobenzene film on Pt(111) using the frequency-doubled Nd:YAG 532 nm laser.

The frequencies of the bands observed agree with the literature values for liquid nitrobenzene and have been assigned as follows⁹: the NO₂ symmetric and asymmetric stretches at 1345 and 1530 cm⁻¹, the ring stretches, breathing and bending at 1590, 1100 and 1000 cm⁻¹ and the C-H bending and stretches at 1160 and 3080 cm⁻¹. With a high signal to noise ratio and a maximum intensity of 5 counts/s for 60 L exposure, the optical setup of our Raman detection system is found to be as sensitive as that reported by the Campion group⁷.

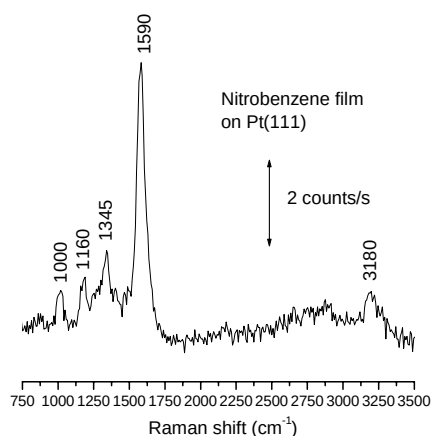


Figure 3. Raman spectrum of nitrobenzene film on Pt(111) using the argon ion frequency-doubled (FreD) 244 nm laser.

Figure 3 shows the Raman spectrum of nitrobenzene film on the single metal crystal Pt(111) using the argon ion FreD laser at 244 nm. The main nitrobenzene bands at 1000, 1160, 1345 cm⁻¹ can be clearly seen and their positions are identical to those obtained previously with the visible light (532 nm).

The intensity ratios differ from the visible Raman spectrum but this behaviour, accredited to resonance effects, was predicted and expected. The band at 3180 cm⁻¹ has been attributed to combinations of carbon-hydrogen bending and carbon ring motions as observed in a benzene resonance study¹⁰. However, the broad band at 1590 cm⁻¹ is not due to the presence of nitrobenzene molecules. Indeed, this broad feature has been frequently observed in SERS experiments and has been explained by the presence of amorphous carbon on the surface. Photodissociation due to intramolecular charge transfer (CT) in the nitrobenzene molecule at resonance frequencies may result in carbon species formation. In order to avoid nitrobenzene dissociation at 244 nm (5 eV), benzene was then dosed on Pt(111).

Adsorption of Benzene on Pt(111)

The Pt(111) sample was carefully cleaned and cooled to 120 K followed by dosing 120 L of benzene. To observe the spectrum shown in Figure 4, the entrance spectrometer slit had to be widely opened, resulting in the observed broadening of the vibration bands. However, the ring-breathing mode at 990 cm⁻¹ is clearly observable and a broad band at 1600 cm⁻¹ is found. In addition, C-H deformations and carbon motions at 1380 and 3170 cm⁻¹ are detected.

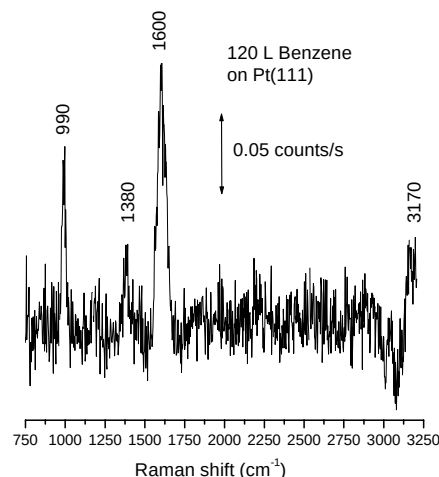


Figure 4. Raman spectrum of 120 L benzene on Pt(111) using the argon ion frequency-doubled (FreD) laser -244 nm laser.

As previously observed for nitrobenzene films, the broad band (200 cm⁻¹) at 1600 cm⁻¹ may be characterised as due to amorphous carbon on the surface. The platinum sample was then flashed at 300 K, in order to desorb the benzene multilayer. Unfortunately, only the broad band at 1600 cm⁻¹ assigned to carbon contamination was detected. Laser damage effects seem to dominate the observed Raman signal once again.

Laser damage effects

Figure 5 shows the spectra recorded as a function of laser exposure after 120 L of benzene was dosed. Each spectrum of 30 seconds acquisition is vertically offset for display purpose. The bottom spectrum was recorded with the laser turned off, and then the laser was directed at the sample surface for 15 minutes.

A resonance Raman study of benzene reported Raman spectra dominated by the overtones and combinations of the active e_{2g} modes in this dipole forbidden transition. Four e_{2g} modes are found in benzene, two have been attributed to carbon bending and stretching motions (strongly scattered) while the other are

due to hydrogen bending and stretching¹⁰). This intense Raman signal at 3170 cm⁻¹ was detected for the first 30 s exposure. However, as the laser exposure increased, the intensity of the Raman mode detected decreased and remained observable for the next 180 s. It is then difficult to distinguish this mode of vibration from the noise level. However, by adding all the spectra recorded a broad band centred at 1600 cm⁻¹ is observed (top spectrum).

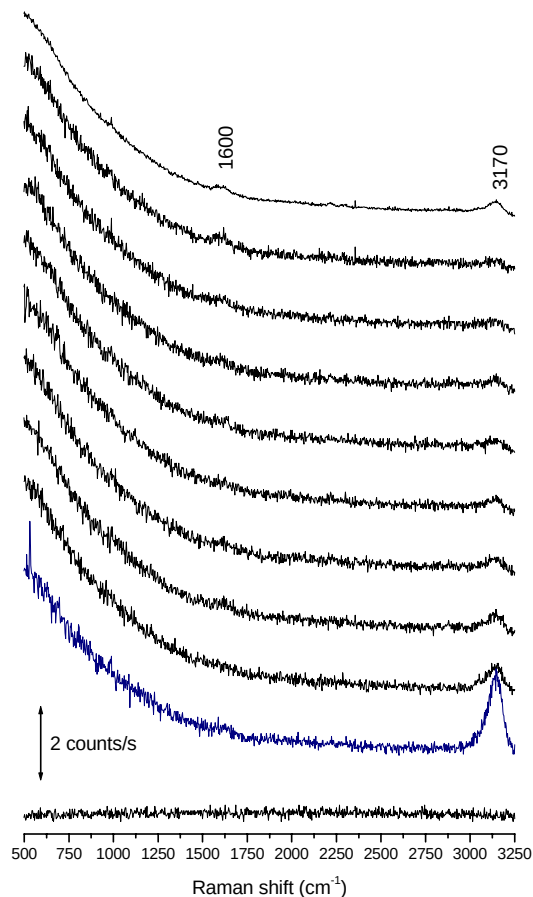


Figure 5. Raman spectrum recorded after desorption of the benzene multilayer using the argon-ion frequency-doubled (FrED) 244 nm laser.

These observations clearly showed the instability of the benzene multilayers under UV light exposure. There are two potential explanations:

- Heating effect of the laser
- Photoinduced hot electron desorption mechanism, which may only be important for the first benzene layer.

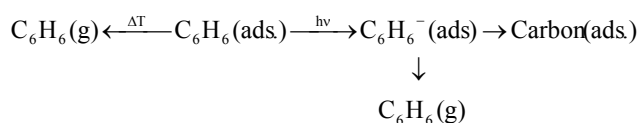
In considering the former, the heating effect of the benzene multilayer under the laser spot has been calculated. The estimated temperature rise in isolated benzene films produced by the laser is in the order of 1-2 K. However, in order to estimate the significance and importance of such heating further investigation and measurements are required.

Conclusion

The Raman spectra of nitrobenzene and benzene multilayers on Pt(111) have been observed. Using the frequency-doubled Nd:YAG (532 nm) laser, the spectra recorded are in good agreement with previous studies. The sensitivity of the UHV-Raman system designed was sufficient to detect 60 to 100 L of nitrobenzene (and benzene) for 20 minutes accumulation time. The Raman bands observed have been assigned and agreed well with liquid phase data and the previously reported studies. These first experiments allowed optimization of the system

detection and setting up a reproducible laser alignment procedure based on the Raleigh scattering. Thus, starting from a clean surface, monolayer to multilayer of adsorbates could be prepared for Raman detection.

The use of the argon-ion laser (244 nm) as an incident source was expected to provide enhanced Raman scattering. Both the ω^4 effect in light scattering and resonance by charge transfer (CT) mechanism should give rise to important enhancement scatterings (10^2 - 10^3). Nitrobenzene and benzene films deposited on Pt(111) have been observed. However, weak intensity signals were recorded and amorphous carbon species were formed under laser exposure. Photodissociation due to intramolecular charge transfer (CT) in the nitrobenzene molecule was expected. However, benzene photodissociation and /or photodesorption suggest a stronger and unpredicted laser damage effect. Thermal desorption (ΔT), photodesorption and photodissociation mechanisms combined and may explain the spectra observed. The diagram below shows the different process in competition.



Acknowledgements

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Optical trapping of droplets from an oil mist

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Introduction

In this work, we utilise the higher trapping efficiency provided by a high numerical aperture (NA) microscope objective lens to generate a trapping environment which is robust enough to immobilise single oil droplets from a nebulised mist passing the point of laser focus. Once captured, the droplets can be held for periods up to 30 minutes whilst the surrounding mist dissipates.

The optical levitation of liquid droplets in the gas phase was pioneered by Ashkin and Dziedzic¹⁾ and the technique has since formed the basis of studies into atmospheric physics, cloud physics, and aerosol science. The optical arrangements for the levitation of aerosol droplets can be broadly divided into two different methods. The first method of optical levitation is based on balancing gravitational forces with those of the radiation pressure from an upward pointing and weakly focused laser beam. The numerical aperture of the focusing lens is typically ²⁾ in the range of 0.01 to 0.25 and thus the convergence angle, θ , of the cone of focused laser light is between 0.5° and 12.5° . Under these conditions the axial trapping efficiency, Q , is approximately 0.05. With this efficiency, great care has to be taken to present single droplets in an environment amenable to levitation trapping that prevents collisions from other particles or disruption from air currents. The trapped droplets diameters are usually in the size range of 12 to 150 μm (diameter). The trapped particles vertical position is dependent upon laser power, but this can be stabilized using a feedback control between a position sensitive diode and the laser power control.

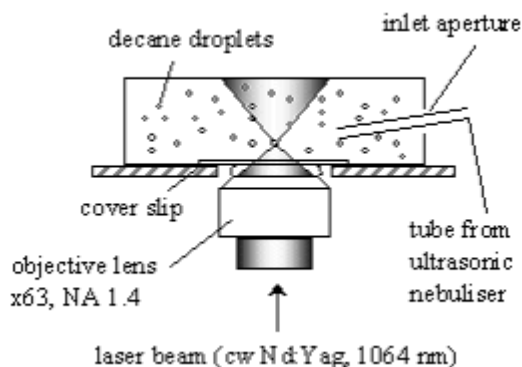


Figure 1. Schematic diagram of the optical trapping arrangement and sample chamber.

The second method of optical levitation uses high numerical aperture microscope objective lenses, which tightly focus the laser beam to form a single beam optical gradient trap. This type of trapping has been documented for a number of years, but is normally associated with trapping particles dispersed in liquid media. Importantly, gradient trapping does not depend on balancing gravitational forces and can be achieved in any optical orientation. Magome *et al.*²⁾ have used a NA 1.3 ($\theta = 60^\circ$), oil-immersion, x100, microscope objective lens to capture water droplets nucleating *in situ*. They observed the trapping of the aerosol droplet at the focal point of the laser beam, an optical arrangement similar to that associated with single beam optical gradient trapping. This appears to offer significant increases in trapping efficiency as Q increases to a value of 0.46. Similarly, Omori *et al.*³⁾ have demonstrated an analogous

arrangement to levitate glass spheres using an air objective lens, NA = 0.95, $q = 71^\circ$.

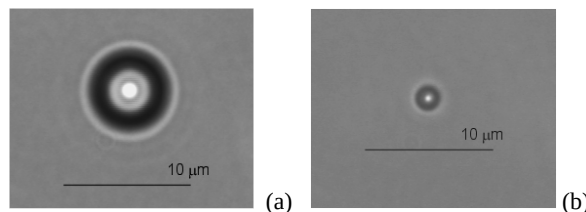


Figure 2. Images of trapped aerosol droplets of (a) 6.7 μm and (b) 2.0 μm diameter.

Experimental Study

The optical trap was created by focusing a continuous wave, TEM00, Nd:YAG diode laser (Laser 2000) with a wavelength of 1064 nm and a variable power output of up to 1 W. From the laser source the beam was expanded and directed into Leica DM IRB microscope where it was reflected upwards, using a dichroic mirror, such that the back aperture of the objective lens was slightly overfilled. The lens used was an oil-immersion objective with NA = 1.40 and $q = 67^\circ$. In addition, the beam could be steered and multiplexed in the plane of focus using a pair of orthogonally mounted acousto-optic deflectors (Isle Optics Ltd). An oil mist (n-decane, refractive index = 1.41) containing droplets in the size range of 1 to 7 μm was generated using a commercial ultrasonic nebuliser (Omron NE-U07). A schematic diagram of the chamber and trapping environment is shown in Figure 1. Experiments were performed at a temperature of $19^\circ\text{C} \pm 0.5^\circ\text{C}$. Images of the droplets were taken from underneath the droplets using a CCD camera mounted on to the conventional optics for inverted microscopy.

Results and Discussion

Injection of the oil mist into the sample chamber resulted in the microscopic observation of numerous droplets passing across the field of view. Within a few seconds a large fraction of these droplets had collided with the upper surface of the cover slip to form a thin condensed film. The thickness of the decane film could be easily determined from the reflection of a focused laser spot from the glass-decane and decane-air interfaces. The decane film varied in thickness from 5 to 15 μm , depending on the volume of mist injected into the sample chamber. The position of the focal spot was adjusted to be above the decane film (see Figure 1). After a few seconds, a single droplet became trapped at the point of focus. This was followed by a short period of droplet growth through multiple collisions that were observed with other droplets. These collisions did not result in ejection of the droplet from the trap. Droplet growth slowed as the droplet concentration diminished and the mist dissipated. The maximum diameter attained through collision was approximately 10 μm . Following growth, the droplet appeared to undergo a low frequency oscillation, whilst it gradually reduced in volume. This behaviour was noted in all aerosol trapping experiments and appears similar to that reported by Keifer *et al.*⁴⁾ where the droplet, at certain sizes, behaves as a resonator and absorbs laser energy, resulting in a localized increase in temperature. The droplet eventually stabilised to a fixed volume and could be held and manipulated for periods in excess of 30 minutes. Throughout this stable

period, droplet volume remained constant at the set laser ping power of 20 mW indicating that evaporation through normal laser heating was minimal.

To assess the robustness of the optical trapping, the chamber cover was removed and the droplet exposed to the open laboratory environment. This created a turbulent flow across the sample area, but even under these conditions, the droplet remained optically trapped. It was found that the final size of the trapped droplet was related to the position of the laser focal point above the cover slip. Smaller droplets were trapped close to the surface. Images of the droplets are displayed in Figure 2 and the variation in the droplet sizes at equilibrium is shown in Figure 3. This behaviour appears to be dependent on the relative position of the decane film surface and the focal point of the laser beam. Specifically, larger diameter droplets could not be trapped just above the decane film surface without undergoing coalescence with bulk decane.

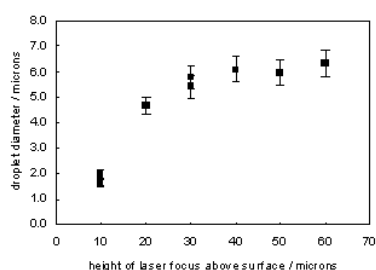


Figure 3. Plot of the diameter of the optically trapped aerosol droplets as a function of the height of laser focus above the cover slip.

The trapping efficiency was determined by gradually reducing laser power whilst holding a droplet of 5.9 μm (diameter). The minimum power just sufficient to retain the droplet was found to be 1.7 mW. The droplet did not change significantly in either size or focal position during the reduction of laser power. The axial trapping efficiency, Q , is ²⁾:-

$$Q = \frac{fc}{nP}$$

where f , c , n and P are the trapping force, velocity of light, refractive index of medium, and laser power, respectively. For levitation, the trapping force along the vertical axis is:-

$$f = mg = \frac{4}{3}\pi r^3 \rho g$$

where m , r , ρ and g are the droplet's mass, radius and density and the gravitational constant respectively. This results in the value of Q as 0.12. Although higher than that of conventional levitation traps, this is still less than that reported for trapped water droplets. A possible cause for this is that the design of the sample chamber is significantly different here and premature loss of the droplet could occur through increased air turbulence created by the open inlet aperture within the chamber.

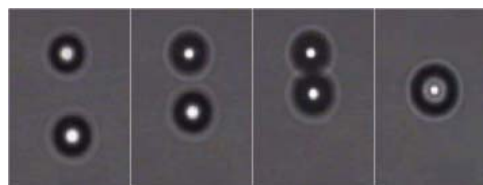


Figure 4. Image sequence showing the capture of two aerosol droplets that are then brought together until the droplets coalesce.

Two optical traps were simultaneously created using a pair of acousto-optic deflectors to multiplex a single laser beam. These traps could be independently steered and were used to capture, manipulate and control the approach of two droplets as shown in Figure 4. Coalescence was observed and recorded using video capture techniques. Image analysis of the resulting frames indicated that the total droplet volume remained constant during coalescence. The coalescence process was noted to occur over a timescale of less than one video frame (less than 40 milliseconds).

Conclusions

Within this research we have demonstrated a method for the robust optical trapping of single and multiple aerosol droplets from a nebulised mist of droplets, having sizes commensurate with respirable therapy applications. This has been achieved using a high numerical aperture microscope objective lens. We have shown that the trapped droplet sizes can be controlled by either adjustment of the depth of the laser focus in the sample chamber or by manipulation and coalescence of multiple droplets. The described methodology is anticipated to have application in the study of aerosol droplet stability and droplet interactions.

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The vibrational quenching of NO($v = 1-16$) by NO₂ and O₂

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Introduction

Nitric oxide is known to be a prominent infrared atmospheric emitter and knowledge of its vibrational energy transfer rates with atmospheric species is needed to gauge their effects on the conversion of measured emission rates to global NO concentrations. The vibrational quenching of NO($v = 1-16$) has been studied by Time-Resolved Fourier Transform Infrared (FTIR) emission spectroscopy. The 193 nm photolysis of NO₂ and N₂O has been employed to generate highly vibrationally excited NO which can then be quenched upon addition of a third body, M. Here we report measurements for M = O₂ and NO₂.

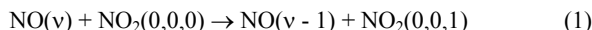
Experiment

Radiation at 193 nm from an ArF excimer laser (Lambda Physik Compex 205, 100 mJ pulse⁻¹, 20 Hz) was directed into a stainless-steel reaction vessel equipped with a multi-pass mirror system (11 passes of the UV photolysis beam) and Welsh collection optics. Emission was collected by a series of parabolic mirrors and focused in to an FTIR spectrometer (Bruker IFS/66), and detected with an InSb (Graseby IS2) detector, operating in the range 1–5.5 μ m. The optical path was purged with N₂ to reduce atmospheric absorption. The signal was amplified with 1 Hz – 1 MHz bandwidth before time-resolved digitization and the response time of the set-up is measured as 2 μ s. Data were taken in step-scan mode, with signals accumulated for a given number of shots (typically 20), before the interferometer mirror was moved a preset distance δ and the process repeated, generating a series of time traces as a function of mirror position. These traces are processed to yield interferograms and thus spectra as a function of time. The values of δ and the total mirror movement determine the frequency range (Nyquist criterion) and resolution of the instrument.

NO₂ (BOC>99.5%) was purified by reaction with O₂ in excess of the NO impurity level, with O₂ removed by freeze-thaw cycling. N₂O (BOC>99.997%), Ar (BOC>99.999%), O₂ (BOC>99.5%) and N₂ (BOC>99.998%) were used without further purification. Measured flows of gases were introduced in to the reaction vessel, with partial pressures calculated from flow rates and total pressure measurement. Measurements were carried out at room temperature, 295 K.

(1) The vibrational quenching of NO($v = 1-16$) by NO₂

The 193 nm photolysis of NO₂ yields vibrationally excited NO($v = 1-16$) and O(¹D)/O(³P). The O(¹D) quantum yield has been measured to be $\Phi = 0.55^{(1)}$ and the nascent vibrational distribution of NO is bimodal, with maxima at $v = 5$ and $v = 14^{(2)}$. We have previously used the photolysis of NO₂ at longer wavelengths (308 nm and 248 nm) to observe relaxation of NO($v = 1-3$)⁽³⁾ and NO($v = 5-8$)⁽⁴⁾ by NO₂. The energy exchange process (1) was found to occur with less than unit efficiency for $v = 1-3$, but was believed to have increasing importance for $v \geq 5$.



Here we extend our observations to the higher vibrational levels ($v \leq 16$) observed through fundamental emission between 1800 – 2000 cm⁻¹ ($v = 1-4$, dictated by the sharp cut-off of the InSb detector at 1750 cm⁻¹) and overtone emission between 2900 – 3900 cm⁻¹ ($v = 2-16$). Fundamental and overtone data

sets at pressures ranging from 50 – 200 mTorr NO₂ in 150 Torr Ar were analysed to yield populations as a function of time at 1 μ s intervals. From the overtone bands, time-dependent populations were extracted for $v = 3-16$, discarding the data for $v = 2$ because of its low Einstein A-factor ($< 1 \text{ s}^{-1}$). Low vibrational levels were analysed through the fundamental emission bands between 1800 – 1970 cm⁻¹. Although this meant that emission from $v > 4$ was cut off by the detector, it resulted in accurate, relative analysis of these low vibrational levels and allowed a complete picture to be formed of the vibrational levels and subsequent quenching by NO₂.

The time-dependence of the levels clearly shows the data is consistent with a single-quantum cascade mechanism as the populations peak at successively longer times for lower v . Rates were found to increase linearly with NO₂ pressure, and rate constants shown in Table 1 and Figure 1 clearly indicate a maximum value attained near $v = 11$ where the energy discrepancy ΔE in process (1) is minimised. The data are also plotted in Figure 2 as reduced probabilities P/v , where P is the probability of a gas kinetic collision between NO(v) and NO₂ leading to single quantum loss in NO, as a function of ΔE . Where applicable an exothermic correction has been made. The reduced probability allows for a harmonic oscillator increase in transition moment of NO with v and thus allows the effect of simply the energy mismatch to be seen.

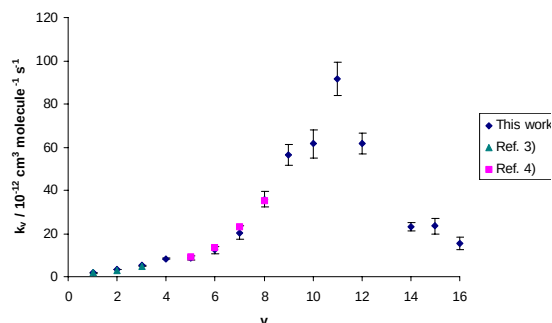


Figure 1. Rate constants, k_v , for the quenching of NO(v) by NO₂, clearly showing a resonant process for process (1).

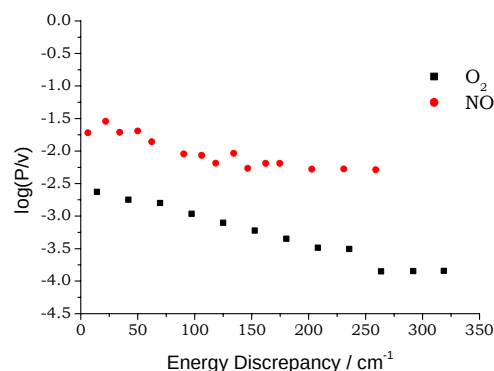


Figure 2. Reduced probabilities for the quenching of NO(v) by O₂ (black squares) and NO₂ (red circles).

ν	This work	Ref. 3)	Ref. 4)	$\Delta E / \text{cm}^{-1}$
1	1.7±0.1	1.9±0.2	-	-258
2	3.4±0.2	2.9±0.3	-	-230
3	5.1±0.2	4.8±0.7	-	-202
4	8.3±0.3	-	-	-174
5	8.7±0.8	-	9.1±0.8	-145
6	12.5±1.7	-	13.6±0.9	-117
7	20.4±3.2	-	23±2.3	-89
8	35.8±3.6	-	35±3.8	-61
9	56.4±4.9	-	-	-34
10	61.6±6.5	-	-	-6
11	91.6±7.8	-	-	22
12	61.9±4.8	-	-	50
13	-	-	-	78
14	23.2±1.9	-	-	106
15	23.4±3.8	-	-	134
16	15.3±2.8	-	-	162

Table 1. Rates constants $k / 10^{-12} \text{ cm}^3 \text{ molecule}^{-1}$ for the quenching of $\text{NO}(\nu)$ by NO_2 and those of Bohn *et al.*³⁾ and Morrell *et al.*⁴⁾. Errors shown as $\pm 1\sigma$.

ν	This work	Ref. 6)	Ref. 3)
1	3.4±0.9	2.7	3.6
2	6.8±0.9	6.7	5.3
3	10.1±2	13.5	12
4	30±2	27	-
5	39±2	51	-
6	64±5	64	-
7	100±11	97	-
8	151±13	-	-
9	233±14	-	-
10	380±34	-	-
11	468±47	-	-
12	675±100	-	-

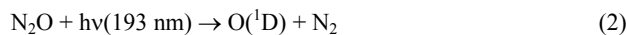
Table 2. Rates constants $k / 10^{-12} \text{ cm}^3 \text{ molecule}^{-1}$ for the quenching of $\text{NO}(\nu)$ by O_2 and those of Green *et al.*⁶⁾ and Bohn *et al.*³⁾. Errors shown as $\pm 1\sigma$.

From the plot of energy discrepancy vs. reduced probability it can be seen that there are two energy-transfer regimes. Firstly, where the energy discrepancy is less than 150 cm^{-1} , it is apparent that there is a linear decrease in reduced probability with increasing energy discrepancy, as would be expected from process (1). The slope of this region is very similar to the plot suggested by Callear⁵⁾ which represents an empirical relationship correlating the early results on V-V exchange between non-hydride diatomic molecules with vibrational frequencies close to 2000 cm^{-1} . It should also be noted, however, that Callear's plot is somewhat lower in magnitude than the data presented here, suggesting the influence of chemical interaction in the $\text{NO}(\nu)/\text{NO}_2$ system, and hence higher rates of quenching, rather than a pure V-V exchange process. The second regime occurs where $\Delta E > 150 \text{ cm}^{-1}$. In this region (principally the quenching of $\text{NO}(\nu = 1 - 4)$) the slope flattens out so that there is a negligible variation in P/ν with ΔE , and the reason for this might be that V-V energy transfer being dominated by chemical interaction.

(2) The vibrational quenching of $\text{NO}(\nu = 1-12)$ by O_2

In order to study the vibrational quenching of NO by O_2 , the 193 nm photolysis of N_2O was employed. This was preferable to NO_2 photolysis as the relaxation of NO by NO_2 is fast. N_2O , on the other hand, quenches NO at rates which are two orders of magnitude lower and is therefore more suitable for these kinds of studies.

Photolysis of N_2O at 193 nm produces $\text{O}(^1\text{D})$ with a quantum yield of unity. $\text{O}(^1\text{D})$ then reacts with N_2O , where $k_3 + k_4 = 1.17 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$:



The branching ratio for channel (3) is 0.61. Vibrationally excited NO is produced up to $\nu = 16$ with a nascent distribution that decreases monotonically with ν . The vibrational relaxation of $\text{NO}(\nu = 1-7)$ has been studied by Green *et al.*⁶⁾ who found that the quenching occurred via single quantum transitions with strong V-V transfer to O_2 . These rates were later studied and confirmed by Bohn *et al.*³⁾ in the region $\nu = 1-3$.

In this work the data set has been increased up to $\nu = 12$. Data were taken with a constant pressure of N_2O (1 Torr) and the pressure of O_2 varied from 0.2 – 3 Torr. NO fundamental and first overtone bands were observed in the same manner as for NO_2 photolysis and data were extracted in a similar fashion. The kinetic scheme incorporated the known rates of quenching by N_2O . Again, the time-dependence of the levels clearly shows the data is consistent with a single-quantum cascade mechanism. Rates increased linearly with O_2 pressure and the rate constants for $\nu = 1-12$ are displayed in Table 2. Clear agreement has been found between our work and that of Green *et al.*⁶⁾ and Bohn *et al.*³⁾ for $\nu = 1-7$ and the rates for $\nu > 7$ clearly show a continuing increase in rate expected of V-V transfer with O_2 . For $\text{NO}(\nu = 1)$ the energy discrepancy between donor and acceptor is 320 cm^{-1} whereas for $\text{NO}(\nu = 12)$ it is reduced to 11 cm^{-1} . This approach to resonance is reflected in the rates measured; that is, as the energy discrepancy decreases with increasing ν , the rate of vibrational quenching increases. These rates are again plotted as reduced probabilities, $\log(P/\nu)$ in Figure 2, where it can be seen that they are an order of magnitude lower than those of energy transfer to NO_2 , indicating that complex formation is a minor factor in the $\text{NO}-\text{O}_2$ system. A slope of similar value and position to that of Callear is noted, indicating dominant V-V transfer.

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Photoluminescence of $\text{Y}_2\text{O}_3\text{:REE}$ phosphors under 257 nm excitation

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Introduction

The present investigations into the visible emissions of rare earth doped Y_2O_3 phosphors under ultraviolet (257 nm) excitation were undertaken in order to examine the mechanisms of their emission processes. This makes possible a comparison with the corresponding emissions that are observed under 244 nm excitation, as well as with upconversion visible emissions that are obtained from these phosphors when they are excited with red light of wavelength equal to 632.8 nm¹⁻⁵). The motivation for these studies is to develop new, improved photoluminescent phosphors for lighting applications that can be excited in the ultraviolet region. The current studies use an excitation wavelength of 257 nm as this comes in the same region as the mercury emission line at 253.7 nm that is commonly used to excite phosphors in fluorescent lights. Our ultimate aim is to obtain quantum cutting in oxide lattices which are doped with two different rare earth ions, whereby more than one visible photon is emitted for each ultraviolet photon that is absorbed.

Experimental

The urea homogeneous precipitation method was used to prepare spherical $\text{Y}_2\text{O}_3\text{:REE}$ hydroxycarbonate sub-micrometre phosphor precursor powders. Following the addition of urea the mixture was heated to boiling and this was maintained for two hours after precipitation had begun. These powders were then fired at 980°C for 6 hrs to convert to the oxides¹⁻⁵). Vanadate samples were prepared by both precipitation and combustion methods. For the precipitation method aqueous nitrates of yttrium and dopants were added to aqueous ammonium metavanadate and EDTA. A literature method was followed for the combustion method⁶).

The resultant phosphors were excited with 257 nm laser light provided by an intracavity frequency-doubled argon ion laser (Coherent Ltd.) which is a loan pool laser (CWL3) from the Central Laser Facility. Emission spectra were collected with a Spex 1877 Triplemate Raman spectrometer equipped with a Peltier-cooled open electrode CCD detector (Wright instruments).

Results and Discussion

Visible emissions were obtained from $\text{Y}_2\text{O}_3\text{:M}^{3+}$ phosphors (where $\text{M}^{3+} = \text{Pr}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Er}^{3+}$ and Ho^{3+}) under 257 nm excitation, as can be seen from Figure 1, with particularly strong red emission being observed from $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ under 257 nm excitation. This result was expected as $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ is a red photoluminescent phosphor that is used in fluorescent light tubes, the phosphors being excited by the light emission from mercury vapour.

The visible emission spectra of the $\text{Y}_2\text{O}_3\text{:REE}$ phosphors are very similar under 244 and 257 nm excitation, as can be seen for $\text{Y}_2\text{O}_3\text{:Tb}^{3+}$ in Figure 2a and 2b, respectively. A notable difference in behaviour was observed for $\text{Y}_2\text{O}_3\text{:Er}^{3+}$ under excitation at wavelengths of 244 and 257 nm, however. In the former case the spectrum was too weak to be observed, whereas in the latter case an intense spectrum was obtained (see Figure 1).

The spectrum of $\text{Y}_2\text{O}_3\text{:Er}^{3+}$ under 257 nm excitation exhibited emissions in the green region over the ranges 520-540 (${}^2\text{H}_{11/2} - {}^4\text{I}_{15/2}$ hot band) and 540-565 nm (${}^4\text{S}_{3/2} - {}^4\text{I}_{15/2}$), and in the blue region over the ranges 400-420 (${}^2\text{H}_{9/2} - {}^4\text{I}_{15/2}$) and 465-480 nm (${}^4\text{F}_{5/2} - {}^4\text{I}_{15/2}$). In addition weak emission features occur in the red region over the ranges

605-635 (${}^4\text{F}_{5/2} - {}^4\text{I}_{13/2}$) and 645-690 nm (${}^4\text{F}_{9/2} - {}^4\text{I}_{15/2}$). This last feature is much weaker than in complementary upconversion luminescence studies using 632.8 nm excitation^{1,2}), where the ${}^4\text{F}_{9/2}$ level is more readily populated following absorption of the incident radiation.

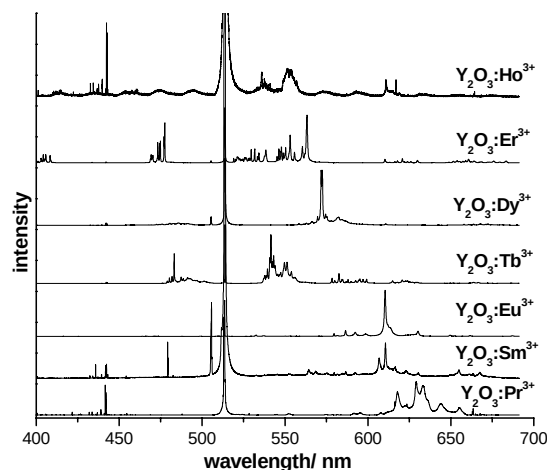


Figure 1. Visible emission spectra obtained from $\text{Y}_2\text{O}_3\text{:M}^{3+}$ ($\text{M}^{3+} = \text{Pr}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Er}^{3+}, \text{Ho}^{3+}$) phosphors under 257 nm excitation. The line at 514 nm is due to the 257 nm laser line in second order.

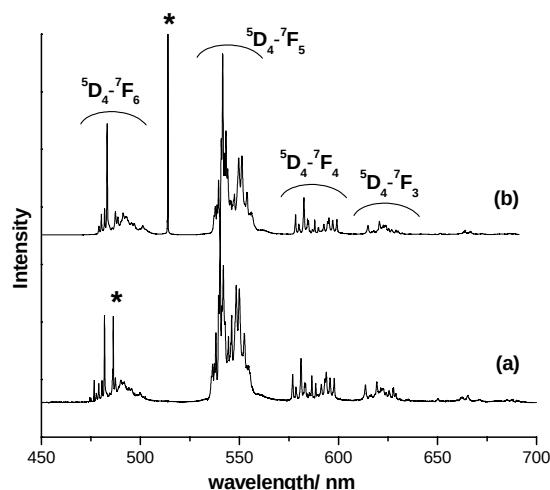


Figure 2. Visible emission spectra obtained from $\text{Y}_2\text{O}_3\text{:Tb}^{3+}$ phosphor under (a) 244 nm and (b) 257 nm excitation. The asterisks denote the lines at 488 and 514 nm due to the laser line in second order in (a) and (b), respectively.

Figure 3 shows a comparison of the emission spectra obtained from $\text{Y}_2\text{O}_3\text{:Er}^{3+}$ and $\text{YVO}_4\text{:Er}^{3+}$ phosphors under 257 nm excitation, which demonstrates the effect that the host lattice can have on the emissions of rare earth cations. In the case of the cubic Y_2O_3 lattice, the rare earth cations can occupy either C_2 or S_6 sites which are present in a ratio of 3:1⁷). The f-f transitions are only electric dipole allowed when the cations occupy the former sites, however, because these are non-centrosymmetric. For the $\text{YVO}_4\text{:Er}$ phosphor, the rare earth

cations replace the yttrium ions and thus occupy sites of D_{2d} symmetry in the tetragonal YVO_4 lattice⁸⁾. The striking contrast in the emission spectra shown in Figure 3 is due to the influence of the site group symmetry (which partially removes the degeneracies of the LSJ states) in addition to the different extents of electron-phonon coupling in the two lattices. As can be seen from Figure 3, the emission spectrum of $YVO_4:Er$ is dominated by the strong green emissions due to the $^4S_{3/2} - ^4I_{15/2}$ and the hypersensitive $^2H_{11/2} - ^4I_{15/2}$ transitions. It is noteworthy that the emission due to the latter transition is comparable in intensity to that of the former transition in the case of the YVO_4 host lattice, but considerably weaker in intensity in the case of the cubic Y_2O_3 lattice. Another striking difference between the emission spectra shown in Figure 3 is that the blue and red emissions originating from the Er^{3+} activator ions are much stronger in the cubic Y_2O_3 host lattice than in YVO_4 .

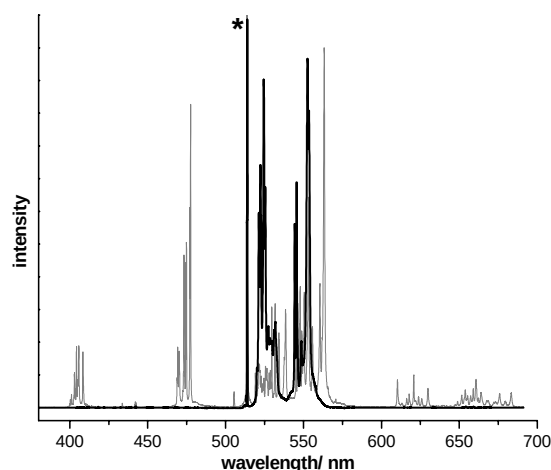


Figure 3. Visible emission spectra obtained from $Y_2O_3:Er^{3+}$ (grey trace) and $YVO_4:Er$ (black trace) phosphors under 257 nm excitation. The asterisk denotes the line at 514 nm due to the laser line in second order.

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Unraveling the mechanism of 4-aminoquinoline antimalarial action

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Introduction

Invasion of host erythrocytes by *Plasmodia* during a malarial infection allows deconstruction of haemoglobin within acidic vacuolar compartments, providing a vital nutrient source for parasite replication. Successive release of four, redox active, toxic porphyrins per molecule of haemoglobin prompts a biomineralization process producing an inert, redox inactive malarial pigment (haemozoin)¹. Host defense mechanisms tightly regulate concentrations of toxic free haemin (heme) using a high affinity ($K_d < 1$ pM) plasma protein scavenger, hemopexin. Current evidence suggests that certain 4-aminoquinoline compounds, especially amodiaquine and chloroquine, inhibit biomineralization allowing translocation of complexed haemin to loci sensitive to oxidative stress^{2, 3}. Knowledge of both binding geometry and stoichiometry within putative antimalarial drug-receptor complexes may allow: i) a deeper understanding of the mechanism of *mono*- and *bis*-4-aminoquinoline antimalarial action, and ii) facilitate design of compounds superior to chloroquine. Previous investigations have allowed definition of a functional antimalarial receptor *in vivo* that has been used to design a highly active, orally bioavailable aryl bridged bisquinoline antimalarial called metaquine⁴. Since related cycloalkyl bridged compounds e.g. Ro 47-7737 demonstrate phototoxicity in animal models⁵, the potential for incurring phototoxicity within the metaquine class of compound requires investigation before further development.

Depiction of parallel π - π interaction between the quinoline and the porphyrin is persistently favoured in antimalarial modeling studies⁶ despite overwhelming evidence from geometrical investigations that confirm such face to face π - π alignments, where the ring plane area overlaps, is a rare phenomenon⁷. The most common geometry is an offset, or slipped interaction (i.e. parallel displaced) revealing important contribution from π - σ contacts⁷. Three possible binding geometries involving monomeric haem and 4-aminoquinolines merit further investigation namely π - π alignments, parallel displaced and an exogenous axial ligand binding mode involving a Fe-N bond. However, the presence of a (+ π , + σ) substituent e.g. chlorine, essential for high antimalarial activity, prevents binding to flat porphyrins.

This study consists of a combination of structural, computational and spectroscopic approaches to explore the putative mechanism(s) of action of 4-aminoquinoline antimalarials by defining their geometrical interaction(s) between drug and receptor.

Methods

Modelling calculations were performed using Molecular Mechanics (Cerius2). A 440nm pulsed dye laser was used to investigate singlet oxygen generating capacity of putative drug candidates. An argon-ion laser with 457.9 and 514.5 nm output was employed for resonance Raman (RR) experiments⁸. Metaquine was synthesised according to reported methods⁴.

1:1 complexes were generated by mechanical grinding in the solid state between haemin chloride and corresponding antimalarial salt.

Results and Discussion

Conversion of an established binding assay⁹ to a high throughput mode, confirms that a 1:1 haem: drug binding interaction persists in aqueous HEPES buffered DMSO (23° C pH 7.4: Log K chloroquine: 5.5; Amodiaquine 5.4; Metaquine 6.1 [pH 5.6: log K = 5.7, 23° C, MES).

Resonance Raman (RR) spectra between various drugs, including 4-aminoquinolines and their putative receptor, haemin, were recorded (using 457.9 and 514.5 nm outputs of the argon-ion laser) by probing into the absorption bands of the quinoline ring that interacts with the haem receptor. RR spectra of the hydroxyl and drug coordinated haemin (in SDS and wet DMSO) display the typical spectroscopic marker bands of a pentacoordinate high-spin ferric iron derivative¹⁰. RR spectra of metaquine and quinoline were obtained. Interaction of metaquine and haem in DMSO provided RR spectra were similar in terms of the peak frequencies of different marker bands. Only small shifts (within 2 cm⁻¹) are observed for the iron core size marker band (ν_4) as well as for other bands in the 1400-1600 cm⁻¹ region. In conditions favouring μ -oxo dimer formation, a moderate (2-3 cm⁻¹) frequency shift was observed for the vinyl-stretching band ($\nu_{C=C}$) at 1624 cm⁻¹ for the alkaline haemin with respect to 1629 cm⁻¹ for metaquine and amodiaquine-complexed haemin (See close contact G in Figure 2). In pure DMSO, molecular ions for such complexes were not detected in our high resolution (accurate) electrospray mass spectrometry (HRESMS) studies suggestive of weak complex formation.

RR experiments reveal, in the absence of water, such interactions between the 4-aminoquinolines and haemin (or haemin chloride) are extremely weak. HRESMS confirm that haemin chloride forms a 1:1 complex with various 4-aminoquinolines (including chloroquine and amodiaquine) and bisquinolines (e.g. Ro 47-7737 and metaquine) in protic solvents such as methanol, but not in DMSO¹¹. RR experiments with haemin (buffered SDS pH 4.7 - pH 14) and various antimalarials showed little evidence of covalent Fe-N bond formation (expected: 215-222 cm⁻¹)¹⁰, suggesting that axial coordination of haemin by 4-aminoquinolines does not displace an axially coordinated hydroxyl group, a result consistent with modeling studies. Artemisinin, which also acts at haeme, generated an unstable radical cation complex which was detected in HRESMS and RR experiments in which solutions were flowed past the light source, a result that requires further TR³ investigations.

Docking calculations between haemin and chloroquine (or metaquine) generate complexes of lowest energy favoring an out of plane displacement along the lowest frequency coordinate of the porphyrin¹² that predominate over parallel π - π motifs. Furthermore, a 'normal coordinate analysis'¹³

suggests that such deformations are a generalized phenomenon in porphyrins and haem proteins. Modeling investigations (Figures 1 and 2) reveal a linear correlation between the total energy (of the monomeric complexes) and the sum of the Van der Waals and electrostatic energy terms (c.f. ⁶⁾ and note)

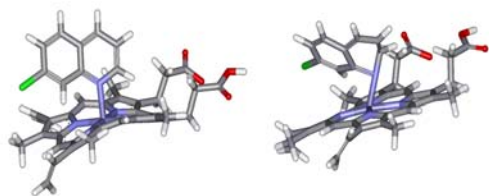


Figure 1. Highest energy conformation of 7-chloroquinoline bound to 7-chloroquinoline (restrained torsion angle = -40°) and the lowest energy conformation (restrained torsion angle = -140°). Drug complexation induced similar changes to ligand induced heme ruffling ¹⁴⁾.

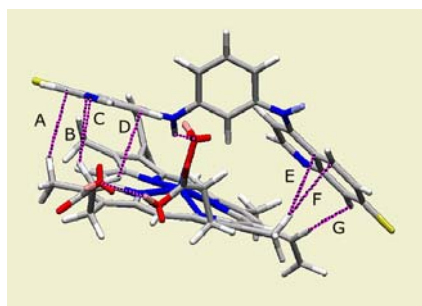


Figure 2. Lowest energy docking interaction showing close contacts. Incorporation of suitable bioisosteres at E, F and G could be used to modulate antimalarial activity.

In contrast, experiments in the solid state suggest that reactions between 4-aminoquinoline and hemin chloride form stable 1:1 complexes, which persist in methanol, whose strong molecular ions in HRESMS experiments suggest axial ligation.

The structure of the reciprocal dimer subunit present in haemozoin, characterized using synchrotron studies ¹⁾, has been detected in our HRESMS studies. Importantly, the currently favored ether bridged μ -oxo dimer was not found either in Raman investigations (at pH 4.7) nor in corresponding HRESMS experiments and may be a desalting artifact or a complex formed at basic pH during preparation of solutions ¹²⁾. Binding to the reciprocal dimer involves weak π - π stacking interactions ($\sim 2 \text{ kJ mol}^{-1}$) ⁷⁾ and displays correspondingly weak mass ions and, as this study shows, is unlikely to represent the currently favored haemin: 4-aminoquinoline binding geometry. Recent NMR investigations involving chloroquine-ferriprotoporphyrin IX complex in the solid state also support our conclusion that orthogonal binding to haemin is possible through the formation of a Fe-N bond. If indeed this is the case, than axial binding by chloroquine and related compounds is only possible with non-planar haemin ¹³⁾, because unfavorable contacts between the essential 7-halogen would prevent this type of complex formation. Monomeric haemin demonstrates antimalarial ²⁾ and immunological effects whereas haemozoin is pharmacologically inert (Dascombe *et al.* unpublished) providing additional support for the success of this *Plasmodium* detoxification mechanism. Experiments involving quantum mechanical calculations and crystallography are in progress to identify and quantify the binding interaction between various

4-aminoquinolines and porphyrins as well as investigating the spectroscopic properties of such adducts in the solid phase.

Photochemical Investigations

In this study we also evaluated the capacity for singlet oxygen ($^1\text{O}_2$) generation from known antimalarials such as quinine, amodiaquine, chloroquine and mefloquine in SDS micelles. As expected, quinine readily generated $^1\text{O}_2$, with amodiaquine and chloroquine less so. Gratifyingly, preliminary investigations confirm that mefloquine does not generate $^1\text{O}_2$. The recent introduction of a combined dosage form of artemisinin with a bisquinoline (Artekin) suggests that bisquinolines may be useful for treating multi-drug resistant malarias.

Conclusion

A combination of *in silico*, spectroscopic and spectrometric experiments suggest that docking motifs other than cofacial π - π interaction between the quinoline and the porphyrin could explain antimalarial drug action. Modeling investigations reveal close contacts between the porphyrin ring and selected atoms within the compounds such as mefloquine, which upon modification could be used to modulate antimalarial activity and further clarify the mechanism of antimalarial activity.

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Nanosecond temperature-jump studies of azo dye dimerisation kinetics

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Introduction

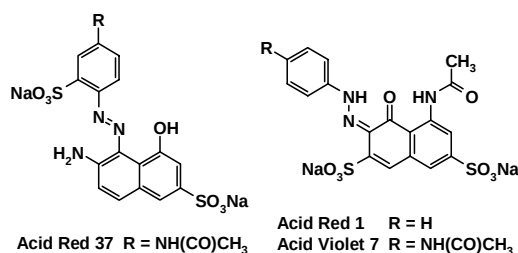
Azo dyes are the dominant class of commercial dyes, and the emergence of new technologies has stimulated a renewed interest in their chemistry. Interest now extends from the more traditional fields of textile dyeing and effluent degradation to areas as diverse as optical data storage, ink-jet printing, biochemical assays, and potential pharmaceutical treatments.

One important area of study is that of intermolecular interactions. This includes the dipole-dipole, hydrogen-bonding, and other interactions between dye molecules and molecular surfaces which are important in their applications,¹⁾ such as those provided by cellulose, synthetic polymers, and proteins. It also includes the π -stacking interactions between identical dye molecules that result in the dimers or higher aggregates which many azo dyes form at high concentrations in aqueous solution.^{2,3)} In some situations, these two types of intermolecular interaction are competitive, with the stronger interaction governing the resultant properties of the dye.

The aggregation of azo dyes in aqueous solution has received significant attention. Several techniques have been applied, including UV-visible and NMR spectroscopy, and they have shown that the nature and strength of aggregation is strongly dependent on the structure of the dye. The thermodynamics have been studied in many cases,³⁾ and dimerisation constants (K_{dim}) have been measured; in general, it has been shown that the process can be either enthalpy- or entropy-driven, and that it is promoted at high ionic strength. By contrast, the kinetics of dimerisation are surprisingly unreported,³⁾ apart from one study of a large bis-azo dye (Congo Red) reported in 1972.⁴⁾

The revitalised interest in azo dyes includes a need to understand their aggregation kinetics because they have a direct impact on some of their new applications. For example, ink-jet printing involves the rapid deposition of a concentrated dye solution onto a molecular surface: the rapid development of the competitive intermolecular interactions, under initial conditions which may be far from equilibrium, can determine the overall properties and long-term stability of the dye.

We have been studying the dimerisation of several 1- and 2-aryazonaphthol dyes. A combination of UV-visible, resonance Raman, and 1D- and 2D-NMR techniques has been used to study the internal structure and bonding within the dye, as well as the sites and geometries of dye-dye interactions. UV-visible spectroscopy has been used to determine dimerisation constants, and changes in free energy, enthalpy, and entropy. Here, we have studied the dimerisation kinetics of three typical azo dyes which have significantly different dimerisation constants: Acid Red 37, Acid Red 1, and Acid Violet 7 (below).



The principle of the nanosecond T-jump experiment is that a near-IR laser pulse is absorbed by the aqueous solvent and induces a temperature jump on a time scale of ca. 10 ns. The kinetics of the sample relaxing to the new equilibrium at the higher temperature are measured using UV-visible absorption. Measurements across a range of concentrations enable the forward and reverse rate constants to be determined.

Experimental

The output from a Q-switched Nd:YAG laser was Raman shifted in H₂ to provide near-IR pulses to induce the T-jump (1.9 μm , 7 ns, 10 Hz, 22 mJ at the sample). A cw diode laser provided the probe beam (532 nm, ≤ 0.2 mW at the sample). The pump and probe beams were counter-propagated through the sample, with diameters of ca. 1 and 0.1 mm, respectively.

Solutions of the purified dyes were prepared in D₂O at concentrations in the range of ca. $(0.5\text{--}5.0) \times 10^{-3}$ mol dm⁻³, and at a fixed ionic strength of 0.03 (adding NaCl). The solutions were flowed through a demountable cell with CaF₂ windows and a pathlength of 100 μm . The reservoir was cooled to maintain a sample temperature of 282 K, at the cell, at which (dP/dT) is minimised for D₂O. This greatly reduced but did not entirely eliminate the well-defined and reproducible shock waves which dominated at higher temperatures, and which are a well-known and well-analysed difficulty with this technique.⁵⁾

The data were collected as kinetic traces at 532 nm, averaged over 8192 shots. Kinetic traces were also collected from D₂O alone, and scaled subtractions from the sample traces were used to remove the shock waves. The data were then converted to $\Delta\text{Absorbance}$ ($\Delta A = \log_{10}[I_0/I_t]$) for analysis.

A temperature jump of 14 K in these experiments was estimated by two independent methods: by using the experimental parameters for the laser, solvent, and cell,⁶⁾ and by comparing the T-jump ΔA signals with those from steady-state UV-visible spectra measured across a range of temperatures as part of our thermodynamic studies. The ΔA signals were measured to decay on a time scale of >1 ms, due to cooling, which was much longer than the time scale of ≤ 10 μs on which the monomer-dimer equilibria were measured to relax.

Results and Discussion

The steady-state UV-visible spectra recorded at different temperatures define the changes that occur in the T-jump experiment, as shown in Figure 1 for Acid Red 37.

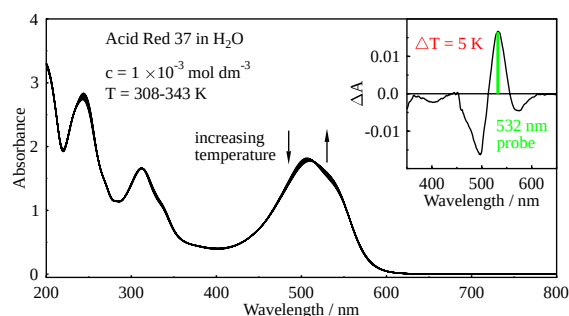


Figure 1. Steady-state UV-visible spectra of Acid Red 37.

Similar spectra to those in Figure 1 were obtained for the other two dyes. Along with concentration-dependent spectra, they have enabled us to determine thermodynamic parameters and the monomer and dimer spectra. For the present study, they show (inset) that the dimerisation kinetics can be probed readily at the convenient wavelength of 532 nm because there is a large increase in absorbance at this wavelength on going from the dimer to the monomer, as induced by a temperature increase.

The T-jump kinetics of all three dyes were measured successfully at 532 nm, as shown by the sample trace from Acid Red 1 in Figure 2. The data were fitted well by a single exponential rise to a fixed offset, as also illustrated in Figure 2, providing an observed rate constant, k_{obs} . Similar traces were obtained across a range of concentrations for each of the dyes (ca. $0.5\text{--}5.0 \times 10^{-3} \text{ mol dm}^{-3}$; limited to a relatively narrow range by constraints in observable absorbances for a fixed pathlength cell), and the observed rate constants were found to increase with concentration. Although the specific rate constants were different for different dyes, and for different concentrations, the relaxation times were generally on the order of ca. $0.5\text{--}5 \mu\text{s}$ under the conditions studied.

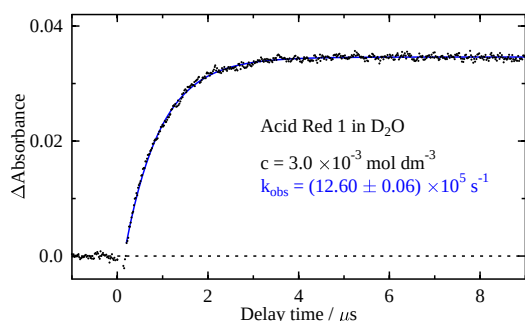
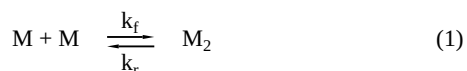


Figure 2. Sample T-jump kinetics from Acid Red 1.

The analysis for a monomer-dimer equilibrium is given by Equations (1-3).^{4,7)}



$$K_{\text{dim}} = k_f / k_r \quad (2)$$

$$k_{\text{obs}}^2 = 8K_{\text{dim}}k_r^2c + k_r^2 \quad (3)$$

The observed rate constants were fitted to Equation (3), using the appropriate K_{dim} values at 296 K (the temperature after the T-jump) obtained from steady-state experiments across a wide range of concentrations for each of the dyes (ca. $10^{-6}\text{--}10^{-2} \text{ mol dm}^{-3}$). The fit for Acid Red 1 is shown in Figure 3, giving the reverse rate constant from the fit to Equation (3) and then the forward rate constant from Equation (2). Similar fits were obtained for the other dyes, and the results are given in Table 1.

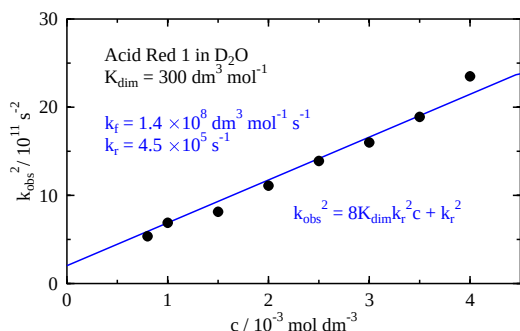


Figure 3. Rate constant analysis for Acid Red 1 at 296 K.

Dye	k_f	k_r	K_{dim}
Acid Red 37	2.2×10^8	8.8×10^4	2500
Acid Red 1	1.4×10^8	45.0×10^4	300
Acid Violet 7	2.7×10^8	3.4×10^4	7800

k_f in $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$; k_r in s^{-1} ; K_{dim} (296 K) in $\text{dm}^3 \text{mol}^{-1}$

Table 1. Rate constants and dimerisation constants at 296 K.

The values in Table 1 show that the rate constant for dimer formation (k_f) is similar for all three dyes, whereas the rate constant for the reverse reaction (k_r) varies significantly between the dyes. This indicates that k_r is the parameter which controls the variation in the dimerisation constant between these dyes, as given by Equation (2). This general trend has been reported for other types of dye,³⁾ and the present data indicate that it is likely to apply to azo dyes. Importantly, for the design of new azo dyes, it indicates that controlling the structural factors which determine the magnitude of k_r is likely to be the key to controlling the magnitude of K_{dim} , and hence the tendency of the dyes to dimerise.

Conclusions

We have demonstrated that the T-jump technique can be applied successfully to study the dimerisation kinetics of azo dyes in aqueous solution. The three dyes studied here gave relaxation times on the order of ca. $0.1\text{--}10 \mu\text{s}$, demonstrating that nanosecond time resolution is required under the conditions necessary for such studies. The concentration dependence of the relaxation times enabled the forward and reverse rate constants in the dimerisation equilibrium to be determined. This analysis indicates that the reverse rate constant varies significantly between the dyes and, therefore, controls the magnitude of the dimerisation constant. The dyes studied here have dimerisation constants which are on the same order as those of many small azo dyes, and therefore many azo dyes are likely to show kinetic behaviour which is broadly similar to that reported here.

In a more general context, this study has defined a time scale of $\leq 10 \mu\text{s}$ for the relaxation of monomer-dimer equilibria of azo dyes under conditions which are relevant to their commercial applications.

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Picosecond time-resolved infrared studies of light-controlled ion switches

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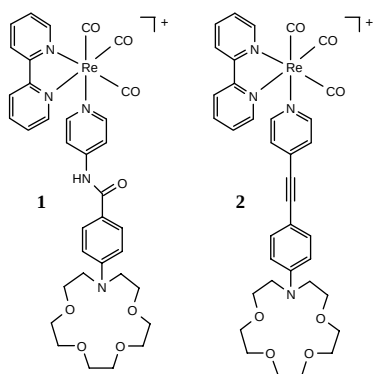
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Introduction

The development of light-controlled ion switches is of interest because of potential applications that range from optical computing to mimicking ion-signalling systems in nature, such as the Ca^{2+} signalling that regulates many activities. Our recent work has centred on $[(\text{bpy})\text{Re}^{\text{I}}(\text{CO})_3(\text{L})]^+$ complexes where L is a functionalised pyridine ligand with a pendant azacrown ether; the azacrown binds a metal cation from solution, and photon absorption by the chromophore changes the charge distribution to lower the binding constant and induce ion release. We have been studying one set of systems that give short ion pulses due to changes only in electronic state, with excited-state release being followed by ground-state recapture, and another set which can give sustained ion release due to photoisomerisation. Two systems which give pulsed ion-switching are the amide-linked complex **1**,¹⁻³⁾ and the alkyne-linked complex **2**.^{4,5)} :-



We have studied **1** and **2** extensively with a variety of steady-state techniques,⁵⁾ with nanosecond time-resolved UV-visible absorption, emission,^{3,4)} and resonance Raman spectroscopy,⁶⁾ and with picosecond time-resolved UV-visible absorption and emission spectroscopy.²⁾ These earlier studies have enabled us to demonstrate that reversible ion-switching occurs. They have also enabled us to develop a detailed understanding of many aspects of the two different mechanisms that operate for these two complexes, including kinetic information across all time scales, and structural information on the excited states and intermediates present at >10 ns obtained from time-resolved resonance Raman spectroscopy. In the present study, we have used picosecond time-resolved infrared (TRIR) spectroscopy to obtain structural information on the excited states present at <10 ns: these studies are important because it is the charge distribution in these states which drives the effect of ion release.

Amide-linked complex

It has been established that the photochemical mechanism of **1** involves a $\text{Re} \rightarrow \text{bpy}$ metal-to-ligand charge-transfer (MLCT) state, $[(\text{bpy}^{\bullet-})\text{Re}^{\text{II}}(\text{CO})_3(\text{L})]^+$, and a ligand-to-ligand charge-transfer (LLCT) state, $[(\text{bpy}^{\bullet-})\text{Re}^{\text{I}}(\text{CO})_3(\text{L}^{\bullet+})]^+$.^{1,2)} The MLCT state is formed on excitation, the LLCT state then forms by $\text{L} \rightarrow \text{Re}$ electron transfer on a time scale of 500 ps, and it decays to the ground state in ca. 19 ns.²⁾ The photochemical mechanism for several systems in which a metal cation is bound to the azacrown, $\mathbf{1-M}^{n+}$, has been proposed to involve ion release in the MLCT state, with subsequent formation of the LLCT state providing a barrier to geminate rebinding.³⁾ The aim of this

TRIR study was to substantiate this proposed mechanism, through the observation of unambiguous $\nu(\text{CO})$ marker bands for these states, and to study their structure, bonding, and charge distribution via the positions of both $\nu(\text{CO})$ bands and L-ligand bands in the fingerprint region.

Steady-state and TRIR spectra of **1** without a metal cation bound to the azacrown are shown in Figure 1. The up-shifted $\nu(\text{CO})$ bands at short delay times are unambiguous markers for the MLCT state, due to a Re^{II} centre which has lower electron density than the Re^{I} centre in the ground state. The down-shifted $\nu(\text{CO})$ bands which form in ca. 500 ps, as the MLCT bands decay, are unambiguous markers for the LLCT state: they report that the electron density at the Re^{I} centre is higher than that in the ground state, due to the presence of the reduced $\text{bpy}^{\bullet-}$ ligand in the LLCT state.

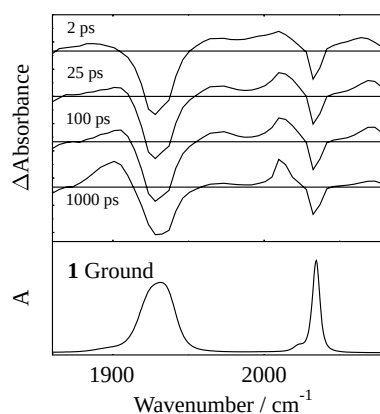


Figure 1. Ground-state IR spectrum of **1** in the $\nu(\text{CO})$ region, and excited-state spectra obtained on 400 nm excitation.

TRIR spectra of **1** were also recorded in the fingerprint region, at 1280-1720 cm^{-1} . They show the loss of ground-state bands and the formation of several excited-state bands from modes localised on the L ligand; some bands show up-shifts and others show down-shifts. The MLCT state band positions indicate clearly that the oxidised Re^{II} centre increases the charge-transfer character of the L ligand; importantly, this substantiates the proposal that MLCT excitation at the $(\text{bpy})\text{Re}(\text{CO})_3$ group lowers the electron density at the azacrown nitrogen atom.

TRIR spectra of $\mathbf{1-Ba}^{2+}$ were recorded in $\nu(\text{CO})$ and fingerprint regions. Both regions show bands which are characteristic of an MLCT state in which the metal cation remains associated with the azacrown at delay times of ≤ 1000 ps; the longer lifetime of the MLCT state of $\mathbf{1-Ba}^{2+}$ is attributed to the electrostatic effect of the metal cation preventing the electron transfer that occurs for **1**.¹⁾ Thus, the TRIR spectra provide conclusive evidence for the proposed mechanism of ion release in the MLCT state of $\mathbf{1-M}^{n+}$, and they are fully consistent with our other observations that this release occurs on a time scale of ca. 40 ns for Ba^{2+} .³⁾ In addition, the MLCT state band positions of $\mathbf{1-Ba}^{2+}$ approach those of **1**, indicating that the charge distribution within the L ligand of $\mathbf{1-Ba}^{2+}$ is similar to that for **1**. This provides crucial evidence that the increased electron demand at the Re^{II} centre in the MLCT state of $\mathbf{1-M}^{n+}$ is strong enough to increase the charge-transfer character of the L ligand, even though there is a metal cation bound to the azacrown.

Alkyne-linked complex

The photochemical mechanism of **2** is not yet established, but our studies to date indicate that both the Re→bpy MLCT state and an intraligand charge-transfer (ILCT) state, centred on the L ligand, are important; these two states are close in energy. The presence of a low-lying ILCT state arises from the fully conjugated alkyne-linked L ligand, and the binding of a metal cation at the azacrown raises the energy of the ILCT state.⁵⁾

TRIR spectra and kinetics were recorded from **2**, from 2-M^{n+} (for $\text{M}^{n+} = \text{Li}^+, \text{Na}^+, \text{Ca}^{2+}, \text{and Ba}^{2+}$), from model complexes in which the azacrown is replaced by $-\text{NEt}_2$ or $-\text{H}$, and from a model L ligand without the $(\text{bpy})\text{Re}(\text{CO})_3$ group attached. The analysis of this substantial data-set is on-going, and illustrative results are shown here.

Steady-state and TRIR spectra of **2** at $1850\text{--}2240\text{ cm}^{-1}$ are shown in Figure 2. They are more complicated than those of **1** due to the presence of both $\nu(\text{CO})$ and $\nu(\text{C}\equiv\text{C})$ bands, and they show inter-converting excited states with overlapping spectra. The $\nu(\text{CO})$ and $\nu(\text{C}\equiv\text{C})$ bands show down-shifts on excitation, and they may be assigned to ligand-centred charge-transfer states in which the electron density at the Re centre increases, and the $\text{C}\equiv\text{C}$ bond weakens; no clear evidence for an MLCT state of **2** is observed.

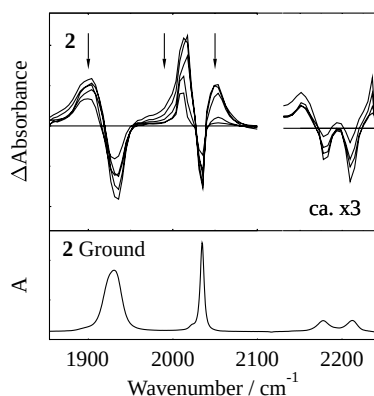


Figure 2. Ground-state IR spectrum of **2** in the $\nu(\text{CO})$ and $\nu(\text{C}\equiv\text{C})$ region, and excited-state spectra at 5, 10, 25, 100, and 1000 ps after 350 nm excitation.

TRIR spectra of **2** were also recorded in the fingerprint region, as shown in Figure 3. The strong bands arise from L ligand modes: some show up-shifts and others show down-shifts from the ground-state bands, consistent with the observation of charge-transfer states centred on the L ligand. As in the $\nu(\text{CO})$ and $\nu(\text{C}\equiv\text{C})$ region, the spectra and kinetics are indicative of two inter-converting excited states with overlapping spectra.

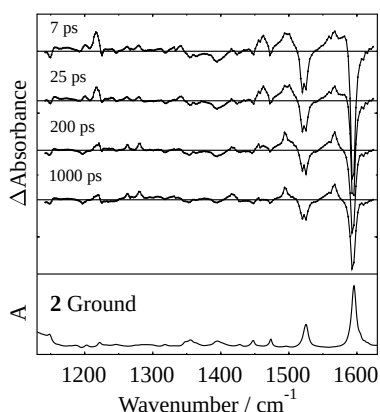


Figure 3. Ground-state IR spectrum of **2** in the fingerprint region, and excited-state spectra obtained on 350 nm excitation.

TRIR spectra and kinetics of 2-M^{n+} were recorded in both the $\nu(\text{CO})/\nu(\text{C}\equiv\text{C})$ and fingerprint regions; illustrative data from 2-Ca^{2+} are shown in Figure 4. The spectra from all of the 2-M^{n+} systems are indicative of charge-transfer states centred on the L ligand. The spectra and kinetics of 2-M^{n+} are different from those of **2**, and they vary between the different metal cations studied. The data from 2-M^{n+} are more complicated than those from **2**: there are some changes which may be indicative of steps in the ion-release process, and others which may be indicative of the participation of MLCT states due to the metal cation raising the energy of the ligand-centred charge-transfer states. A detailed analysis of the data is in progress.

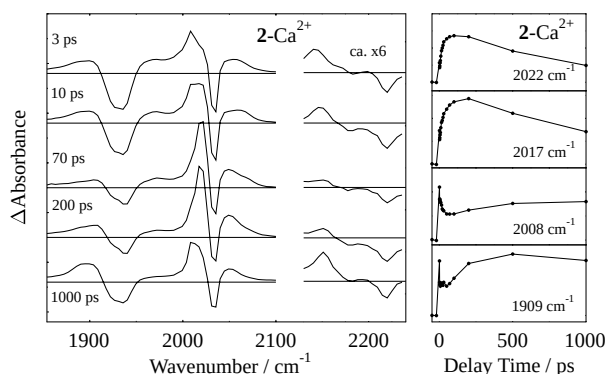


Figure 4. Excited-state IR spectra and kinetics of 2-Ca^{2+} in the $\nu(\text{CO})$ and $\nu(\text{C}\equiv\text{C})$ region on 350 nm excitation.

Conclusions

Picosecond TRIR spectroscopy has provided important information on the structure, bonding, and charge distribution in the excited states responsible for ion release in two types of light-controlled ion switch. The TRIR spectra from the amide-linked system, 1-M^{n+} , show unambiguously that ion release occurs in the MLCT state, and the band positions indicate that the effect can be attributed to an increase in the charge-transfer character of the L ligand in this MLCT state. By contrast, the TRIR spectra from the alkyne-linked system, 2-M^{n+} , show that charge-transfer states centred on the L ligand, rather than the MLCT state, are responsible for the photochemistry. More detailed information on the structure, bonding, and charge distribution in the various excited states observed is being elucidated from an ongoing analysis of the TRIR spectra allied with DFT calculations.

Acknowledgements

We thank Dr A W Parker for helpful discussions and advice, and we acknowledge financial support from EPSRC.

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Atmospheric reactions of OH with unsaturated hydrocarbons

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The kinetics of small hydrocarbons with the hydroxyl radical at have been investigated to investigate the possible effects of a pre-reaction complex. Unpublished work by Lester et al. has demonstrated that OH and C₂H₂ form a complex with a well depth of ~1000 cm⁻¹, prior to forming the adduct, HOC₂H₂, which is the main reaction product at low T. The project involves investigation of OH + C₂H_n (n=2,4), over the temperature range 200 – 300 K, where the effects of the pre-reaction complex will be most apparent.

The reaction rates we observe were determined by the Laser Flash Photolysis-Laser Induced Fluorescence technique. OH was generated by the pulsed photolysis of HNO₃ at 248 nm using a KrF excimer laser and observed by LIF with use of a frequency-doubled Nd:YAG-pumped dye laser system. The dye laser was operated with Rhodamine-590 dye, pumped by the second harmonic of a Nd:YAG laser, producing a doubled output at 283nm, at the Q-branch of the OH A²Σ⁺-X²Π₁ transition. The fluorescence was then observed at 308 nm by a photomultiplier tube mounted 90 degrees from the intersection of the two laser beams.

The first-order kinetic decays of OH were monitored via the delay between the photolysis and excitation pulses (Figure 1). The Laser Loan Pool 30 Hz Nd:YAG laser provides ample power and stability for these experiments.

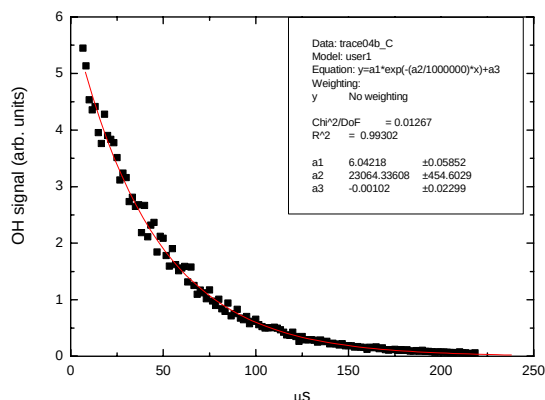


Figure 1. Typical kinetic trace of OH in the presence of excess C₂H₄. The OH signal is normalized to excitation laser power fluctuations. (Laser Loan Pool Nd:YAG 30 Hz laser).

The Nd:YAG pump laser that had been used previously malfunctioned regularly from temperature-control problems. Figure 2a and 2b show traces with the use of the malfunctioning laser. The fluctuations in laser power increased throughout the day until no useful data could be procured from the experiments.

Pseudo-first order rate constants were determined over a wide range of C₂H₄ concentrations to deduce bimolecular rate constants for a set of temperature and pressure conditions (Figure 3).

The studies completed thus far have encompassed the pressure dependence of the OH + C₂H₄ reaction over 3 different temperatures: 295, 260 and 195 K. The extensive data set is represented in Figure 4. The increase in the high-pressure limit at low temperatures has been observed in another study recently¹⁾, although is not consistent with kinetic evaluations from both IUPAC²⁾ and NASA³⁾.

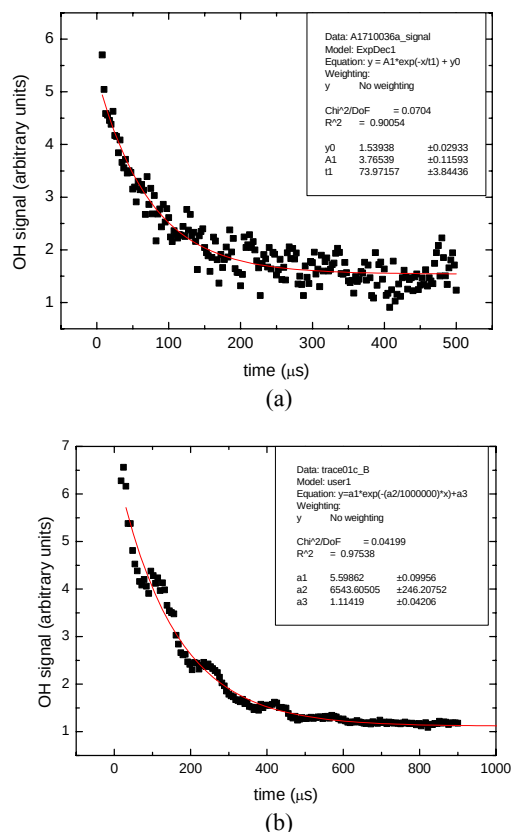


Figure 2. Traces with malfunctioning laser showing a) the noise in the 5 pt average data points and b) wide laser fluctuations that increase over the course of the day.

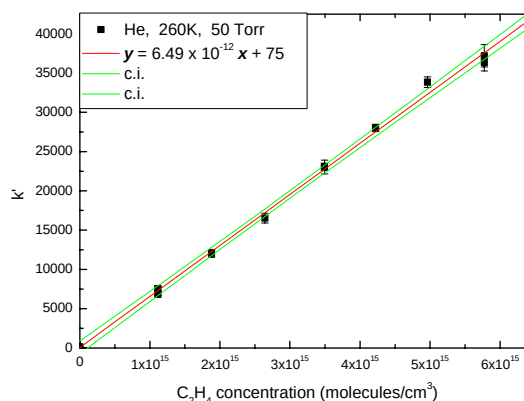


Figure 3. Determination of the bimolecular rate constant for OH + C₂H₄ at 260K and 50 Torr.

Figure 5 shows the fit of the low temperature data to $A(T/300K)^n$, which gives $n = -0.87$ and $A = 8.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

In order to confirm the derived value of n , more low temperature data points are needed. However, our value of $n = -0.87$ is similar to the value determined by Vahtkin et al.¹⁾ of -0.85 , at temperatures significantly lower than 195K. It is the

mid-region, relevant to the atmosphere, which is crucial to assess. The fit of this data corresponds well to the very low temperature data from Vakhtin *et al.*¹⁾ but varies from the high temperature data from Tully⁴⁾. This aspect is being investigated further using higher T measurements.

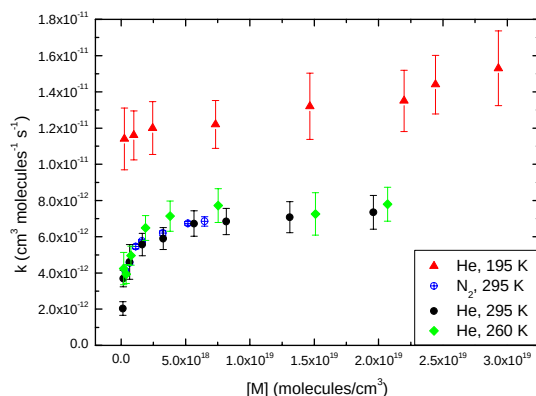


Figure 4. Kinetic data for the reaction $\text{OH} + \text{C}_2\text{H}_4$ as a function of bath gas pressure.

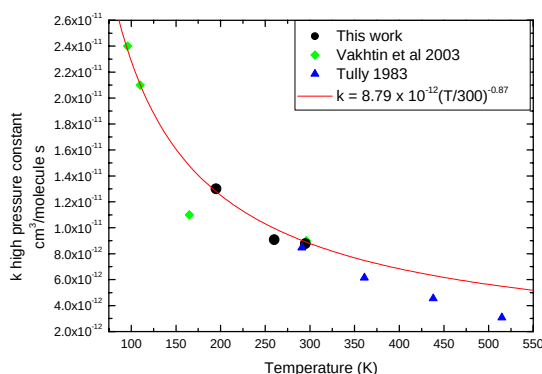


Figure 5. Plot of k_∞ versus temperature and best fit to the expression $k_\infty = A(T/300)^n$. Studies at higher and lower temperatures are also shown.

Complementary theoretical calculations of this system are also underway. We have constructed potential energy surfaces for the two reactions using *ab initio* techniques and then used these to carry out master equation calculations to investigate the pressure dependence and the effects of the pre-reaction complex. Interestingly, these show that the rate coefficient increases at very high pressures, as stabilization in the complex occurs. The pressure region where the increase occurs depends on the depth of the well. It is easier to observe in $\text{OH} + \text{C}_2\text{H}_2$.

Once the $\text{OH} + \text{C}_2\text{H}_4$ system is adequately characterized experimentally, we wish to move on to the $\text{OH} + \text{C}_2\text{H}_2$ system. Similar studies of the fall-off parameters of the $\text{OH} + \text{C}_2\text{H}_2$ system at various temperatures will be investigated. We are also investigating the behaviour of the reactions in high pressures of SF_6 , using laser flash photolysis coupled with cavity ring down spectroscopy.

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Resonance Raman studies of Fe-S cluster containing enzymes

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Introduction

Resonance Raman (RR) spectroscopy is a valuable technique to study [Fe-S]-cluster containing enzymes¹. We seek to utilize this to characterize the ligand and active site environment around [Fe-S]-clusters in enzymes belonging to the 'radical SAM' family that are involved in 1) sulphur insertion chemistry in particular biotin synthase (BioB) and lipoic acid synthase (LipA) and 2) thiazole formation, the 4-methyl-5-β-hydroxyethyl-thiazole phosphate synthase (ThiGH complex).

The common reaction of the 'radical SAM' proteins is the formation of a 5'-deoxy adenosyl radical (5'DOA), where an electron is donated by a [4Fe-4S]¹⁺ cluster. The 5'DOA radical is thought to abstract a specific hydrogen selectively from the substrate to generate a radical intermediate. In the case of LipA, two hydrogen atoms are abstracted from C6 and C8 of an octanoyl substrate, and replaced with sulphur atoms, a process requiring two mole equivalents of 5'DOA² (Figure 1).

The [4Fe-4S]-clusters in these proteins are ligated by three cysteine residues which poses an intriguing question; what is the fourth ligand. Furthermore the source of the inserted sulphur is an issue of debate, which might be solved using RR spectroscopy to examine the differences in spectra obtained for various Fe-S clusters. The EPR, Mossbauer and RR spectra for BioB³) and LipA⁴) have been reported in the literature, whereas the ThiGH complex⁵) has only been characterized by EPR. Unfortunately the [4Fe-4S]²⁺ state of the cluster is EPR silent and limits the use of this technique in the study of protein-ligand interactions. Thus far, no RR data of protein-ligand interactions for any of these proteins has been published.

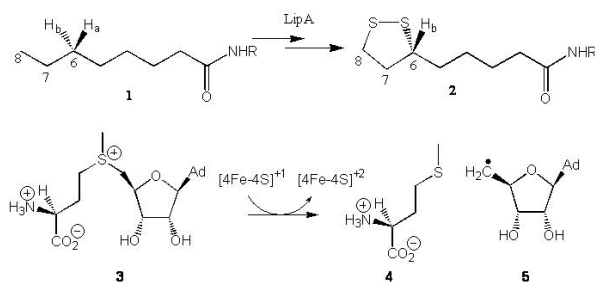


Figure 1. The reactions catalysed by LipA. The enzyme contains a [4Fe-4S]¹⁺ cluster that donates an electron to SAM (3) which cleaves to form a 5'-deoxyadenosyl radical. This radical (5) subsequently abstracts a specific hydrogen from an octanoic acid (1) derivative followed by the insertion of a sulphur atom. This cycle is then repeated to obtain a lipoic acid derivative (2).

Practical difficulties of RR spectroscopy of these Fe-S containing proteins arise from the fact that the signal is temperature dependent⁶) and the clusters are liable to oxidation. We have developed a new method to mount low volume frozen samples into a laser beam. The method was tested with horse heart myoglobin and 4-thiouracil.

Designed experimental set-up

The set-up for RR spectroscopy comprised an argon-ion laser (363.8 or 457.9 nm), collection optics, Raman spectrograph, CCD detector and a sample holder. The sample holder, a modified nickel top hat, similar to those used in protein crystallography, was magnetically held on a goniometer head for positioning. The sample sits in a photo-etched brass loop of 1.5 mm internal diameter attached to an integral stem of 40 mm length. The brass stemloops were either glued or spot-welded to the top hat. Samples were prepared and stored in cryotubes immersed in liquid nitrogen. The sample was loaded from this cryotube onto the goniometer head and when the cryotube was removed the sample was continuously cooled by the nitrogen stream from a cryostream (Figure 2).

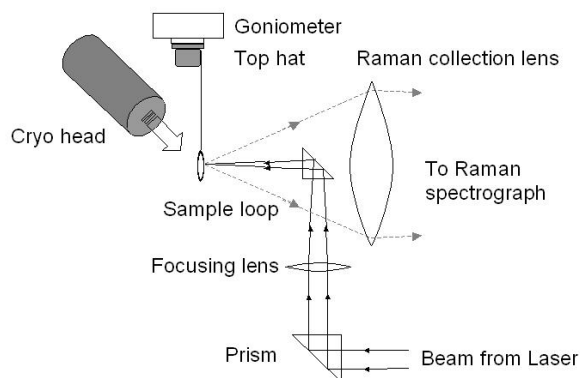


Figure 2. Experimental back-scattering set-up for the resonance Raman experiment on frozen samples.

Method verification

Following initial alignment a series of sample loops were tested to establish their accuracy by measuring the signal intensity when loaded with solvent. In each case minimal adjustment of the sample position was required to obtain the maximal signal.

RR spectra of a frozen solution of 4-thiouracil were recorded. Figure 3 shows such a spectrum using an excitation wavelength of 363.8 nm. The data obtained is in excellent agreement with data published by Ghomi and coworkers⁷). 4-thiouracil is a compound that can be considered as a simple analogue for the unnatural nucleotide 4-thio-deoxythymidine. Since this methodology requires only minute amounts of sample, it becomes feasible to study the interaction between expensive 4-thio-deoxythymidine containing oligonucleotides and DNA binding proteins.

Finally, horse heart myoglobin was used to verify the methodology. Horse heart myoglobin (5 mg/ml) was dissolved in Hepes buffer (50 mM, pH 7.5) and frozen in a sample loop. RR spectra were collected for 1 hour using an excitation wavelength of 457.9 nm, the preferred wavelength for the [Fe-S] clusters. After subtraction of the buffer background the spectrum of horse heart myoglobin was obtained (Figure 4). Again, the obtained spectrum was in good agreement with the literature⁸), both for the high intensity resonances at 1371, 1483, 1561 and 1617 cm⁻¹ as well as the low intensity bands at 930,

1133 and 1172 cm^{-1} . Furthermore the absence of a RR band at 1357 cm^{-1} indicates that under these conditions photoreduction of the sample did not occur.

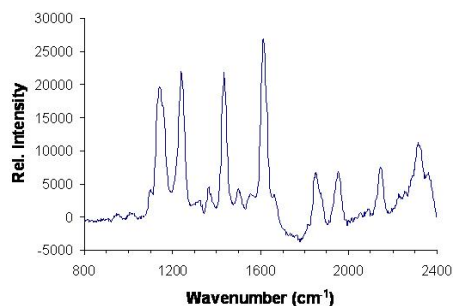


Figure 3. Summed RR spectra of 4-thiouracil (1 mM) in water recorded between 800 and 1500 cm^{-1} for 3 times 20 sec using laser light to excite at 363.6 nm (15 mW power at sample).

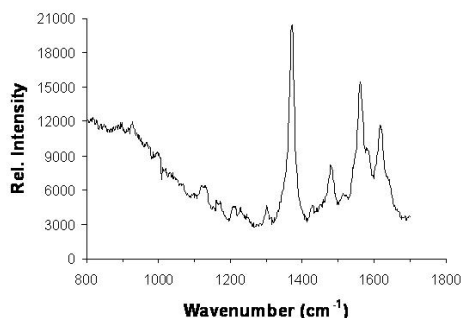


Figure 4. RR spectrum of horse heart myoglobin. Spectrum was recorded in 50 mM Hepes buffer pH 7.5 for 1 hour using an excitation wavelength of 457.9 (40 mW power at sample), background subtracted.

A possible complication of this methodology when studying [Fe-S] cluster proteins might be the sample temperature. When using a series of simple alcohols the temperature of the frozen sample was found to be -43 °C, which is far higher than the temperature reported by the cryostream controller -170 °C. This difference can be explained by the different position of the cryostream temperature probe, which is positioned in the core of the nitrogen stream and the turbulence of the stream caused by the size of our sample loop.

Future work

The developed methodology appears to be suitable to study [Fe-S] clusters. The method will be used to characterize synthetic clusters at high concentrations. Future studies will be conducted to obtain RR data for BioB, LipA and the ThiGH complex and to study the changes in the RR spectra upon substrate binding for each of these proteins.

Conclusions

A successful method to obtain RR spectra on frozen samples has been developed using a cryostream and accurately manufactured brass sample loops.

The methodology allows small samples to be studied (5 μl) in frozen solution without the interference of quartz.

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Kerr-gated picosecond Raman spectroscopy and Raman photon migration of equine bone tissue

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Introduction

Most tissue specimens exhibit intense fluorescence when excited with visible laser light and scatter light at all wavelengths at which Raman spectroscopy with silicon photodetectors is feasible. For these reasons workers in Raman tissue spectroscopy have generally employed near-infrared lasers to obtain spectra from specimens. The most common sources have been diode lasers operating at 785 nm or 830 nm. While this approach is satisfactory in many cases, it is well understood that excitation with blue or green lasers would provide inherently greater scattering efficiency, provided that the fluorescence problem could be overcome.

In tissue multiple scattering is a more important source of attenuation of light in the 400-1000 nm range than absorption, except for wavelengths at which hemoglobin absorbs. Light propagation under these conditions is called photon migration. To a good first approximation, multiple scattering can be modeled as a random walk, analogous to diffusion. Photons that are detected after multiple scattering events are generally called diffusive photons. This scattering is the dominant phenomenon when using near-infrared radiation that is preferred for deep penetration into tissue.

Despite the extensive literature of time-resolved photon migration measurements in absorption and fluorescence spectroscopies, the Raman photon migration has been studied only infrequently. Systematic studies of Raman photon migration have been carried out by Everall and co-workers at RAL¹⁾. They have shown that Raman spectra of finely divided powders excited by 400 nm illumination are recovered from depths of several mm and that the total photon migration distance is at least 3 cm as determined by monitoring the delay between the 1 ps excitation pulse and detection of the late-arriving Raman photons. They found $t^{1/2}$ time decay of the Raman scattering intensity observed at a single point outside the powder and $t^{-3/2}$ decay of elastically scattered light where t is the time following the 1 ps excitation pulse. In recent work the group have presented Monte Carlo simulations of the decay of Raman and scatter under realistic boundary conditions for a laboratory optical system²⁾.

Bone tissue is a composite material. The extra-cellular matrix contains a carbonated apatite mineral phase and an organic phase that is about 90% type I collagen. Both Raman and infrared spectroscopy are used to study composition and materials properties of bone³⁾. Both methods of obtaining vibrational spectra provide similar information on the composition and local structure of both the mineral and matrix components. Raman spectroscopy is advantageous for ease sampling of wet, solid specimens, such as tissue. In the Raman the major characteristic band of phosphate is ν_1 , the P-O symmetric stretch. The most prominent Raman marker for carbonate is at 1070 cm^{-1} . Bone matrix amide I (C=O stretch) and amide III (C-N stretch, C-H bend) contain a wealth of information. Both bands are envelopes that are resolvable into three or more components. The relative intensities of the bands in the amide I envelope relative intensity vary with the number and type of interfibril cross-links and in normal mature tissue

the most intense component is at 1665 cm^{-1} . In immature tissue or in tissue in which the cross-links have been severed mechanically or in tissue in which the cross-links have been severed mechanically or partially disrupted chemically, a band at 1685 - 1690 cm^{-1} is prominent.

However, Raman spectroscopy of bone tissue suffers from fluorescence interference from collagen if visible or near-UV excitation is used, and from haem iron if NIR excitation is used. Kerr-gated spectroscopy provides means to overcome these problems. While the principal research interests of the external investigators are in the function and pathologies bone and other musculo-skeletal tissues, techniques developed for Kerr-gated Raman spectroscopy of bone tissue can be easily modified for use with many other tissue types as well.

Experimental

Standard beam samples of equine cortical bone tissue (10 mm wide, 5 mm deep and 45 mm long) were cut under constant irrigation from the proximal, cranial cortex of the third metacarpal (canon). These samples were collected from UK registered abattoirs and frozen within 24 hours of death and thawed immediately before tissue preparation, then wrapped in gauze soaked in saline and refrozen to be thawed immediately before spectroscopic examination.

Kerr-gated picosecond Raman spectroscopy was performed on the CLF picosecond spectroscopy facility. The instrument was adjusted for 16 cm^{-1} resolution to match the transform-limited resolution of the 1 picosecond pulse train. Most experiments were performed with 400 nm light using the second harmonic of the fundamental laser output. The pulse energy at the specimen was 8 μJ and the average power was 8 mW.

Measurement of the depth of penetration through bone specimens and measurement of migration properties was performed on specimens ground to about 0.22 mm and mounted at a 45° angle to the incident laser beam as described above to give an effective depth of 0.31 mm. The time dependence of the signals was found by varying the opening of the Kerr gate from 0 to 30 picoseconds in 4 to 10 picosecond increments relative to the incident Raman gating pulse. A small sample of powdered polystyrene placed against the back of the specimen was used to identify Raman scatter arising from beyond the depth of the specimen. The time dependence of the laser light scattering from the sample was used to further characterize the depth of penetration.

Results and Discussion

In Figure 1 we show two Raman spectra from two regions, about 1 cm apart, of a specimen of equine cortical bone tissue. The 4 picosecond gate is adjusted for maximum signal (zero delay). Because the pulse width is only 1 psec, bands are broadened to about 15 cm^{-1} . Each spectrum rides on a background of about 2400 counts that has been removed by subtracting a fitted third order polynomial background function.

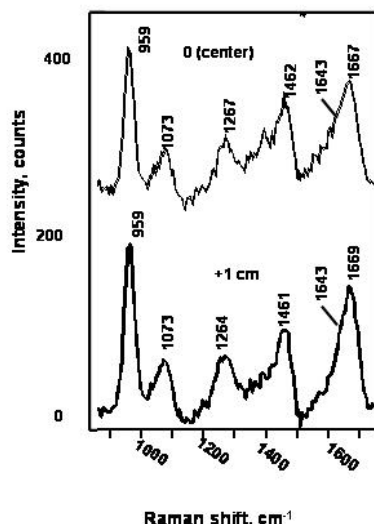


Figure 1. Kerr-gated Raman spectra of equine bone tissue. The spectra were obtained from the same specimen, at locations 1 cm apart.

The bands are readily identified as mineral and matrix (protein) bands of mature cortical bone tissue. The labeled bands include mineral markers phosphate ν_1 (P-O symmetric stretch) at 958 cm^{-1} and carbonate ν_1 (C-O symmetric stretch) at 1073 cm^{-1} and matrix markers: amide III at 1262 cm^{-1} , CH_2 wag at 1460 cm^{-1} and the amide I envelope with peak at 1667 cm^{-1} . Some detail that of conventional bone tissue Raman spectra obtained with $3\text{--}5\text{ cm}^{-1}$ resolution is obscured. The low frequency shoulder on phosphate ν_1 usually observed at ca. 945 cm^{-1} is not readily visible. Additionally, some bands are slightly displaced from their positions in conventional Raman spectra of similar bone tissue because the spectrograph resolution was set to match the transform-limited band width inherent in the time-resolved spectroscopy.

Spectra are reproducible. Two spectra taken on the same specimen at points approximately 1 cm apart are nearly identical. Band positions are the same within experimental error and there are only small differences in relative intensities of less intense bands. While spatial variation of bone tissue composition is often encountered, the laser beam in this case was focused to a spot about $200\text{ }\mu\text{m}$ diameter, blurring any spatial information.

Although fluorescence rejection was not our only goal, it is worth noting that fluorescence makes Raman spectroscopy of bone tissue with 430 nm CW excitation difficult or impossible. If Kerr gating was not used, the only signal observed from this specimen was an intense, featureless fluorescence arising from collagen, hemoglobin and other components of the tissue.

We studied photon migration properties of the tissue using time-delayed opening of the Kerr gate relative to the excitation pulse to follow temporal evolution of the Raman signals and determine the depth of light penetration through a specimen of bone tissue. The spectrum of a piece of polystyrene placed behind the bone tissue identified arrival of Raman photons generated at depths greater than the tissue thickness.

A Kerr gate delay time-sequence of spectra for a 0.2 mm thick bone specimen is shown in Figure 2. The specimen is placed in the optical path at 45° giving an effective depth of $\sqrt{2} \times 0.5 = 0.31\text{ mm}$. At 10 picosecond delay the bone tissue spectrum has been attenuated to about $2/3$ of its zero-delay intensity. The spectrum of a piece of polystyrene placed behind the bone tissue serves as a marker of the arrival of Raman photons generated from depths greater than the tissue thickness. The polystyrene spectrum is just discernable at 7 picoseconds delay and dominates the spectra at 10 psec and longer delays. At 20 picoseconds delay both the bone tissue and polystyrene

spectra were undetectable. Further confirmation that Raman photon migration occurs is found by fitting the time dependence of the integrated area under the phosphate ν_1 band to a $t^{-1/2}$ decay. Linear regression with $t^{-1/2}$ as the independent variable yields $r^2 = 0.99$, as expected in the simplest model of a diffusive process.

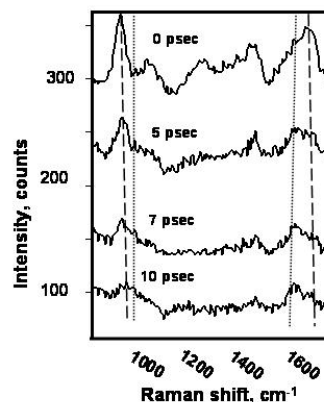


Figure 2. Time-delayed Kerr-gated Raman spectra of a 0.5 mm thick specimen of equine cortical bone. The gate delay times are 0- 10 psec. Dashed lines: bone 957 cm^{-1} and 1667 cm^{-1} bands. Dotted lines: polystyrene 992 cm^{-1} and 1590 cm^{-1} bands.

Conclusions

We have presented the first Kerr-gated Raman spectra of tissue specimens. Spectra are easily recorded even with the exciting laser at 431 nm , a wavelength at which intense fluorescence of hemoglobin, flavins and many other molecules is also excited. Raman photon migration has been demonstrated and shown to provide spectra of subsurface materials.

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Time-resolved fluorescence spectroscopy on single oligophenylenevinylene nanoparticles

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Introduction

Semi-conducting polymers such as polyphenylenevinylenes are attractive materials for optoelectronic devices. However, molecular engineering suffers from the lack of quantitative understanding of structure-property relationships due to (i) the distribution of effective conjugation lengths in the polymers and (ii) inhomogeneities of the polymer film morphology, resulting in dispersive energy and charge transport. We combine two approaches to overcome these difficulties: (i) the use of oligomers with well-defined π -conjugation lengths and (ii) the preparation of self-organized oligomer films or nanoparticles¹. Despite the high degree of order in oligomer films and nanoparticles, macroscopic samples still show non-exponential fluorescence decay traces. In order to find out whether these nonexponentialities are due to intra-particle or rather to inter-particle inhomogeneities, single nanoparticles of distyrylbenzene (2PV, see Figure 1) are investigated by time-resolved fluorescence microscopy under two-photon excitation. Bimolecular contributions to the deactivation of excited states are detected by investigating the intensity dependence of fluorescence decay curves. By doping the particles with energy acceptors (B5PV, 5T, see Figure 1), details of the excitation energy transfer processes are investigated.

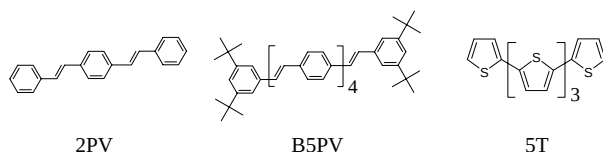


Figure 1. (Substituted) oligophenylenevinylenes (2PV, B5PV), quinquethiophene (5T).

Experimental

Nanoparticles with diameters of 100 to 200 nm were prepared by precipitation of 2PV (see Figure 1) from methanol solution ($c_{2PV} = 2 \cdot 10^{-5}$ M) by addition of water (methanol:water 1:4 v/v). Doped nanoparticles were precipitated in the same manner from solutions containing both, 2PV and the dopant (5T or B5PV) at concentrations corresponding to the desired doping ratio. The nanoparticles were drop-coated onto fused silica or silicon substrates and the solvent was removed by blow-drying.

Fluorescence lifetime images were obtained by scanning the sample through the optics of a Nikon inverted microscope in steps of $\Delta x = 1.25 \mu\text{m}$ (at optical resolutions of $0.2 \mu\text{m}$ in the radial and $0.7 \mu\text{m}$ in the axial directions). Decay traces were recorded by the single-photon counting technique, using the B&H SPCM700 for data acquisition. The samples were excited at $\lambda = 362 \text{ nm}$ by two-photon absorption of 100 femtosecond pulses from an Ar ion laser pumped Tsunami Titanium:Sapphire (Ti:S) laser at a repetition frequency of 80 MHz. The fluorescence light was detected by a microchannel plate photomultiplier tube, yielding an instrument response of 200 ps FWHM. Emission wavelengths were selected by band-pass and interference filters.

Results and Discussion

Undoped Nanoparticles The fluorescence spectra of 2PV nanoparticles in methanol/ water suspension (Figure 2) show a vibrationally structured emission between 25000 cm^{-1} and

19000 cm^{-1} with its maximum at 22900 cm^{-1} . Fluorescence decay curves of 2PV nanoparticle suspensions are strongly nonexponential with mean decay times of $\bar{\tau}_F \approx 2.7 \text{ ns}^{(2)}$.

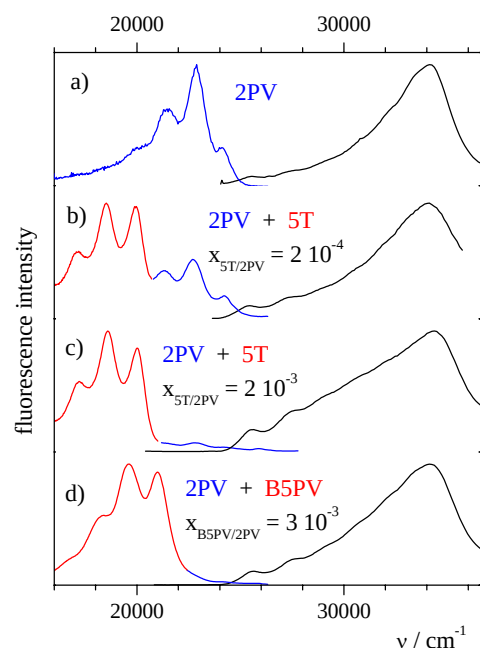


Figure 2. Fluorescence emission (left) and excitation spectra (right) of 2PV nanoparticles (NP): a) undoped, b) doped with 5T, doping ratio $x_{5T/2PV} = 2 \cdot 10^{-4}$, c) doped with 5T, $x_{5T/2PV} = 2 \cdot 10^{-3}$, d) doped with B5PV, $x_{B5PV/2PV} = 3 \cdot 10^{-3}$.

Figure 3 shows the fluorescence life time images of 2PV nanoparticles on silanized silicon/SiO₂ for two perpendicular polarizations. The decay curves of single nanoparticles are fairly exponential with life times varying between the extremes of 0.6 ns to 2 ns (Figure 4). The maximum of the lifetime distribution is found at $\bar{\tau}_F \approx 1 \text{ ns}$. Obviously, the emitting molecules within a single nanoparticle show the same decay kinetics, whereas the fluorescence lifetimes of molecules in different nanoparticles are significantly different. Considering that the fluorescence life time of 2PV is very sensitive to the environment of the molecule, especially to the local refractive index, n , ($\tau_F^{-1} \approx \tau_F^{-1}(n=1) + \text{const} \cdot n^2$), it seems that the structure of the nanoparticles is homogeneous throughout, i.e., at least on the 100 nm scale.

Single 2PV nanoparticles are highly ordered systems with the long molecular axes being aligned in the direction of the optical axis of the particle. This leads to dichroic absorption by single nanoparticles, as demonstrated by the polarized fluorescence intensity profiles in Figure 5. For the particle at the position of $20 \mu\text{m}$ a dichroic ratio of $D > 10$ is observed, due to the preferential alignment of the optical axis of the nanoparticle with the x-axis (see Figure 3). Due to the random orientation of the nanoparticles on the surface the maximum value of the dichroic ratio is rarely reached. For most particles smaller

values are observed, as for example for the particle at the position of 10 μm in Figure 3.

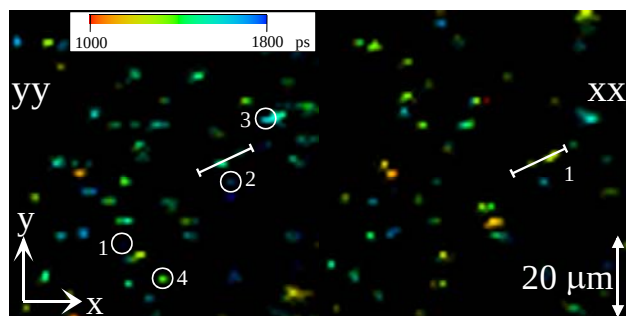


Figure 3. Fluorescence lifetime image of 2PV nanoparticles. Left: excitation and emission y polarized (yy). Right: excitation and emission x-polarized (xx). The pseudocolors represent fluorescence decay times, see insert.

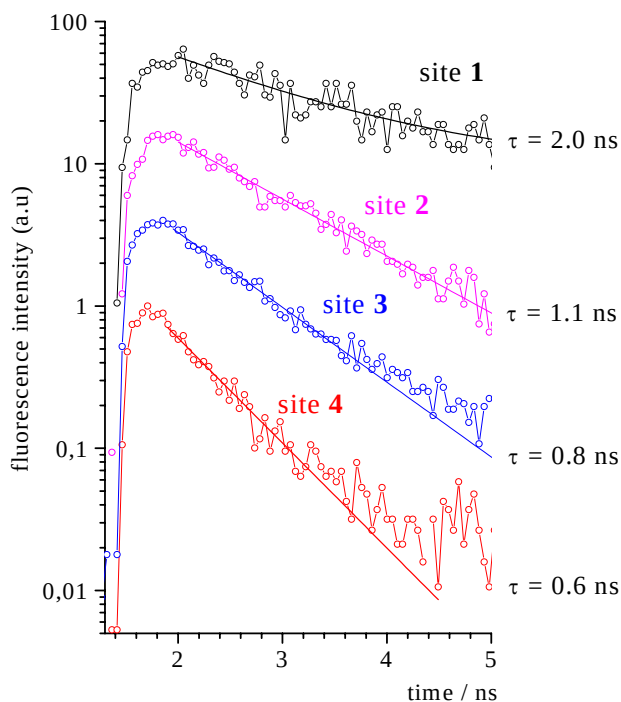


Figure 4. Fluorescence decay traces of different 2PV nanoparticles. The positions (sites 1 - 4) are indicated in Figure 3. The decay traces are shifted along the ordinate.

Doped Nanoparticles. Doping of 2PV nanoparticles with B5PV at a molar ratio of $x_{\text{B5PV}/2\text{PV}} = 3 \cdot 10^{-3}$ leads to almost complete quenching of 2PV fluorescence. Due to the good spectral overlap of 2PV fluorescence and B5PV absorption, efficient energy transfer from the 2PV matrix to the B5PV dopant takes place, so that practically only B5PV contributes to the fluorescence spectrum (Figure 2). The decay curves of B5PV are exponential, with lifetimes which are significantly longer than both, the fluorescence lifetime of undoped nanoparticles and the B5PV fluorescence lifetime in solution of $\tau_F = 1.1$ ns (Figure 6). This implies that energy transfer from 2PV to B5PV is not the only effect of doping. An additional process, e.g., the formation of a long lived intermediate species, must be active, which slows down the emission process. As for the undoped particles, high values of fluorescence anisotropy are observed for B5PV (Figure 7), indicating that the dopant molecules are aligned with their long axes parallel to the optical axis of the nanoparticle (i.e., parallel to the long axes of the host molecules). For this kind of system, where both guest and host molecules are parallel, high values of fluorescence anisotropy are observed even if energy transfer does not only occur by direct donor-acceptor transfer, but also involves energy

migration by donor-donor transfer. Depolarization is only caused by lattice imperfections.

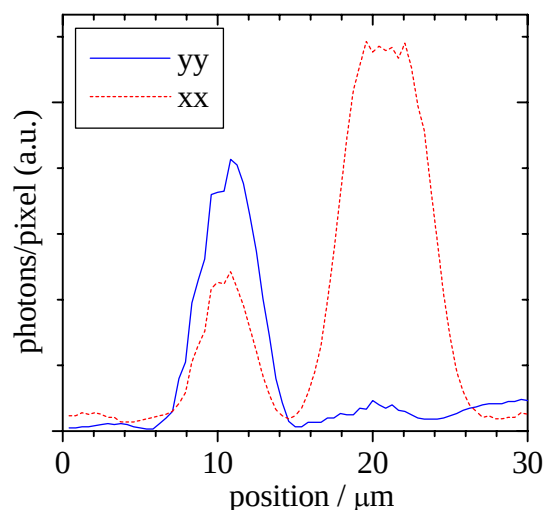


Figure 5. Lateral fluorescence intensity scans of 2PV nanoparticles along the line indicated in Figure 3. Excitation and emission are either both y-polarized (yy) or both x-polarized (xx). The scans are corrected for the intrinsic polarization of the set-up.

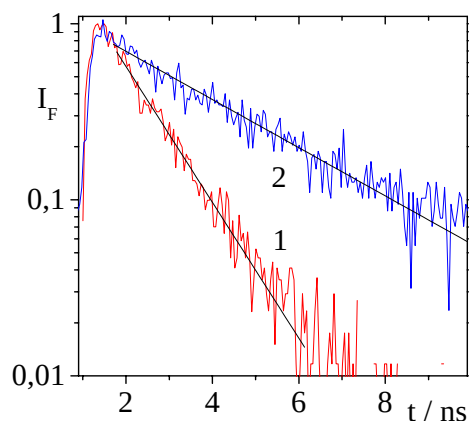


Figure 6 Typical fluorescence decay curves of (1) an undoped and (2) a B5PV-doped 2PV nanoparticle ($x_{\text{B5PV}/2\text{PV}} = 3 \cdot 10^{-3}$). Fluorescence lifetimes are $\tau_F = 1.1$ ns and $\tau_F = 3.2$ ns, for undoped and doped nanoparticles, respectively.

2PV nanoparticles doped with 5T at a doping ratio of $x_{\text{5T}/2\text{PV}} = 2 \cdot 10^{-4}$ exhibit spectrally separated 2PV and 5T fluorescence bands of about equal intensities (Figure 2). The fluorescence lifetime images of 5T doped 2PV nanoparticles show significantly different lifetimes, depending on the respective emission wavelength ranges (Figure 8). The mean fluorescence decay time of the host lattice is reduced by doping from $\tau_F \approx 1.1$ ns in undoped particles to $\tau_F \approx 0.35$ ns (Figure 9). The fluorescence of 5T, which is sensitized by energy transfer from 2PV, reveals a broad distribution of lifetimes, centered around $\tau_F = 0.95$ ns. The comparison of the two lifetime images in Figure 8 reveals that all detectable nanoparticles show both host and guest fluorescence, which indicates that none of the particles is undoped. However, although the decay of 5T fluorescence is exponential for single nanoparticles, the overall distribution of 5T lifetimes (Figure 9) is very broad. This suggests that the environment of the dopant molecules is homogeneous within the same nanoparticle but differs greatly from nanoparticle to nanoparticle. As in the case of B5PV, the lifetimes of 5T in the nanoparticles are close to or longer than the lifetime in solution. This indicates that energy transfer is not direct, but involves some additional process. This is supported

by the observation that the 5T decay curves are exponential, while the 2PV decay curves are not.

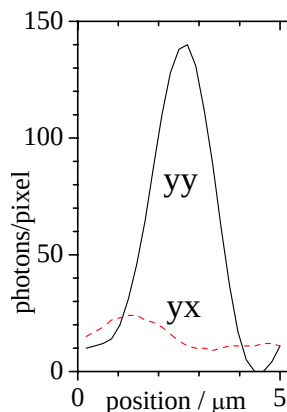


Figure 7. Lateral fluorescence intensity scans of a 2PV nanoparticle doped with B5PV ($x_{\text{B5PV/2PV}} = 3 \cdot 10^{-3}$). Excitation y-polarized (for polarization directions see Figure 3), emission y-polarized (yy) and x-polarized (yx), respectively.

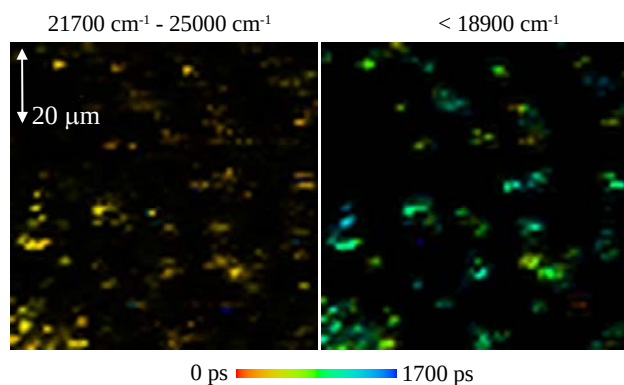


Figure 8 Fluorescence lifetime images of 5T-doped 2PV nanoparticles ($x_{\text{5T/2PV}} = 2 \cdot 10^{-4}$) for two different emission wavelength ranges, corresponding to emission of the 2PV matrix (left) and of the 5T dopant (right), respectively. The pseudocolors present fluorescence decay times.

Excitation Intensity Dependence At low excitation intensities ($I < 20$ mW) the decay curves of single 2PV nanoparticles are fairly exponential. At higher excitation densities the decay curves become non-exponential and the mean lifetimes become shorter (Figure 10). This effect has been observed before in thin OPV films³⁾ and is ascribed to bimolecular deactivation of photogenerated transients, e.g., singlet excitons³⁾. At incident light intensities of $I = 50$ mW and two-photon absorption cross sections⁴⁾ of $d = 10^{-50}$ cm⁴photon⁻¹ the initial density of excited states is approximately 10^{19} cm⁻³. At these excitation densities singlet-singlet annihilation by both, direct energy transfer and energy migration via the host lattice contributes significantly to excited state deactivation³⁾.

Conclusions

It could be shown by polarized fluorescence lifetime imaging that single nanoparticles are highly ordered systems with the long axes of the constituting molecules oriented parallel to the optical axis of the particle. However, large differences in the photophysical processes have been found among the particles. For example, fluorescence decay curves of single particles are fairly exponential, whereas they are non-exponential for macroscopic samples. Thus, the photophysical processes are much easier to analyze in single particles than for macroscopic ensembles. This advantage has been made use of in the elucidation of the mechanisms of deactivation and energy transfer processes. It could be demonstrated that the deviation of fluorescence decay curves from exponentiality at high excitation intensities is not due to inhomogeneities but rather to

the contribution of bimolecular deactivation of photogenerated transients. Progress has also been achieved in the study of energy transfer, which is often complicated by broad distributions of photophysical properties in macroscopic samples. The comparison of the fluorescence decay curves of host lattice and dopant in the same nanoparticle enables us to analyze the energy transfer process quantitatively.

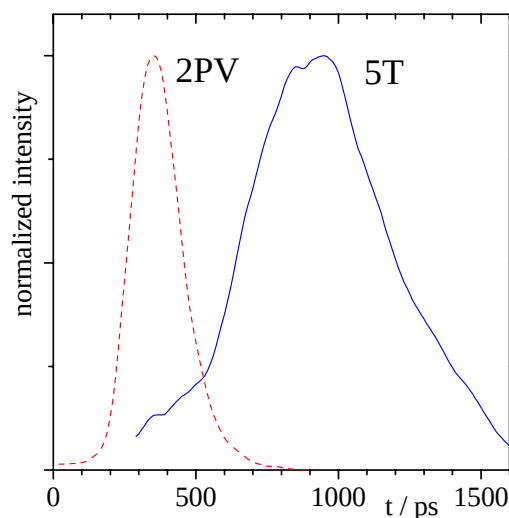


Figure 9 Fluorescence lifetime distributions obtained from Figure 8 for 5T-doped 2PV nanoparticles ($x_{\text{5T/2PV}} = 2 \cdot 10^{-4}$) for two different emission wavelength ranges, corresponding to emission of the 2PV matrix ($\tilde{\nu} = 21700$ cm⁻¹ to 25000 cm⁻¹) and of the 5T dopant ($\tilde{\nu} < 18900$ cm⁻¹), respectively)

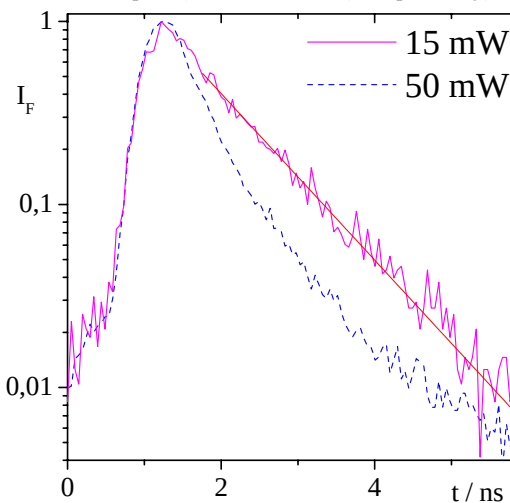


Figure 10. Normalized fluorescence decay curves of a single 2PV nanoparticle at two different excitation intensities. The fluorescence lifetime at 15 mW is $\tau_F = 0.95$ ns.

Acknowledgements

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Probing the structure of charge-separated excited state in Pt(II) diimine (bis)thiolates by time-resolved resonance Raman spectroscopy

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Introduction

This contribution reports preliminary ps TR³ studies into the structure of the charge-transfer excited state in metal thiolates.

It has long been desired to control light-induced properties through deliberate chemical changes. Photoinduced electron transfer is one of the elementary processes, which is utilized in light energy conversion, such as photosynthesis or vision.¹⁾ In these processes, a Donor-Spacer-Acceptor (D-sp-A) unit is the component responsible for the photoinduced-electron transfer step, with a charge-separated excited state, [D⁺-sp-A]^{*}, as a key transient.¹⁾ However, the fate and reactivity of this state is too often dictated by thermodynamically favourable back electron transfer that regenerates the ground state. A key challenge is to design a way to control back electron transfer so that the excited state can become engaged in a "chemical event" in a rational manner. Our approach is to exploit *structural reorganisation in the excited state*, namely formation of a transient sulfur-sulfur three-electron bond, S $\cdots$ S,²⁾ on a metal template, as a tool to control back electron transfer.

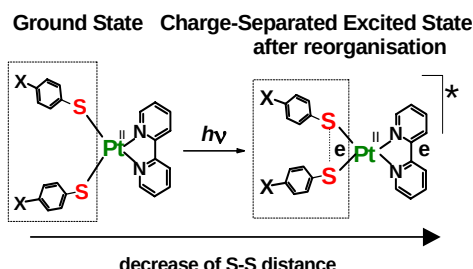


Figure 1. Suggested formation of a three-electron sulfur-sulfur bond with a concomitant shortening of the sulfur-sulfur distance in the excited state of metal thiolates.

The Pt(II) diimine (bis)thiolates have acted as model compounds in our studies, since the HOMO in these systems has thiolate/Pt(d) origin, while the LUMO is predominantly localised on the diimine ligand. In these systems (Figure 1), light induces electron transfer from the thiolate moiety to the diimine,³⁻⁵⁾ forming a system with a thiolate anion and thiyl radical, which can interact with each other via the metal centre. These systems are therefore suitable for formation of a transient sulfur-sulfur bond, accompanied by a decrease in the S-S distance in the excited state if compared to the ground state. The formation of a new bond in the excited state, which is not present in the ground state, creates an activation barrier for back electron transfer, thus giving one a tool to control the rate of this undesired process.

The formation of a transient S $\cdots$ S bond have been probed so far by the studies of dynamics and photoreactivity of the lowest excited state in the diimine (bis)thiolates as a function of thiolate ligand, and by quantum-chemical calculations.⁶⁾

(I) Studies on excited state dynamics and on photoreactivity as a function of thiolate showed that changes in the thiolate structure and donor capability allows one to vary the lifetime from 9 to

840 ps; and photooxidation quantum yield from 10⁻³ to 0.1. The trend in photoreactivity and lifetimes correlates directly with the estimated energy of the transient S $\cdots$ S bond (32 to 6 kcal/Mol).⁶⁾

(II) The quantum-chemical calculations (HF/6-31G*) have shown that the HOMO of the triplet state of the model system is a singly-occupied antibonding, and HOMO-1 – doubly-occupied bonding combination of p-orbitals of the two S atoms, suggesting a presence of a S-S bond in this excited state.⁷⁾

The results summarized above provided significant indirect support of the presence of S $\cdots$ S bonding in the lowest triplet *charge-separated excited state* of model chromophores. This contribution is concerned with the preliminary studies onto the *structure* of this excited state.

Experimental arrangements

The picosecond TR³ experiments on the Kerr gate apparatus described in detail in²¹⁾ were performed in DMF, under vertically flowing open jet sample arrangement. The 400 nm pump and 500 nm probe wavelengths were used, with typical pulse energies ca. 10 μ J (pump) and 3 μ J (probe), and both beam diameters being ca. 300 μ m at the sample. Acetonitrile Raman bands were used for calibration the spectra, with an estimated accuracy of the absolute frequency ± 10 cm⁻¹. Approximately 1000 s integration time was used for each time delay. The ground state Raman spectrum was obtained from the spectrum at -50 ps time delay after scaled subtraction of the solvent spectrum. All the TR³ spectra were first corrected for the solvent absorptions by the scaled subtraction of the solvent spectrum. The pure excited spectra were then obtained by a scaled subtraction of the spectrum at a negative time delay from the spectrum at the time delay of interest

Results and discussion

Time-resolved resonance Raman (TR³) is an excellent method for obtaining direct structural information on the excited states of metal chromophores.⁸⁾ The picosecond TR³ provides a direct route to probe the sulfur-sulfur interaction directly in the excited state of Pt(NN)(RS)₂. The TR³ is particularly useful for following S-S bonding since ν (SS) is strongly Raman active. For disulfides RSSR, the ν (SS) energy is strongly dependent on "R", ranging from 550 to 450 cm⁻¹. Since ν (SS) in disulfide radical anions, [RSSR]^{-•}, occurs at the energies lower than that in disulfides due to a single-occupied antibonding character of the HOMO in the S $\cdots$ S species (e.g., 450 in (SCN)₂ versus 218 cm⁻¹ in (SCN)₂^{-•}),⁹⁾ one can expect this vibration in our systems to occur in the region below 500 cm⁻¹.

The TR³ experiments were performed for the (NN)Pt(RS)₂, and presented in Figure 2. The excited state was generated by 400 nm pump pulse (150 fs), and then probed by 500 nm pulse at different time delays (Figure 2, left). Under these experimental conditions, the compounds studied all show the similar Raman pattern, with ca. 390, 1020 and/or 1180, and 1520 cm⁻¹ vibrations being most pronounced. The excited states of all of the compounds exhibit the vibration at

ca. 390 cm^{-1} , where $\nu(\text{SS})$ can be anticipated. No Raman signal was detected for $\text{Pt}(\text{bpy})(\text{PhSe})_2$, $\text{Pt}(\text{bpy})(4\text{-MeO-PhO})_2$, and $\text{Pt}(\text{bpy})\text{Cl}_2$, in which the lowest excited state retains {charge-transfer to bpy} nature, but is not suitable for S...S interaction. So far, the assignment of individual vibrations in the TR^3 spectra obtained remains ambiguous for a number of reasons:

- the $\nu(\text{SS})$ vibration will only be resonantly enhanced if the probing wavelength in TR^3 is in resonance with the transition involving either bonding, or anti-bonding S-S orbitals;
- The absorption spectrum of NN radical-anion, which is present in the charge-separated excited state of $\text{Pt}(\text{NN})(\text{RS})_2$, overlaps with that of the RS-ligand (Figure 3);
- The Raman vibrations of NN and RS ligands overlap across the whole spectral region. E.g., bpy-anion has characteristic Raman bands at 1558, 1497, 1205, 1151, 1033, 986, 740, 660, 370 cm^{-1} ,¹⁰ and PhS-radical - at 1551, 1180, 1073, 724 cm^{-1} .¹¹

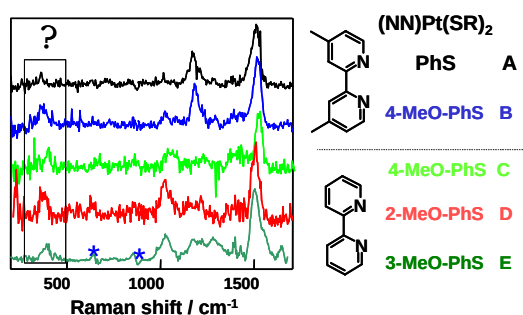


Figure 2. The TR^3 spectra of A - E obtained under 400 nm pump / 500 nm probe configuration. * indicates non-compensated solvent absorptions. Please note the differences in (i) the data obtained for the compounds containing 4,4'-diMe-2,2'-bpy (A,B) and 2,2'-bpy (C, D, E); (ii) in the ratio between the intensities of the 390 cm^{-1} and ca. 1500 cm^{-1} band.

The preliminary considerations onto the assignment of the Raman spectra observed (Figure 2) are summarised below.

1000 – 1700 cm^{-1} . The Raman spectrum of bpy radical-anion as obtained from $[\text{Ru}(\text{bpy})_3]^+$ under 514 nm excitation, exhibit vibrations at 1496 and 1007 in the ca. 2:1 ratio.¹² This intensity ratio was observed for $1520/1180\text{ cm}^{-1}$ bands in A, B (diMe-bpy) and for $1520/1020\text{ cm}^{-1}$ bands in C-E (bpy), Figure 2. The bands at 1163 and 1009 cm^{-1} were assigned to C-H deformation of bpy-radical anion.¹⁰ We thus tentatively assign 1520, 1180 and 1010 cm^{-1} bands to intra-bpy anion vibrations; the change in the enhancement from 1020 to 1180 cm^{-1} band on changing from bpy to 4,4-diMe-bpy supports this assignment.

The region below 500 cm^{-1} is of particular interest as that is where $\nu(\text{SS})$ can be anticipated. However, it is also characteristic for $\nu(\text{Pt-S})$, $\nu(\text{Pt-N})$ and some intra-ligand modes.

a) Let us first consider $\nu(\text{Pt-S})$ vibration. By application of normal coordinate analysis to the $(n\text{-Bu}_4\text{N})_2[\text{Pt}(\text{SCN})_6]$, a number of vibrations in the region $143 - 299\text{ cm}^{-1}$ were attributed to Pt-S modes. The $\nu(\text{Pt-S})$ was reported to appear at 405 and $<310\text{ cm}^{-1}$ for $\text{Pt}(\text{S}_2\text{C}_2\text{Me}_2)_2$, 403 & 373 cm^{-1} for $\text{Pt}(\text{S}_2\text{C}_2\text{Ph}_2)_2$; 375 & 288 cm^{-1} for $\text{Pt}(\text{S}_2\text{CNH}_2)_2$; and $298\text{-}350\text{ cm}^{-1}$ for $[\text{cis-PtCl}_2(\text{SMe}_2)_2]$.¹⁴

For $[\text{Bu}_4\text{N}]_2[\text{Pt}(\text{mnt})_2]$ (mnt = meleonitrile=dithiolate), the $375\text{-}380\text{ cm}^{-1}$ polarised vibrational band was assigned to a $\nu(\text{Pt-S})$ by analysing the vibrational satellites in the emission and polarised absorption ($T = 2\text{ K}$) spectra of single-crystals.¹⁵ For the related compounds $\text{Ni}(\text{baba})(\text{mnt})$ and $\text{Pd}(\text{baba})(\text{mnt})$

(baba=bis-acetyl-biantryl),¹⁶ the bands at 330 and 360 cm^{-1} were attributed to the M-S bond.

Thus, various bands in the region $140 - 405\text{ cm}^{-1}$ have been assigned to $\nu(\text{Pt-S})$, but no definitive assignment for the case of $\text{Pt}(\text{diimine})(\text{thiolate})$ has been made.

b) Another vibration possible in the region $< 500\text{ cm}^{-1}$ is $\nu(\text{Pt-N})$. The $\nu(\text{Ru-N})$ assignment was made for the 370 cm^{-1} band observed in the resonance Raman spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$.¹⁷ The vibrational satellites at 296, 349, 370 and 420 cm^{-1} observed in the emission spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ at 1.2 K ¹⁸ by high-resolution emission spectroscopy were also assigned to Ru-N vibrations. For $[\text{cis-Pt}(\text{glycine})_2]$ a strong vibration at 389 cm^{-1} was assigned to $\nu(\text{Pt-N})$.¹⁹ For $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$ and $[\text{Pt}(\text{bpy-h}_8)(\text{bpy-d}_8)]^{2+}$, on the basis of a comparison of the

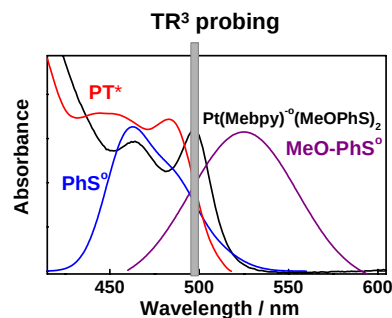


Figure 3. Absorption spectra of electrochemically generated radical-anion $[\text{Pt}(4,4'\text{-diMe-2,2'-bpy})(4\text{-MeO-PhS})]^-$ (Figure 2, compound B) in DMF, black line; of uncoordinated $\text{PhS}^\bullet$, blue line, of uncoordinated $4\text{-MeO-PhS}^\bullet$, purple line,² and transient absorption spectrum of $[\text{Pt}(4,4'\text{-diMe-2,2'-bpy})(4\text{-MeO-PhS})]^*$ probed 10 ps after 616 nm 15 fs pulse, red line.¹³

Raman data and highly-resolved emission spectra at 1.3 K , the band at 382 cm^{-1} was assigned to a bpy mode, and the bands at 417, 437 and 471 cm^{-1} to $\nu(\text{Pt-N})$ since the latter were not affected by the deuteration of bpy.¹⁸

In the Raman spectrum of $\text{Pt}(\text{bpy})\text{Cl}_2$ obtained under a 457.9 nm excitation, we observed the bands at 295, 387, 417 and 430 cm^{-1} in the region $<500\text{ cm}^{-1}$. 457.9 nm is in a pre-resonance with the lowest MLCT transition (390 nm), and therefore $\nu(\text{Pt-Cl})$ is unlikely to be enhanced. Hence, each of the above bands could be assigned to either $\nu(\text{Pt-N})$, or intra-bpy vibrations.

Similarly to $\nu(\text{Pt-S})$, three different regions, 290 cm^{-1} , $370\text{-}380\text{ cm}^{-1}$ and $417\text{-}478\text{ cm}^{-1}$ have been assigned previously to $\nu(\text{Pt-N})$ vibration, with no definitive assignment being made.

c) The third category of vibrations possible at the energies below 500 cm^{-1} are intra-ligand vibrations. To the best of our knowledge, no Raman data have been reported for thyl radicals in this region. However, thyl radicals are known to isomerise into pseudo-quinoidal structures, which can give rise to low-frequency vibrations. To this end, the very similar Raman pattern observed for the complexes with *ortho*-, *meta*- and *para*-MeO-PhS- (Figure 2, C-E) renders this suggestion unlikely.

In the Raman spectrum of $[\text{Fe}^\text{II}(\text{bpy})_3]^{2+}$, the vibration at 370 cm^{-1} was assigned to bpy, to bpy^- for $[\text{Fe}^\text{II}(\text{bpy})_2(\text{bpy})]^+$, and to intra-phenanthroline (phen) mode for $[\text{Fe}^\text{II}(\text{phen})_3]^{2+}$.²⁰ It therefore seems possible that the band at 390 cm^{-1} observed in Raman spectra of the charge-transfer excited state of the model chromophores A-E (Figure 2) is due to an intra-ligand vibration of a coordinated bpy-radical anion. Several observations are not in line with such an assignment:

(i) In the Raman spectrum of $[\text{Fe}^\text{II}(\text{bpy})_2(\text{bpy})]^+$ (501.78 nm)¹⁰ the band at 370 cm^{-1} of bpy^- , is accompanied by a 30% weaker band at 519 cm^{-1} , and a 50%-weaker band at 740 cm^{-1} .

Although the S/N ratio should allow us to detect these vibrations, they are not seen in the spectra obtained (Figure 2).

(ii) The intensity ratio between the “390” band and the high-frequency bands depends on both diimine and thiolate ligand (Figure 2). Should the 390 cm^{-1} vibration be localised on bpy^- , the ratio of these intensities would be independent on the structure of the compound under the same probing wavelength.

Summary

The absorption spectra of the species of interest (Figure 3) clearly suggest an overlap of several electronic transitions at 500 nm, one of which might be localised on bpy^- , and the other one(s) of possibly intra-thiolate or charge-transfer origin. The difference between the Raman pattern observed and the one expected for bpy -radical anion also suggests that 500 nm probing light in TR^3 experiments is in resonance with several electronic transitions. While the position of the 390 cm^{-1} band might suggest that it is an intra- bpy -radical anion vibration, the lack of other low-frequency bands associated with this one,²⁰ and the dependence of the relative intensities of the Raman vibrations observed on the structure of the compounds makes this assignment less likely. The absence of Raman data for $\text{Pt}(\text{bpy})(\text{PhSe})_2$, $\text{Pt}(\text{bpy})(4\text{-MeO-PhO})_2$, and $\text{Pt}(\text{bpy})\text{Cl}_2$, under identical experimental conditions does *not* support either $\nu(\text{Pt-N})$ or intra- bpy^- assignments of the band at 390 cm^{-1} .

Therefore, a creation of an excitation profile, in combination with isotopic substitution experiments and quantum chemical calculations into vibrational spectra deem essential for an assignment of the vibrations discussed above, for identifying $\nu(\text{SS})$ in the TR^3 spectra, and for the further insight into the transient sulfur-sulfur bonding as a mechanism of tuning excited state properties in metal chromophores.

Acknowledgements

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Monitoring the C-H Activation of methane by $\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$ in solution at room temperature

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Introduction

There is considerable interest in the photochemistry of $\text{M}(\eta^5\text{-C}_5\text{R}_5)\text{CO}(\text{L})$ ($\text{M} = \text{Rh}, \text{Ir}$; $\text{R} = \text{H}, \text{CH}_3$; $\text{L} = \text{CO}, \text{H}_2$), since these complexes undergo photolytic oxidative addition via alkane C-H bond activation.¹⁾ Several experimental techniques have been employed to elucidate the activation mechanism, including matrix isolation,^{2,3)} liquefied noble gases,^{4,5)} laser flash⁶⁾ and steady state photolysis.⁷⁾ It has been shown that the initially formed unsaturated $\text{M}(\eta^5\text{-C}_5\text{R}_5)(\text{CO})$ complexes are responsible for the C-H activation. In solution these exist as solvated adducts,⁸⁾ and oxidative addition occurs at room temperature on timescales $\ll 1 \mu\text{s}$.^{8,9)}

Picosecond time-resolved infrared spectroscopy (ps-TRIR) has previously been used to study alkane C-H activation with $\text{Rh}(\text{Cp})(\text{CO})_2$.^{6,9)} The alkane complex, $\text{Rh}(\text{Cp})(\text{alkane})(\text{CO})$, forms on the 10 ps timescale with a yield of ca. 25%. The remaining 75% of the excited molecules return to the ground state within 200 ps. At 660 ps, $\text{Rh}(\text{Cp})(\text{alkyl})\text{H}(\text{CO})$ begins to appear. The decay rate of the alkane complex was estimated to be $4.0 \times 10^8 \text{ s}^{-1}$. However, the activation of cyclohexane by $\text{Ir}(\text{Cp})(\text{CO})_2$, occurs with a lifetime of 2 ps and a 20% yield.¹⁰⁾

Bergman and Moore have examined the activation of several linear and cyclic alkanes by $\text{Rh}(\text{Cp}^*)(\text{CO})_2$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) in liquid Kr and liquid Xe solution at cryogenic temperatures.⁴⁾ On the μs -timescale, $\text{Rh}(\text{Cp}^*)(\text{CO})\text{Ng}$ ($\text{Ng} = \text{Xe}$ or Kr) was the primary photoproduct. In liquid Xe they found that CH_4 , C_2H_6 and C_3H_8 were not activated and $\text{Rh}(\text{Cp}^*)(\text{CO})\text{Xe}$ was the dominant intermediate. However, in liquid Kr only, CH_4 was unable to compete with the binding strength of the noble gas and the other alkanes were all activated. Notably, for each series of linear and cyclic alkanes, the larger alkanes interacted more strongly, and the cyclic alkanes more strongly than the linear alkanes. It has also been demonstrated, through steady state photolysis studies, that supercritical (sc) CH_4 , C_2H_4 and C_2H_6 are convenient solvents for the activation of the lighter alkanes.¹¹⁾

We have previously characterised organometallic noble gas complexes in solution at room temperature by combining TRIR with supercritical fluid techniques.¹²⁾ In this report we give details of our recent TRIR investigation in sc CH_4 to monitor the C-H activation of CH_4 in solution at room temperature.

Results and Discussion

Figure 1 shows ps-TRIR spectra obtained following 267 nm excitation of $\text{Rh}(\text{Cp})(\text{CO})_2$ in sc CH_4 (4000 psi) in the presence of CO (60 psi).¹³⁾ 2 ps after the laser flash, the parent $\nu(\text{CO})$ bands at 1995 and 2056 cm^{-1} are fully bleached (labelled with "a" in Figure 1). Between 4 and 10 ps, five transient features barely resolve ("b"). These broad transient bands centred at around 1926, 1949, 1972, 2020 and 2037 cm^{-1} are tentatively assigned to absorption of the A1 and B1 symmetric CO stretch vibrations of vibrationally excited ground state and/or electronically excited state $\text{Rh}(\text{Cp})(\text{CO})_2$. During the following 90 ps a subsequent decay of the hot bands (b) takes place. Although subject to considerable error, the lifetimes of these bands were estimated, falling apparently into three groups, 17($\pm$ 2) ps (1926 cm^{-1}), 33($\pm$ 4)-50($\pm$ 20) ps (1949, 2020 cm^{-1})

and 90($\pm$ 30)-110($\pm$ 30) ps (1972, 2037 cm^{-1}). The number and different lifetimes of the hot bands suggests that different levels of vibrational excitation are involved. The above assignment is supported by similar previous findings for solutions of $\text{Rh}(\text{Cp})(\text{CO})_2$ in alkanes, where hot bands have been found at 2020 and 2034 cm^{-1} ,⁶⁾ and by IR pump-IR probe experiments with $\text{Ir}(\text{Cp}^*)(\text{CO})_2$ ¹⁴⁾ and $\text{W}(\text{CO})_6$.¹⁵⁾

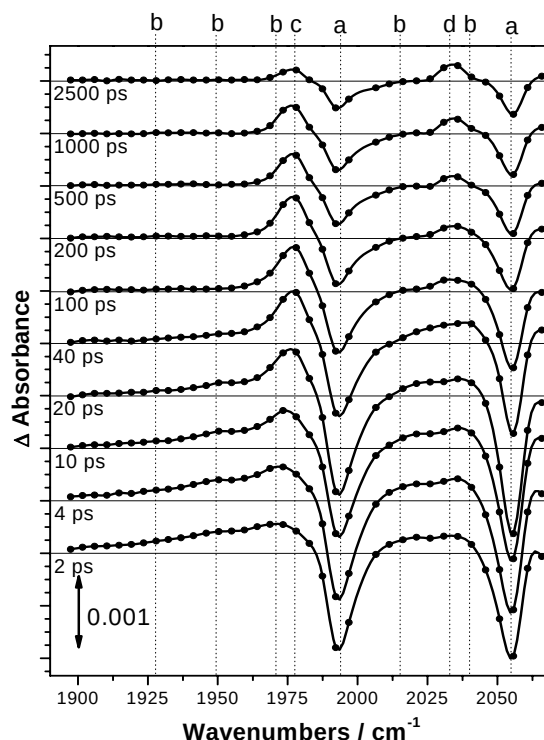


Figure 1. Transient IR difference spectra in sc CH_4 (4000 psi, doped with 60 psi CO), at selected pump-probe delay times.

The 2037 cm^{-1} band could belong to an electronically excited complex $[\text{Rh}(\text{Cp})(\text{CO})_2]^*$. Following an analogy with $\text{Ir}(\text{Cp}^*)(\text{CO})_2$ one would expect its second $\nu(\text{CO})$ absorption at around 2092 cm^{-1} , which is difficult to detect under the current experimental conditions due to the presence of large quantities of CO.

After ca. 40 ps an additional transient absorption becomes clearly visible at ca. 1979 cm^{-1} ("c" in Figure 1). It is assumed that this band is initially formed after the laser flash (2 ps). At 100 ps, this band is the main transient left in the region. It can readily be assigned to the CH_4 complex, $\text{Rh}(\text{Cp})(\text{CH}_4)(\text{CO})$ by comparison with the results of matrix isolation of " $\text{Rh}(\text{Cp})(\text{CO})_2 \cdots \text{CH}_4$ "³⁾ and TRIR studies in *cyclo*-⁹⁾ and *n*-hexane.⁶⁾ $\text{Rh}(\text{Cp})(\text{CH}_4)(\text{CO})$ has an estimated lifetime of 2.2($\pm$ 0.3) ns.

The two parent absorptions recover to 40% of the initial bleach intensity within the first 200 ps (Figure 2). This early recovery of the parent absorption matches the time range of the already estimated range of lifetimes of the hot bands from 17($\pm$ 2) to

110(±30) ps. Photoexcitation of $\text{Rh}(\text{Cp})(\text{CO})_2$ causes two pathways: 60% of the excited molecules dissipate excitation energy non-dissociatively whereas 40% dissociate CO followed by C-H activation (vide supra). Interestingly, Bergman *et al.* found a ratio of 75% and 25%, 200 ps after 267 nm excitation of $\text{Rh}(\text{Cp})(\text{CO})_2$ in cyclohexane.⁹⁾

The methane complex decays to form a new transient with an absorption at 2036 cm^{-1} , see Figure 3 (labeled as “d” in Figure 1). This band is assigned to the hydride complex, $\text{Rh}(\text{Cp})(\text{CH}_3)\text{H}(\text{CO})$, which gives direct evidence for a C-H activation reaction taking place in scCH_4 . The kinetic trace at 1976 cm^{-1} (Figure 3, left) shows an early rise and decay, which is caused by a narrowing of the $\text{Rh}(\text{Cp})(\text{CH}_4)(\text{CO})$ band within 14(±4) ps and the decay of the overlapped hot band (90(±30) ps). The points after 200 ps show the genuine decay of the methane complex. The early decay feature in the 2035 cm^{-1} trace similarly originates from the decay of a hot band (110(±30) ps).

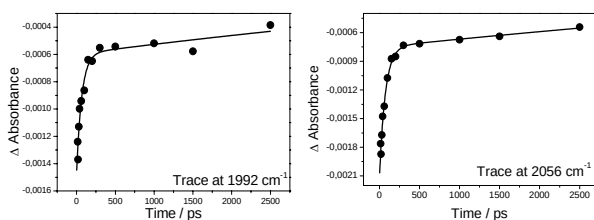


Figure 2. Kinetic traces showing the recovery of the bleached parent absorptions at 1992 and 2056 cm^{-1} .

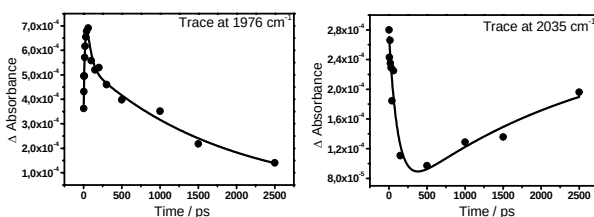
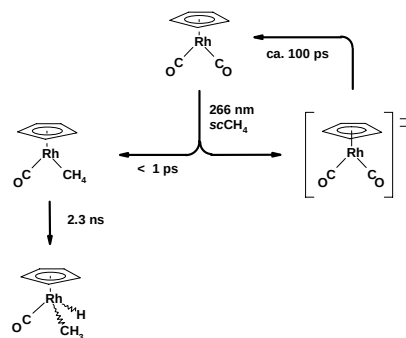


Figure 3. Trace showing the rise and decay of the methane complex (left) and trace showing the early decay of the vibrationally excited complex and the later growth of the C-H activated complex (right).

At the longest delay time available with the ps-TRIR apparatus (2500 ps), $\text{Rh}(\text{Cp})(\text{CH}_4)(\text{CO})$ had not completely decayed and $\text{Rh}(\text{Cp})(\text{CH}_3)\text{H}(\text{CO})$ was not fully formed. However, ns-TRIR investigations showed that this reaction is complete within 7 ns, with $\text{Rh}(\text{Cp})(\text{CH}_3)\text{H}(\text{CO})$ being fully formed and $\text{Rh}(\text{Cp})(\text{CH}_4)(\text{CO})$ no longer detectable. This allows us to estimate the $\text{Rh}(\text{Cp})(\text{CH}_3)\text{H}(\text{CO})$ risetime to be 2.4(±0.5) ns. The first order rate constant for the C-H activation reaction was found to be $4.5(\pm 0.4) \times 10^6 \text{ s}^{-1}$.

The photochemistry of $\text{Rh}(\text{Cp})(\text{CO})_2$ in scCH_4 is summarized in the Scheme 1.



Scheme 1. Summary of the photochemistry of $\text{Rh}(\text{Cp})(\text{CO})_2$ in scCH_4 .

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Lignin radicals in wood cell walls monitored by Resonance Raman spectroscopy

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Analysis of liposomal membrane composition using Raman Tweezers

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Summary

We have developed a methodology for the analysis of liposomal membranes and their contents using near-IR Raman spectroscopy on liposomes held in an optical trap. We were able to detect a variety of membrane components including lipids, cholesterol, and small molecule solutes such as ethanol, DMSO and hexafluoroisopropanol. The methodology is able to distinguish between solutes that equilibrate across the liposomal membrane from those that partition selectively into the lipid bilayer.

Introduction

Optical entrapment, also known as laser tweezing, is an emerging technique that has the potential to be extremely useful for the analysis of liposome properties¹. This technique offers the possibility of manipulating liposomes in order to observe a number of phenomena that would otherwise be difficult to study, and has the advantage of being performed under physiologically relevant conditions. Optical tweezing of liposomes has already been described for applications involving micromanipulation, controlled fusion, and studies of single molecule reactions² and enables measurements to be made on membrane processes with slow kinetics or that require lengthy acquisition times. In this paper we describe a methodology for trapping single liposomes in order to obtain Raman spectra of the membrane components. Although methods for obtaining Raman spectra from lipids have been described, these rely on either measuring bulk properties, which may be difficult in cases where the number of liposomes per unit volume is low, or on detailed preparation procedures that enable supported membranes to be probed using conventional Raman microscopy³. Raman tweezing has previously been applied in a few cases to the study of small particles⁴, although little work has been done with liposomes. It is a technique particularly well suited to liposomes, as potentially any substance that interacts with, or partitions into, a membrane may be studied without the need for labelling and extended sample preparation. Detailed knowledge of the chemistry and biology of natural lipid membranes is essential for understanding a variety of phenomena, including membrane permeability, peptide-lipid interactions and blood-brain permeability. The Raman spectra that were collected were suitable for obtaining analytical information regarding membrane composition, and to determine the permeability of an added solute.

Experimental

Raman Tweezing.

The Raman tweezers apparatus (Figure 1) consisted of a cw Argon ion laser (Innova 90-5-UV, Coherent) with laser beam wavelength of 514.5 nm and maximum power of 2 W. The beam was passed through two sets of expansion optics (L1 to L4), reflected from a 33:67 beamsplitter and directed into the microscope. Here, a dichroic mirror reflected the beam through the objective lens (x63, NA 1.2, Leica Microsystems) where the optical trap was formed. For trapping and acquisition of Raman spectra the laser was attenuated to a power of 12 mW, measured at the entrance aperture of the objective lens.

The Raman light scattered from the focal point was collimated by the objective lens and passed back along the same optical pathway. A holographic notch filter (HNF-514, Kaiser Optical

Systems) was placed after the beamsplitter to transmit only the Raman shifted light above 514.5 nm. The beam was then focussed on to the entrance slit of a spectrometer (SpectraPro-500, Acton Research Company) and detector (LN/CCD-1024, Princeton Instruments). To allow observation of the trapped liposome, filtered light (>700 nm) from the microscope is used to image the particle onto a CCD camera.

Calibration of the spectrometer was performed by focussing the laser into a sample vial of toluene (Spectroscopic grade, Aldrich) and assignment of the peaks was made from standard spectra. Recorded wavenumbers were accurate to within 2 cm^{-1} . Peak positions were reproducible for multiple liposomes from the same preparation to $\pm 1.5\text{ cm}^{-1}$. For a single liposome, the peak height varied by $\pm 3\%$ between acquisitions.

To remove the presence of the dispersion medium from the liposome spectra the background noise was acquired without a vesicle in the optical trap. The background spectrum was as expected for water and showed no sharp features. This was subtracted from the original spectra in a 1:1 ratio to produce the spectra shown. A similar protocol has been routinely used in Raman microscopy studies. Calculations of peak ratios were made from the relative peak intensities in the acquired spectra after subtraction of the background signal.

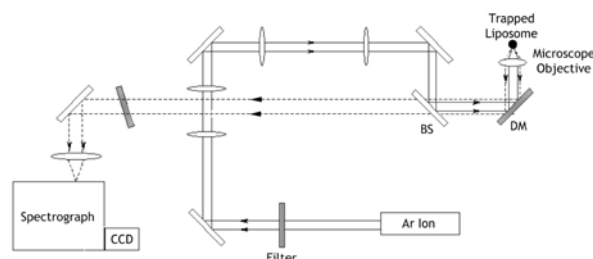


Figure 1. The Raman tweezing system.

Liposome Preparation.

Unilamellar liposomes were prepared by drying chloroform solutions (100 mg/ml) of the lipids *in vacuo* in a 50 ml round-bottomed flask to form a thin film. The dried lipid films were hydrated using phosphate buffered saline (pH 7.2, 1 ml per mg lipid) and vortex mixed for 3 minutes. The lipid emulsions were then subjected to five freeze thaw cycles using liquid nitrogen and a water bath at 40 °C before being extruded ten times through a laser-etched polycarbonate membrane of pore size 2 μm (Whatman). The final liposome preparations were diluted x10 for Raman tweezer experiments.

For membrane partition assays, a solution (900 ml) of the solute under examination was prepared in phosphate buffered saline. This was treated with 100 ml of the liposome preparation to give a final liposome dilution of 1/10 and a solute concentration of 2.5% v/v. The mixture was incubated for 16 h before being subjected to analysis by Raman tweezing.

Spectral Acquisition.

Raman scattering spectra were typically obtained from the trapped particle using a 150 s acquisition time at a laser power of 12 mW. The particle was dislodged and the process repeated to obtain the background spectrum. Both sets of data were

filtered to remove signals due to cosmic radiation, and the corrected spectrum obtained by subtracting the background spectrum from that of the trapped particle. In the case of samples containing DMSO, cosmic filtering removed the sharp peak at 679 cm^{-1} arising from the sample, and consequently data was recorded with a 10 s acquisition time at a laser power of $\sim 40\text{ mW}$ and processed without filtering.

Results/Discussion

In our initial experiments we sought to obtain reference Raman spectra for typical examples of saturated and unsaturated lipids under conditions of physiological relevance, and selected dimyristoyl phosphatidylcholine (DMPC) and dioleoyl phosphatidylcholine (DOPC) respectively. Phosphate buffered saline (PBS) was used as the medium throughout our experiments due to the weak Raman signature of this buffer. Raman spectra were obtained from large unilamellar vesicles of diameter $\sim 1\text{ }\mu\text{m}$ composed of pure DMPC and DOPC that exhibited characteristic spectra. The salient features of the DMPC spectrum (Figure 2A) were bands at 1060 , 1085 and 1125 cm^{-1} (C-C skeletal stretching vibrations), 1296 cm^{-1} (CH_2 twist) and 1445 cm^{-1} (CH_2 bend)⁵. DOPC (Figure 2B) exhibited additional Raman bands at 1264 cm^{-1} and 1655 cm^{-1} (cis C=C stretching vibration).

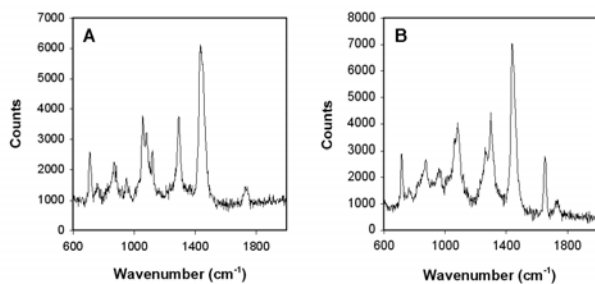


Figure 2. Raman spectra obtained from liposomes composed of pure DMPC (A) and DOPC (B).

Although these spectra have a lower signal-to-noise ratio than those reported⁶, we routinely used a low laser power in order to minimise thermal effects on the liposomal membrane, at the expense of a slight increase in background noise. Liposomal membranes composed of DMPC/DOPC with an approximate DOPC content of 18 mol% were prepared and also subjected to Raman analysis (Figure 3A). By performing a ratiometric subtraction of the peaks arising from DOPC using the spectrum of the authentic sample, we were able to determine the proportion of this lipid in these membranes to be $54 \pm 7\text{ mol}\%$, significantly different from the intended composition. The precise reasons for this discrepancy are uncertain, and future work will be performed to try to determine whether it results from an inherent property of liposomes, or arises as an artefact of the method used to prepare them. A similar analysis was performed on soyabean phosphatidylcholine (SPC, Figure 3B). By comparison of the intensities of the peaks at 1655 and 1450 cm^{-1} , we were able to estimate the olefin content of SPC to be 1.57 ± 0.09 times that of pure DOPC, based on the assumption that the spectrum for DOPC was characteristic of a *cis*-double bond-containing lipid. These values are consistent with published data for the composition of SPC, which contains a high content (43%) of the *cis*-9,12 unsaturated lipid linoleic acid⁷. We were also keen to demonstrate the ability to detect the presence of cholesterol in membranes, particularly as cholesterol is a key modifier of membrane properties but has a less distinctive Raman spectrum than phospholipids. Consequently we prepared liposomes composed of 10% cholesterol/DMPC and obtained spectra for these mixtures from a series of trapped liposomes.

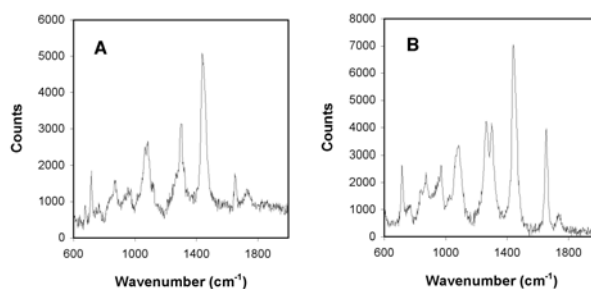


Figure 3. Raman spectra obtained from liposomes composed of 18 mol% DOPC/DMPC (A) and SPC (B).

We were able to subtract the DMPC signals and unambiguously identify cholesterol as a membrane component through the observation of peaks at 1438 and 1669 cm^{-1} (Figure 4), in accordance with the literature data for this compound. The presence of several peaks of low relative intensity below 1400 cm^{-1} is also typical of cholesterol⁸.

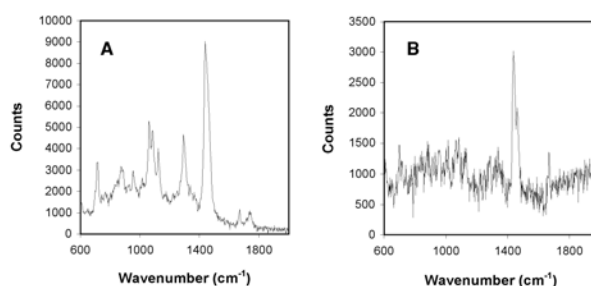


Figure 4. A) Raman spectrum obtained from liposomes composed of 10 mol% cholesterol/DMPC; B) The spectrum in (A) following subtraction of peaks arising from scattering by DMPC.

Additionally, as liposome samples are never monodisperse, we were able to trap a number of DMPC vesicles of varying size in order to examine the effects of particle size on Raman scattering intensity. Interestingly, scattering reached a maximum for particles of size $1\text{ }\mu\text{m}$ and then decreased slightly at larger sizes (Figure 5A). The optimum size will depend primarily on the numerical aperture of the objective lens in the microscope and the size of the diffraction limited focal spot in comparison to the trapped object.

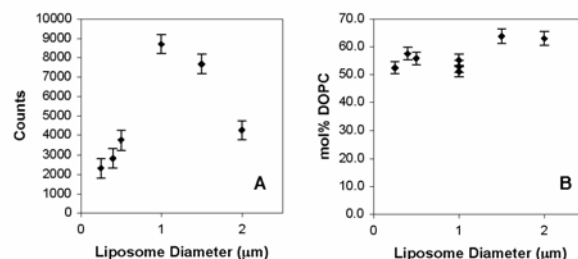


Figure 5. A) Magnitude of the Raman emission at 1440 cm^{-1} as a function of liposome diameter for DMPC liposomes in PBS; B) DOPC composition (mol%) of DOPC/DMPC liposomes as a function of size in a single sample population.

In our experiments the focal spot was $\sim 600\text{ nm}$ in length in the *z*-plane, smaller than the size of the liposomes for which maximum scattering was observed. Further work will be required to determine why these two values are different, although it should be noted that as the lipids are only present in a small layer of approximate diameter 10 nm at the surface of the liposome, the scattering intensity that we observe is determined not only by the quantity of lipid in the liposome, but also the distance of the liposomal membrane from the point of

highest incident light intensity at the centre of the liposome. Thus, as liposomes become increasingly large, the potential scattering intensity is larger as more lipid becomes available to generate the Raman signal. However the actual scattering intensity decreases because the liposomal membrane is further from the focal point of the incident beam.

The ability to determine the partitioning of solutes into the lipid bilayer was of intrinsic interest to us. In order to examine the distribution of a solute added to the solution surrounding the vesicles, a sample of liposomes was diluted in PBS containing the solute (typically at a concentration of 2.5% v/v for liquids). After an overnight incubation period to ensure that equilibrium was obtained, Raman spectra of trapped liposomes were recorded, and a background spectrum obtained as normal. We performed analyses on three solutes, ethanol, dimethyl sulfoxide (DMSO) and hexafluoroisopropanol (HFIP). It was anticipated that the signals resulting from solutes that distributed freely throughout the sample by permeation across the lipid membrane would cancel out during the background subtraction.

This proved to be the case for DMSO and ethanol. For HFIP however, a clear tendency to partition into the membrane was observed, as the Raman spectrum following background subtraction continued to display clear signals for this solute (Figure 6).

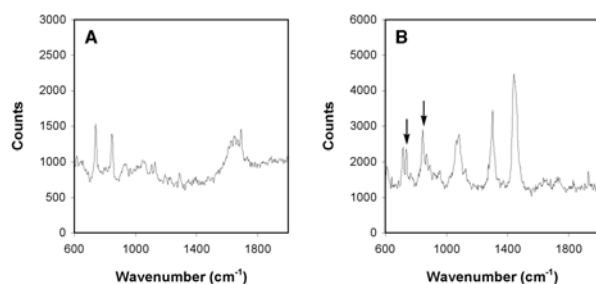


Figure 6. Raman spectra of 2.5% v/v HFIP/PBS (A) and DMPC liposomes following incubation in 2.5% v/v HFIP/PBS (B). Peaks arising from HFIP at 740 cm^{-1} and 846 cm^{-1} are indicated by arrows.

Conclusions

From our data we have shown that Raman analysis of the lipid contents of optically entrapped liposomal membranes is a feasible methodology that can provide analytical data under physiologically relevant conditions that do not denature the membrane structure. Furthermore, these conditions are suitable for measurement of dynamic processes such as solute partitioning that would not be possible by any methodology that would require liposome processing (lyophilisation, centrifugation, dialysis or gel filtration) prior to analysis.

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Characterisation of DNA damage induced by near infrared multiphoton absorption

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Introduction

When cells are exposed to radiation serious cellular lesions are introduced into the DNA. These include random double strand breaks (DSB), single strand breaks (SSB), base damage and clustered damage sites, a specific feature of radiation induced DNA damage. It is known that DNA bases absorb maximally in the UVC wavelength range (200-290nm), resulting in the formation of bulky lesions and complex DNA DSB sites. This complex damage has long been thought to be a critical determinant leading to loss of genome stability^{1,2}. It has previously been shown using 254nm UV excitation that DSB are formed in cells in the presence of BrdU and an intercalator dye³. BrdU is an analog of thymidine and can be integrated into newly synthesised DNA during cell proliferation in place of thymidine. If cells with BrdU are exposed to a NIR ultrashort pulse laser that through multiphoton processes gives an equivalent to a 254 nm UV photon in the presence of Hoechst dye, double strand breaks are introduced into the DNA by the tightly focused laser pulse.

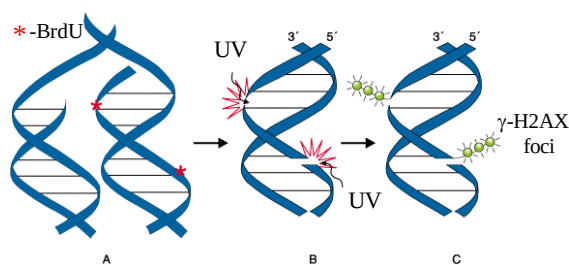


Figure 1. Schematic diagram showing the induction of a DSB followed exposure to UV in BrdU incorporated DNA.

Recently, the substantial phosphorylation of the histone H2AX has been identified as an early step in the response of cells to DSB^{4,5,6}. This response has been used to investigate DSB formation following low LET radiation in a number of studies^{7,8}. H2AX, a 14kDa protein, is one of three conserved H2A histones and comprises 2-10% of the H2A complement in mammalian tissues⁹. Phosphorylation of serine 139, a residue within a conserved carboxy terminus motif (SQ(E/D)-(I/L/Y)), yields the modified γ -H2AX protein⁹. The decay of ¹²⁵I incorporated into genomic DNA¹⁰ has revealed a close correlation between the induction of γ -H2AX foci and the number of predicted DSB events.

We previously undertook preliminary experiments to characterize the DNA damage induced in mammalian cells by near infrared multiphoton processes using the comet assay to visualise SSB and γ -H2AX as a marker of DSB. One of the aims of this current work was to further characterise and quantify the DNA damage induced within cell nuclei via multiphoton absorption. Unlike multiphotonic excitation where the wavelength of the photon must match an electronic absorption band of the molecule under study multiphoton processes occur when a molecule interacts with two or more photons that sum to provide an equivalent quanta of energy to create the electronic excited state or, as in some cases, a photoinitiated species. Table 1 lists the NIR photon energies used in this work and correlates these in terms of two or three photon equivalents. Three photons absorbed by a molecule in a

stepwise fashion from a 750 nm laser source is equivalent in energy to a single photon from a 250nm source being absorbed.

Energy/Photon (eV)	λ /nm	Two photon λ /nm equivalent	Three photon λ /nm equivalent
1.73	715	359	238
1.70	730	365	243
1.65	750	376	250
1.59	780	390	260
1.55	800	400	267

Table 1. Multiphoton irradiation wavelength and single photon equivalents.

In this study we investigated the induction and subsequent repair of DNA DSB induced in individual mammalian cells by multiphoton near infrared irradiation, in the presence or absence of BrdU and Hoechst dye.

Material and Methods

Cell Culture

Mammalian cells (V79-4 cells) were maintained in DMEM supplemented with 200mM L-glutamine, 10U/ml penicillin/streptomycin, 10% FCS and grown at 37°C in a humidified incubator under 5% CO₂, exhibiting doubling times of ~12 hours. Cultures of cells were maintained in exponential growth by routine passage. 2×10^5 cells were seeded into 2.5 μ M hostaphan dishes 40 hours prior to irradiation.

BrdU Incorporation and Hoechst Dye

Cells were cultured with 10 μ M of BrdU in the medium for 24 hours prior to irradiation. Hoechst dye (#33258) was added to the medium 10 minutes prior to irradiation.

Multiphoton Irradiation

Exponentially growing cells (47% S-phase, 45% G0/G1-phase) plated on hostaphan dishes were placed into a cooling rig and cooled to 4°C for 10 minutes. The irradiation was carried out at 10°C. A 1cm x 1cm area at the centre of the dish was irradiated by raster scanning using a 100 femtosecond pulsed Tsunami Titanium:Sapphire (Ti:S) laser. The near infrared (pseudo UV) light was focused in the cell nucleus and generated by multiphoton reactions. Following irradiation the medium was removed, the cells rinsed with 1X PBS and analysed for DNA damage.

γ -Irradiation

Exponentially growing cells (47% S-phase, 45% G0/G1-phase) plated on hostaphan dishes were exposed to 10 Gy γ -irradiation (Cobalt⁶⁰) at a dose rate of 2.9 Gy/min. Following irradiation the medium was removed, the cells rinsed with 1X PBS and analysed for DNA damage.

γ -H2AX Assay

Following irradiation the dishes were placed in an incubator at 37°C for the required repair time. Cells were fixed for 30 minutes in 3% paraformaldehyde dissolved in 1X PBS at 4°C. Fixed cells were rinsed in 1X PBS and permeabilised with

ice cold 1% Triton X-100 in 1X PBS for 8 minutes at room temperature. Cells were blocked for 1 hour in 1% fish skin gelatin (FSG) and 1% bovine serum albumin (BSA), rinsed and incubated with the primary antibody (anti-phospho H2AX ser139 rabbit monoclonal antibody, 5 μ g/ml) raised against γ -H2AX for 1 hour at room temperature. Cells were then rinsed in 1X PBS, blocked for 1 hour in 1% FSG and 1% BSA and incubated with the secondary antibody (fluorescein conjugated F(ab')₂ fragment goat anti-rabbit IgG, 7.5 μ g/ml) for a further 1 hour at room temperature. Cells were rinsed and mounted with vectashield, an antifade medium. Images were captured using a BioRad MRC 600 confocal microscope with 488nm FITC excitation and a x60 oil objective. Images were analysed using Quantity One software (BioRad).

Foci Quantification using Quantity One software

Control samples were transformed using Quantity One software allowing any background to be reduced. Once settings were established using a control, all of the samples were transformed to the same settings. Using the volume contour tool we captured information on the foci (black pixels) present within each sample for a given dose and time point. Optimisation for quantification of the foci has been described in detail (Leatherbarrow *et al.*, paper in preparation). The area of each pixel visualised in Quantity One is 0.079 μ m².

Results

Previously the experimental set up was optimised by investigating (I) temperature of irradiation to minimise DNA damage repair and (II) changing the raster steps of the irradiation stage to optimise the number of cells irradiated (Reference 12). Additionally we were able to visualise the induction of both SSB and DSB in mammalian cells following NIR absorption, using the Comet assay and the γ -H2AX assay respectively.

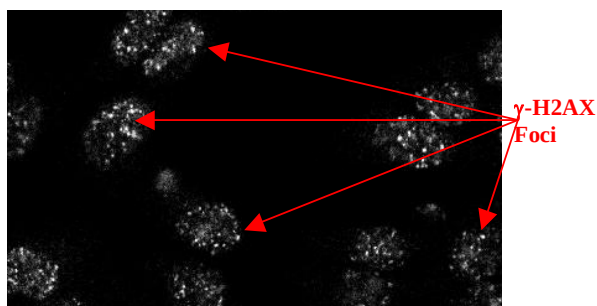


Figure 2. V79-4 cells showing induced γ -H2AX foci following exposure to 1 Gy γ -irradiation (⁶⁰Co).

In our recent study we used the γ -H2AX assay, an immunofluorescence assay capable of detecting DSB, to determine DSB induction in mammalian cells following incorporation of BrdU into the DNA. We exposed V79-4 cells to 730nm multiphoton irradiation and 365nm single photon irradiation in the presence or absence of Hoechst dye. The Hoechst dye/BrdU/DNA complex should absorb maximally at 365nm or 3.4eV, the energy of which can be generated by a single 365nm photon or 2 photons absorbed sequentially at 730nm. Note the 2 and 3 photon excitation cross sections are typically of the order of $\sim 10^{-51}$ and 10^{-75} cm⁴s photon⁻¹ respectively. Thus, 2 photon can be more readily achieved and hence more specific to nucleic acid bases.

Thus we expect to see the greatest levels of DNA damage as detected by immunofluorescence in the samples with BrdU incorporated into the DNA in the presence of Hoechst dye. However, as can be seen in Figure 3, DNA DSB, indicated by lines formed along the raster scanning of the laser, are only seen in some of the cells. Although there is a significant level of

damage throughout the cells, indicated by foci formation irrelevant of the raster path, in much the same way as we see in the γ -irradiated samples.

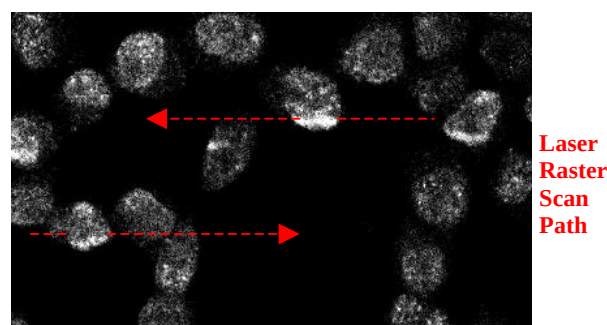


Figure 3. Induction of γ -H2AX foci following multiphoton irradiation in V79-4 cells with BrdU incorporated in the presence of Hoechst dye #33258 (730nm, 25mW, 12 μ m raster steps, 20 minutes post-irradiation at 37°C).

Instead we see a greater level of damage along the laser's raster path in samples without BrdU but in the presence of Hoechst dye (Figure 4). Although the dye will be ubiquitously found throughout the cells the damage, detected as γ -H2AX foci, appears to be mainly confined to the raster path. We also studied the repair of DNA DSB as indicated by the disappearance of the immunofluorescent lines and foci. The lines appeared strongly after 20 minutes incubation time at 37°C and remained strong throughout the first hour of repair. Post 1 hour the lines formed began to fade and after 24 hours the cells showed only low levels of DNA damage.

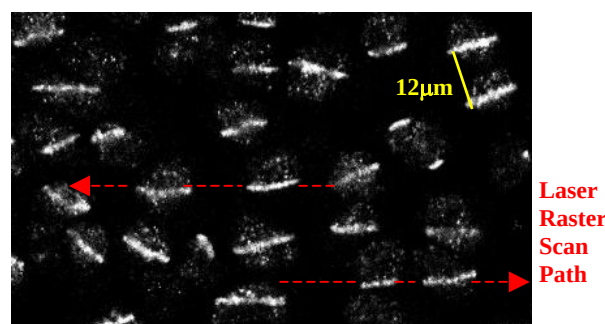


Figure 4. Induction of γ -H2AX foci following multiphoton irradiation in V79-cells in the presence of Hoechst dye #33258 (730nm, 4mW, 12 μ m raster steps, 20 minutes post-irradiation at 37°C). The cell nuclei are seen to rotate within 20 minutes post-irradiation, as shown above.

The DNA damage induced following multiphoton irradiation was quantified and compared to the damage induced following γ -irradiation. At 20 minutes post 1Gy of γ -irradiation the average foci size was found to be 0.2 μ m², Reference 11. However, at 20 minutes repair time (37°C) post multiphoton-irradiation (730nm, 4mW, 12 μ m raster steps) the width of the induced immunofluorescent lines was found to be 0.3 μ m. The multiphoton confocal irradiation site is of the femtolitre volume scale. However, the area of induced damage in each cell is significantly larger than the original irradiation area of the laser. The Hoechst dye, once excited by UV, will induce SSB in the DNA. If two or more SSB are induced in close proximity they will form a DSB and be detected by the γ -H2AX assay. With the dye in excess and found ubiquitously in the samples this may in part explain the additional DNA damage observed in the multiphoton irradiated samples. Further studies will be completed to establish this as a DNA damage pathway.

Conclusions

From the experimental studies carried out to date we have established a DNA damage induction profile using NIR multiphoton processes. We have investigated the formation of DNA DSB through immunofluorescent technology in the presence and absence of incorporated BrdU and an intercalator dye. These studies are currently on going. Future studies will enable us to further investigate the processes involved in the induction of DNA damage and its repair. We will also focus on the repair of DNA damage sites based on their spatial distribution, using immunofluorescence assays and software development, and various repair deficient mutant cells.

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Properties of the excited triplet state of 5-hydroxytryptophan

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Introduction

5-Hydroxytryptophan (5HT) and related molecules such as serotonin have a red-shifted absorption compared with that of tryptophan, and so may be selectively excited in the presence of proteins^{1,2}. Substitution of a single tryptophan residue in a protein with 5HT allows specific investigation of the structure and dynamics of that residue by fluorescence depolarisation and ODMR^{3,4}. The triplet state of tryptophan has been characterised by transient absorption spectroscopy and found to have a lifetime of about 10^{-5} s in deoxygenated aqueous solution^{5,6}. It is rapidly quenched by partial electron transfer to electron acceptors such as oxygen and disulfides. The phosphorescence of tryptophan in aqueous solution with $\tau > 1$ ms may be detected even at room temperature and has been used to investigate proteins^{7,8}, but appears to be formed by a complex mechanism⁹. Phosphorescence from 5HT has also been observed in rigid media at low temperature, but is much shorter-lived than from tryptophan in water above 273 K⁷.

The transient species formed upon excitation of 5HT are being investigated in relation to the visible emission ('hyperluminescence') observed on multiphoton near-infrared excitation^{10,11}. We have now observed the triplet excited state of 5HT by laser flash photolysis at 308 nm, and have investigated singlet oxygen formation and quenching by 5HT.

Results and Discussion

a) Laser flash photolysis

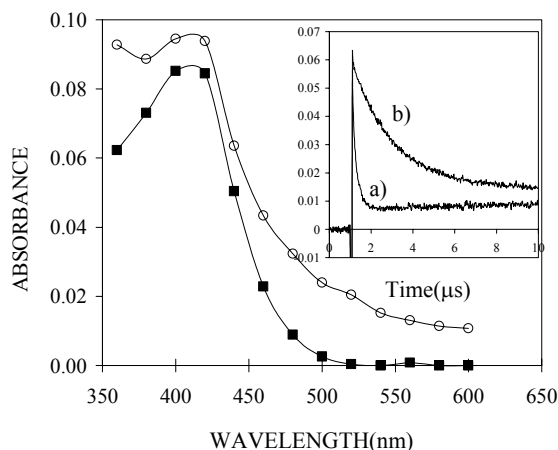


Figure 1. Transient absorption spectra from laser flash photolysis of 5-hydroxytryptophan (0.2 mmol dm^{-3}) in oxygen-saturated solutions at pH 7, measured at 200 ns ($\circ$) and 8 ms ($\blacksquare$) after the laser flash. **Inset:** transient decays at 480 nm in a) oxygen-saturated solution and b) nitrous oxide saturated solution.

Laser flash photolysis of 5HT at 308 nm in deaerated aqueous solution at pH 7.0 resulted in the transient spectra shown in Figure 1. Photoionisation of 5HT, observed previously¹¹, leads to the formation of the 5-indoxyl radical with λ_{max} 400-420 nm and the hydrated electron, λ_{max} 720 nm, which decays rapidly (Figure 1, inset, trace a) by reaction with oxygen ($k = 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). The results of a similar experiment in N_2O -saturated solutions are shown in Figure 2. Although the

hydrated electron is also rapidly scavenged by nitrous oxide ($k = 9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), the spectra show an additional spectral component with λ_{max} 480 nm and which decays with a lifetime of ca. 2 μs (Figure 1, inset, trace b)). This species is rapidly quenched by oxygen ($k = 6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, Figure 2, inset). In solutions containing β -carotene the decay was accelerated with the formation of an absorption at 500-520 nm (results not shown). Since β -carotene is recognized as an efficient triplet state quencher, but cannot be directly excited to the triplet state¹², it is concluded that the transient species with λ_{max} 480 nm is the triplet state of 5HT. The triplet was similarly observed in deaerated methanol and dimethylsulfoxide with lifetimes of 0.56 and 4.0 μs respectively.

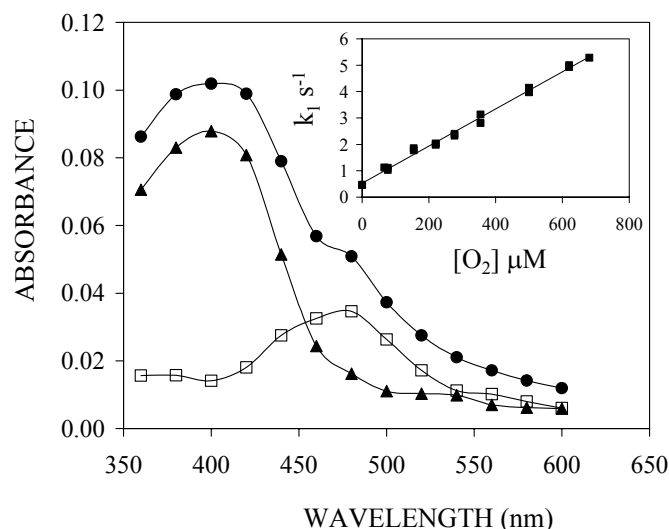
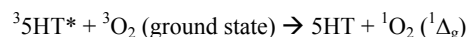


Figure 2. Transient spectra from flash photolysis of 5HT (0.2 mmol dm^{-3}) in N_2O -saturated solution at pH 7 measured 200 ns ($\bullet$) and 6 μs ($\blacktriangle$) after the laser pulse. The difference between the 200 ns and 6 μs spectra is also shown ($\square$). **Inset:** first order rate constant (k_1) for decay of the 480 nm absorption versus oxygen concentration in solutions saturated with oxygen/ N_2O mixtures.

b) Formation of singlet oxygen

The possibility of triplet energy transfer from 5HT to oxygen



to form the $^1\Delta_g$ excited singlet state was investigated by observation of time-resolved luminescence at 1270 nm from solutions of 5HT on excitation by 10 ns pulses at 308 nm from a XeCl excimer laser.

Luminescence intensities, extrapolated back to the laser pulse, were measured from solutions of 5HT with a range of absorbance values at 308 nm, and compared with luminescence from solutions of rose bengal. The quantum yield for singlet oxygen formation from rose bengal has previously been determined to be 0.76¹³.

The results shown in Figure 3 indicate that singlet oxygen near infrared luminescence is observed on pulsed excitation of 5HT

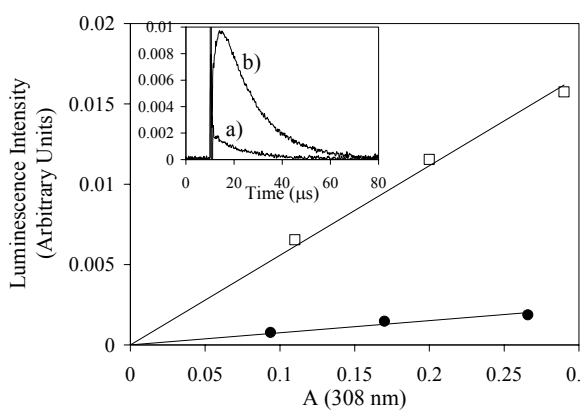


Figure 3. Singlet oxygen luminescence extrapolated to the time of the laser pulse from solutions of 5HT (●) and rose bengal (□) versus absorbance at 308 nm. **Inset:** time-resolved singlet oxygen decays on pulsed laser excitation at 308 nm of from solutions of 5HT ($A_{308} = 0.27$, a) and rose bengal ($A_{308} = 0.29$, b)).

in solutions in D_2O/H_2O (80/20 v/v) buffered with phosphate to pD ~ 7 . That the observed luminescence originates from singlet oxygen is confirmed by the determination of the lifetime of 18 μs , consistent with literature values¹⁴⁾ and is the same as from the solutions of rose bengal. The results in Figure 3 indicate a quantum yield for formation of singlet oxygen from 308 nm excitation of 5HT of 0.10 ± 0.01 .

c) Singlet oxygen quenching by 5HT

The aromatic and sulfur-containing amino acids are recognized as important quenchers of singlet oxygen in biological systems¹⁴⁻¹⁶⁾. The ability of 5HT to quench singlet oxygen was therefore investigated from the effect of 5HT on the lifetime of singlet oxygen formed by pulsed laser excitation of rose bengal at 532 nm. Figure 4 shows the second order plots between 15° and 65° C.

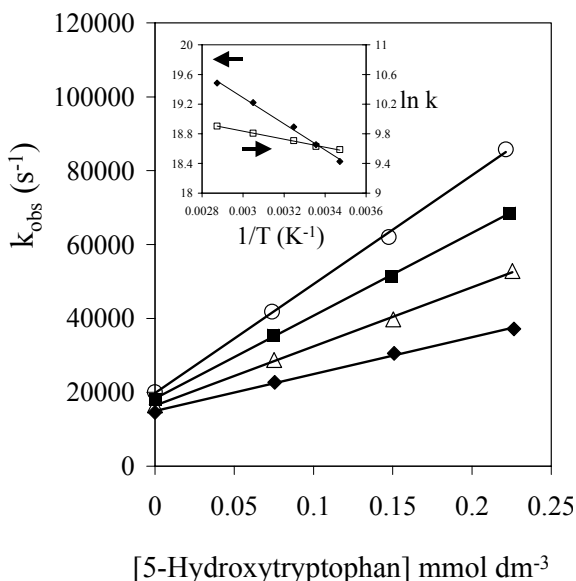


Figure 4. Effect of 5HT concentration on the first order rate constants for singlet oxygen decay in aqueous solution at pH 7 and 15° C (◆), 25° C (Δ), 45° C (■) and 65° C (○). **Inset:** Arrhenius plots for quenching by 5HT (▲) and decay of singlet oxygen alone (□).

At 25° C the second order rate constant for quenching of singlet oxygen by 5HT is $1.3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This is higher than the equivalent rate constants for tryptophan ($4.1 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and tyrosine ($8.5 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) at neutral pH and is consistent with the lower one-electron reduction potential of the indoloxyl radical at pH 7 (640 mV) compared with those of tryptophan (1080 mV) and tyrosine (760 mV). The Arrhenius plots provide the entropy ($-48 \text{ J K}^{-1} \text{ mol}^{-1}$) and enthalpy (12.5 kJ mol^{-1}) of activation and reflect the reversible formation of an exciplex as the quenching mechanism¹⁷⁾.

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Time-resolved depolarisation of ultraviolet and visible luminescence from 5-hydroxytryptophan using multiphoton excitation

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Introduction

The unusual luminescence that is produced on multiphoton excitation of 5-hydroxytryptophan (5HT) is described as “hyperluminescence” and comprises a green emission with a maximum at ~500 nm, compared with the normal one-photon induced fluorescence in the ultraviolet at ~340 nm¹⁾. A similar luminescence was also observed on a nanosecond photolysis employing a 308 nm XeCl laser pulse, followed by excitation at 430 nm using a dye laser pulse²⁾. Shear et al.³⁾ have reported visible fluorescence on multiphoton NIR excitation from several other neurotransmitter molecules in addition to 5-hydroxytryptophan. However, the elusive species responsible for hyperluminescence is yet to be discovered.

There are several advantages of multi-photon excitation in fluorescence microscopy for three dimensional imaging in live cells of cellular systems including reduced degradation and phototoxicity in cells, and reduced interference from background fluorescence. Brindle and co-workers⁴⁾ have been successful in labelling proteins intracellularly with 5-hydroxytryptophan instead of the usual tryptophan, and have studied intracellular location of the labelled protein by fluorescence imaging with multiphoton excitation. Studies of 5-hydroxytryptophan-labelled protein mobility in cells would be greatly extended using time-resolved fluorescence anisotropy measurements. Multiphoton excitation may result in enhanced photoselection processes^{5,6)}, leading to increased values of the initial anisotropy value (r_0). In these experiments we determined the number of photons involved in excitation of both normal UV fluorescence and hyperluminescence from 5-hydroxytryptophan over a range of wavelengths from 315 nm to 810 nm. Time-resolved fluorescence measurements of both emissions have been similarly studied in aqueous solutions of glycerol to provide increasing viscosities.

Materials and Methods

The multiphoton excitation experiments were undertaken with a Spectra Physics Ti-sapphire laser producing 120 fs pulses (80 MHz) between 710 and 820 nm. An OPO (APE, Germany) pumped by the Ti-sapphire laser was used to produce pulses at ~630 nm, which could then be frequency doubled to ~315 nm. The laser beam was focused at a microscope stage (Nikon TE2000) using a x40, na 0.9 objective and the emission wavelengths selected using suitable filters that were shown not to produce significant autofluorescence. Time-resolved fluorescence was detected by time-correlated single photon counting, using a photon-counting photomultiplier (Hamamatsu R3809U) connected to a Becker and Hickl PC card. Data was analyzed using Edinburgh Instruments software.

Results and Discussion

a) Power dependencies for hyperluminescence excitation

Hyperluminescence was observed on multiphoton excitation through a range of wavelengths from 315 to 810 nm. The original work on hyperluminescence from 5-hydroxyindoles by Shear et al.¹⁾ using 830 nm excitation showed that overall six photons were required. Through power modulation studies it was demonstrated that four photons were involved in the photochemical formation of an intermediate from which fluorescence was excited by two further photons. Figure 1

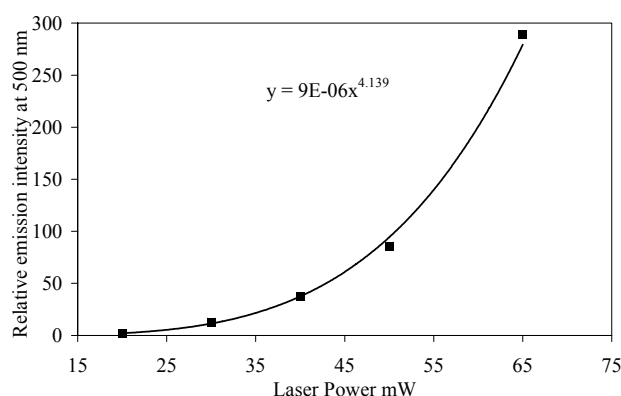


Figure 1. The power dependence of 500 nm hyperluminescence from 5HT on excitation at 628 nm, with the solid curve showing the weighted fit using the power dependence shown.

shows the power dependence for emission at 500 nm on excitation at 628 nm and indicates that the hyperluminescence is excited through an overall four-photon process. It is concluded that the intermediate is created by two photons at this wavelength, since two further photons at 628 nm must be required to excite the luminescence at 500 nm. At 410-420 nm, the power dependence also indicates an overall 4-photon process, whereas at 315 nm the power dependence demonstrates a 2-photon excitation. Between 755 nm and 810 nm a six photon process was indicated in agreement with the original results of Shear et al.¹⁾. The efficiency of excitation decreases with the number of photons required for excitation. Hence anti-Stokes excitation at ca 600-630 nm is expected to be less damaging in cellular systems.

b) Time-resolved fluorescence anisotropy decays

The rotational correlation time (Φ) for a sphere obtained from the Stokes-Einstein equation depends on the volume of the

$$\Phi = \eta V / RT \quad 1)$$

sphere (V), solvent viscosity (η) and temperature (T). The rotational correlation time (Φ) may be measured experimentally from the decay of fluorescence anisotropy (r) and the fluorescence lifetime (τ).

$$r = r_0 \exp(-\tau / \Phi) \quad 2)$$

On one-photon excitation, the value of the initial anisotropy (r_0) is generally determined by the angle between excitation and emission dipoles in the fluorophore, but might be expected to be increased in magnitude on multiphoton excitation^{5,6)}.

Figure 2 shows the fluorescence anisotropy decays for hyperluminescence emission (500 nm) from solutions of 5-hydroxytryptophan in viscous solutions water and glycerol on multiphoton excitation at 315 nm and at 755 nm. On excitation at 315 nm (2-photon) the initial anisotropy is positive, whereas on 755 nm excitation (6 photons) the r_0 becomes negative and with a larger value. A similar reversal in the sign of r_0 on multiphoton near-infrared excitation of

N-acetyl-L-tryptophanamide has been observed by Gryczynski et al.⁷⁾.

Analysis of the decay of fluorescence anisotropy, such as the data in Figure 2, to give values of the rotational correlation time of the fluorophores may then be used to compare the molar volumes of the emitting species according to Equation 1), assuming that the molecules are approximately spherical. Data from time-resolved anisotropy decays determined using the hyperluminescence at 500 nm from 5HT, are shown in Figure 3. The slope gives a molar volume for fluorescing photoproduct from 5-hydroxytryptophan of $151 \pm 19 \text{ cm}^3 \text{ mol}^{-1}$. This appears to be considerably larger than the reported value for 7-azaindole in water ($60 \text{ cm}^3 \text{ mol}^{-1}$)⁸⁾.

The results shown here suggest that time-resolved fluorescence anisotropy measurements using the hyperluminescence from 5-hydroxytryptophan and serotonin may be used to provide information on molecular mobility and flexibility in cellular systems. The use of shorter wavelengths, such as in the region of 620 – 630 nm, may be used to provide hyperluminescence more efficiently using fewer photons than required at 755 nm, and therefore potentially requires lower laser power and will be less damaging to cells.

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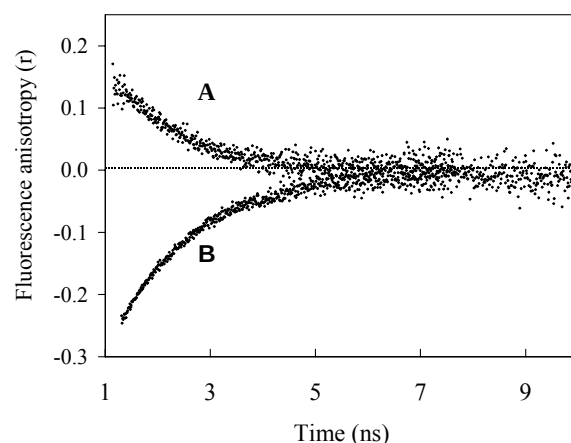


Figure 2. Time-resolved anisotropy decays for fluorescence at 500 nm from solutions of 5HT in an aqueous solution of glycerol with viscosity of 21.5 poise. Excitation at A, 315 nm, B, 755 nm.

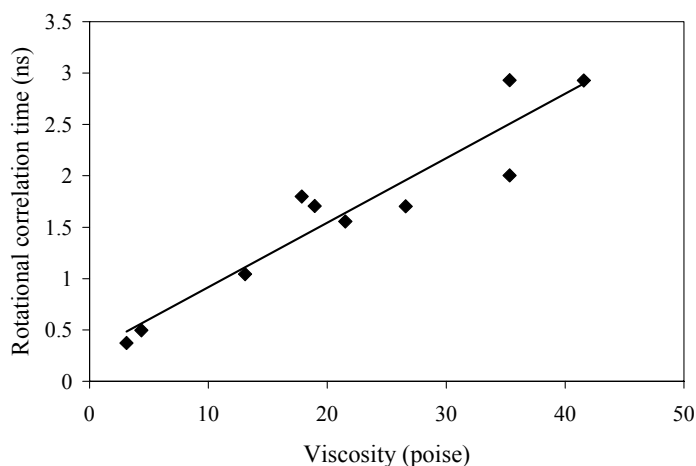


Figure 3. Rotational correlation times plotted against viscosity in water-glycerol solutions of 5HT (2 mmol dm^{-3}). Fluorescence was excited at 755 nm and emission was measured at 500 nm .

Optical control of the quantum state distribution of Rydberg wave packets in Na and NO

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Introduction

Since the first observations of Rydberg wave packets in atoms¹, and more recently in molecules², there has been an increasing interest in controlling the dynamics of these simple systems. Molecular dynamics and even biological systems can be controlled by optimising laser field parameters such as phase, amplitude and intensity of the spectral components in a self-learning feedback loop. However, the resulting pulse shapes can be extremely complex and much of the underlying physics cannot be extracted due to this complexity. One is therefore tempted to revisit some of the more simple systems, such as electron wave packets in atoms, where one can fully determine the quantum interfering paths and wave packet dynamics. This report describes two experiments that exploit electronic and molecular phase to control the quantum-state distributions of Rydberg wave packets in Na and NO.

1. Controlling the electronic orbital angular momentum composition of a Rydberg wave packet in Na

Almost two years ago, we demonstrated that it was possible to control the orbital angular momentum character of an electron wave packet, which was initially created from a superposition of *s* and *d* Rydberg series, using sequences of phase-locked laser pulses³. By an intelligent choice of phase, which depends on the excitation energy and the quantum-defects, we were able to selectively pump down either all, or a fraction of one or other angular momentum component, and by employing MQDT we were able to analyse the quantum-state distribution in detail. In this new work we have taken a new system with 'less convenient' quantum defects and employed state-selective field-ionisation (SSFI) to measure the quantum state distribution as a function of optical phase. In this new experiment, a coherent superposition of Rydberg states of Na, with average principal quantum number in the range $\bar{n} = 28-39$, is excited in a resonance-enhanced one-nanosecond plus one-picosecond ($1_{\text{ns}}+1_{\text{ps}}$) excitation process.

The output of a nanosecond dye laser (2.5 $\mu\text{J}/\text{pulse}$) is tuned to resonance with the $^2P_{3/2} \leftarrow ^1S_{1/2}$ transition in Na at 589.16 nm. The amplified output of a synchronously-pumped picosecond dye laser is frequency-doubled to generate pulses of near-ultraviolet radiation (ca. 410 nm, 20 $\mu\text{J}/\text{pulse}$) with bandwidth $\geq 15 \text{ cm}^{-1}$, which subsequently enter a Michelson interferometer to generate two delayed pulses with a precisely determined phase difference ($\pm\pi/5$). After the interferometer, the nanosecond and picosecond radiation is focused collinearly into an atomic beam of Na to excite a superposition of *s* and *d* Rydberg states converging to the Na^+ ionisation limit. Approximately 100 ns after laser excitation a ramped electric field (slew rate $\approx 700 \text{ V cm}^{-1} \mu\text{s}^{-1}$) sequentially field ionises the Rydberg states and accelerates the electrons towards a multichannel plate detector (MCP). The resultant current is preamplified and monitored on a 500 MHz digital oscilloscope interfaced to a personal computer (PC). In a typical measurement, the electron signal is summed for 1000 laser shots at each value of the optical phase-difference.

Consider the wave packet in Na composed of a superposition of *ns* and *nd* Rydberg series converging to the same ionisation limit. As a consequence of their difference in angular momentum, they can be expected to have different quantum

defects. The wave packet may be regarded as being composed of two separate components, both of which are time dependent. After some time, the pathways connecting the two angular components, i.e. the coupling between the initial *p*-state and the Rydberg states in the two series, may be expected to be phase mismatched. In this case a second optical pulse could be chosen to be in phase with one component, thus interfering constructively, and out of phase with the other, thus interfering destructively. We can quantify the dynamics of the two components by expressing each wave packet as

$$\Psi(r, t) = \sum_{nl} a_{nl} \psi_{nl}(r) \exp(-i\omega_{nl}t) \quad (1)$$

where $\psi_{nl}(r)$ is the radial wave function of the eigenstate $|nl\rangle$, $\omega_{nl} = -1/2(n - \mu_l)^2$ is its energy and a_{nl} is its amplitude in the superposition. Expanding the energy term as a Taylor's series in $\delta n = \bar{n} - n$ gives rise to a term $\exp(-2\pi i(t/t_{cl})\mu_l)$ showing that the wave packet is phase-shifted by $2\pi k\mu_l$ after *k* periods.

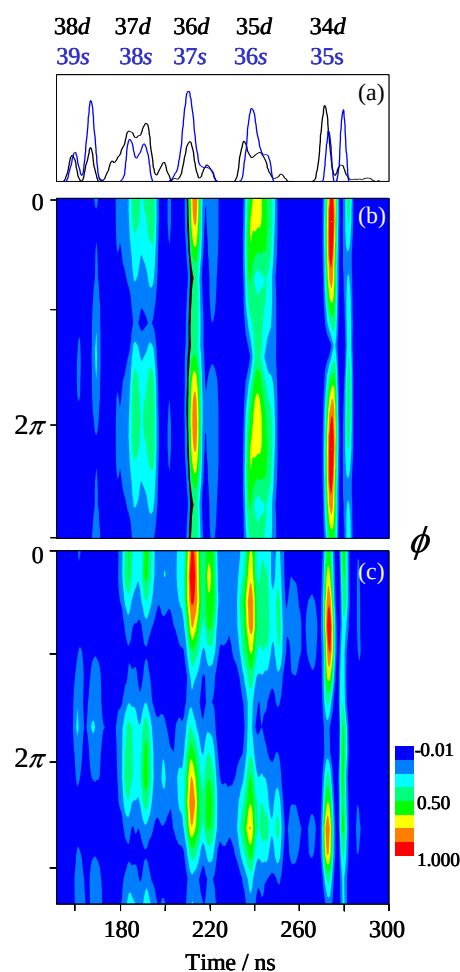


Figure 1. Calculated (b) and experimental (c) SSFI traces illustrating the phase evolution of individual *s* and *d* states in a wave packet excited around $n = 35$. The wave packet excitation was made with a pair of 0.8 ps phase-locked pulses separated by $t_2 = t_{cl} + t_\phi$. The individual states which make up the wave packet are shown in (a).

In Na, the quantum defect difference between the nd and ns Rydberg series is $\Delta\mu_l = 0.35$. Therefore, after one classical period of motion, the two angular momentum components of the wave packet will have a phase difference 0.7π . A second wave packet launched now can be tuned so that it is exactly out of phase with one angular momentum component of the wave packet but not with the other. Removing one of the angular momentum components from the wave packet has the effect of filtering out the oscillation in the angular coordinate to leave only the radial motion. The results of such an experiment are presented in Figure 1. The lower contour plot represents a set of experimentally measured electron time-of-flight traces as a function of the phase difference between two optical pulses separated by one classical orbit period. As the phase is scanned over 2π , Ramsey fringes are observed in each of the constituent Rydberg states. The Rabi frequency is dependent on the energy separation between each Rydberg state in the superposition and the $^2P_{3/2}$ 'launch' state and so the fringes in the populations of the individual quantum states are out of phase with one another. The most significant observation is made in the region of the $35s$ and $34d$ quantum states which can be seen to be phase-shifted with respect to one another. Because $\Delta\mu_l = 0.35$, when the population of the $35s$ component is minimum, the population of the $34d$ component is significant but not at its maximum. Nevertheless, the angular momentum composition of this low energy portion of the wave packet can be seen quite clearly to depend on the phase difference between the two optical pulses. To the best of our knowledge, this is the first direct observation of controlled angular momentum composition of an electron wave packet.

2. Controlling the rotational angular momentum composition of a bound Rydberg wave packet in NO

Last year we demonstrated that it was possible to control the rotational angular momentum character of a Rydberg wave packet composed predominantly of two Rydberg series associated with different rotational states of the ion core⁴). The approach exploited the 'stroboscopic effect' in Rydberg molecules⁵). In this project, we aim to control the rotational composition of a wave packet composed predominantly of three Rydberg series converging to three rotational states of the ion core. To design a coherent control scheme requires knowledge of the phase evolution of the whole system or the use of a genetic algorithm to guide the laser to the correct pulse sequence to achieve the desired outcome. This is the approach we are taking here. First, it is necessary to record a frequency resolved spectrum of the Rydberg states of interest so we have some real idea of the composition of the wave packet at a given excitation energy. We can then determine the population distribution after a sequence of k pulses A_{ω}^2 , assuming the intensity of the laser pulses is sufficiently weak that the population of the 'launch state' remains virtually unchanged

$$A_{\omega}^2 \propto \left[\sum_{N^+} a_{N^+}(\omega) e^{-2\ln 2(\omega - \omega_l)^2 / \sigma^2} \left[1 + \sum_k e^{i\Delta t_k} e^{i(\omega - \omega_l)t_k} \right] \right]^2 \quad (2)$$

We used a genetic algorithm to formulate a pulse sequence to selectively depopulate specific Rydberg series. The population ratio of the series involved is used to determine the fitness parameter. The fitness parameter is then fed back into the algorithm until the desired result is obtained.

To record the frequency spectra and set ourselves up for the coherent control, approximately 50% of a 10 Hz nanosecond Nd:YAG laser (Continuum Powerlite 8010) pumps a nanosecond dye laser (Continuum ND-6000) containing Pyridine 1. The output is then frequency tripled at a series of

crystals to produce light at around 220 nm. The remaining 50% of the nanosecond Nd:YAG pumps another nanosecond dye laser (Sirah Precisionscan) containing DCM. The output is frequency doubled to give light at around 330 nm which can then be scanned over ~ 3 -4 nm to collect a complete Rydberg spectrum from around $n = 22$ to ionisation. Both beams are combined and directed into a pulsed source of NO exciting Rydberg states below the lowest ionisation limit. The Rydberg population is then pulsed field ionised using a delayed (100 ns) pulsed electric field which also serves to guide the ions down a field free time of flight tube towards an MCP detector.

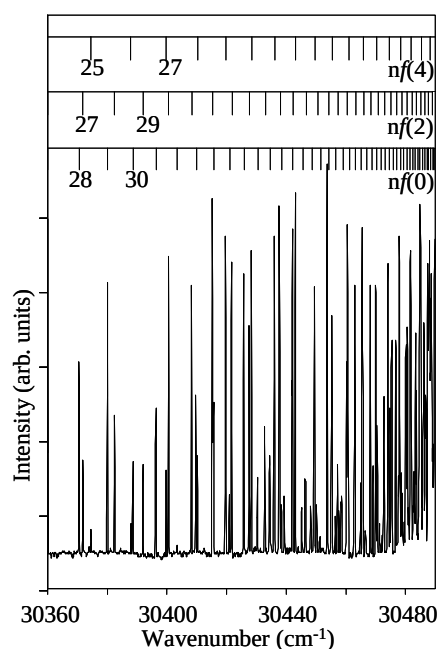


Figure 2. Frequency spectrum recorded via the $v = 0$, $N = 2$ level of the A-state. Three f series can be easily identified converging to three different rotational states of the ion core. The p states are noticeable by their absence from the spectrum, most probably due to fast predissociation to $N(4S) + O(3P)$.

Preliminary results suggest it is possible to remove two of the three Rydberg series excited in the above spectrum, with a sequence of three phase locked pulses. The correct sequence obtained with the genetic algorithm is now being analyzed to discover the exact control mechanism. By slowly building up the complexity of these systems we are beginning to build up a picture of the basic control mechanisms used in larger systems.

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Raman depth profiling in diffusely scattering media using picosecond Kerr gating

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Introduction

Diffusely scattering media are common constituents of living systems and as such are frequently encountered in many biochemical and medical spectroscopic applications. These samples are often highly heterogeneous and composed of several layers of different chemical constituents. A major challenge of analytical sciences is to provide a method capable of determining the chemical composition of these systems in a non-destructive way. Here we examine an approach that utilises temporal characteristics of Raman signals emitted from samples to perform depth profiling in turbid media. The technique can be combined with conventional confocal microscopy, where appropriate, for delivering enhanced depth separation capability. The method relies on impulsive Raman excitation and a fast temporal gating of the inelastically scattered (Raman) light collected at various time delays following the laser pulse.

Despite the extensive literature on time resolved photon migration in absorption and fluorescence spectroscopies^{1,2} there are only a few studies on Raman photon migration^{3,4,5}. In general terms, the deployment of time-resolved Raman migration methodology is more challenging than that for elastic scattering due to much lower levels of photon signals involved and the susceptibility of Raman spectroscopy to interference from fluorescence or sample damage. The inherent difficulties of the technique are partially offset by the slower decay kinetics of Raman signals compared with the elastic ones making the detection of late Raman signals, i.e. those from the deepest regions of sample, somewhat more feasible. The higher effort required when performing Raman microscopy is, however, handsomely recuperated in a form of rich chemically specific information obtainable from Raman spectra that can be indispensable in applications such as disease diagnosis.

The optical Kerr gating technique was first used to improve Raman signal contrast in diffusely scattering media in trial experiments aiming at extracting Raman signals from bone interiors and from bones inside phantoms mimicking living tissue in non-invasive way⁶. However, in these experiments, no detailed quantitative assessment of the performance was carried out. Here we present the first quantitative characterisation of the degree of Raman signal contrast improvement available using the Kerr gating technique and discuss its potential and further ways for advancement. The study was performed in back-scattering geometry, i.e. 180 degree Raman collection geometry, which is best suited for biomedical diagnostics applications. The performance of the system was characterised on two-layer systems by monitoring the improvement of Raman contrast from individual layers. A detailed account of this work is given in Reference 7.

Experimental

The Raman Kerr gated collection system is based on a high throughput 4 ps optical Kerr shutter described in detail in our earlier publication⁸. Raman scattered light was collected in backscattering geometry using a lens with $f^\# \sim 2$, unlike in the original Kerr gate design.

The probe wavelength was 400 nm, the pulse duration 1 ps, the pulse energy $\sim 5 \mu\text{J}$ and the repetition rate 1 kHz. The beam was weakly focused on sample surface to a $\sim 500 \mu\text{m}$ diameter spot size. The laser apparatus is based on a regenerative amplifier

system followed by a two pass linear amplifier (SuperSpitfire, Spectra Physics/Positive Light) providing 800 nm, ~ 1 ps, 2 mJ fundamental pulses at 1 kHz repetition rate.

To demonstrate and quantify the ability to obtain Raman signal from a deep layer we performed an experiment on a two-layer sample consisting of a 1 mm optical path cuvette of 1 cm width and ~ 4 cm height, with 300 μm custom made fused silica front and back windows, filled with PMMA (poly(methyl methacrylate)) spheres of $\sim 20 \mu\text{m}$ diameter. A tablet of trans-stilbene of approximately 10 mm diameter and 4 mm thick, formed by compression packing of stilbene powder, was placed immediately behind the back wall and centred on the optical axis of the incident laser beam. The PMMA and stilbene samples represented the first and second layers of a diffusely scattering medium, respectively. To demonstrate the recovery of a Raman signal from a thin top layer, we used a second sample in which only a 100 μm thick transparent PET (polyethylene terephthalate) foil was placed directly on the stilbene powder tablet.

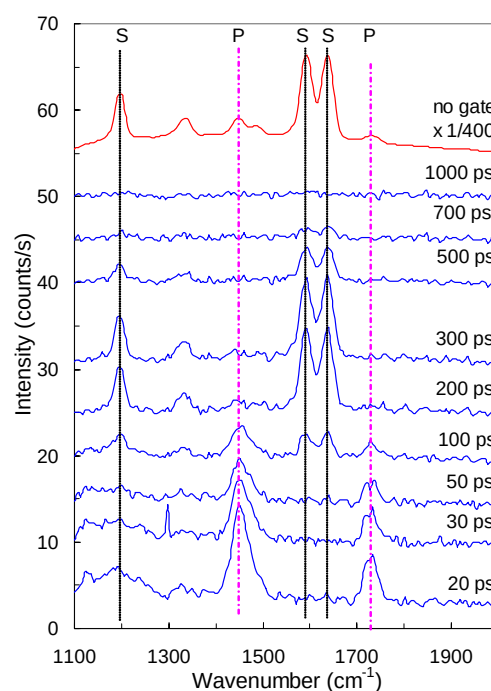


Figure 1. The Kerr gated Raman spectra of a two-layer system consisting of PMMA spheres (P) followed by trans-stilbene powder (S). The top spectrum is obtained with no Kerr gating. The acquisition time was 200 s for each spectrum.

Results

Figure 1 shows Raman spectra measured from the PMMA/stilbene two-layer system as a function of the time delay of the Kerr gate. The top spectrum is that measured without the Kerr gate and consequently contains contributions from both the layers. The early time delay spectra (up to 50 ps) are clearly dominated by the Raman spectrum of the top, PMMA layer. This is initially surprising, since in the absence of diffusion the photons would pass through a 1mm layer in just

5ps. However, because the diffusing photon wavefront progresses more slowly than the speed of light in the medium, coupled with the fact that the Raman photons are biased towards longer times⁵⁾, the net result is that below 50 ps the photons do not have sufficient time to diffuse to the second, stilbene layer and back, and therefore no Raman signal from the second layer is present. Only at 50 ps does one begin to discern a contribution from the stilbene layer with its characteristic doublet appearing at around 1600 cm^{-1} . The stilbene signal then continues to grow, peaking at around 200-300 ps from which point it gradually dies away. The PMMA signal on the other hand decays monotonically from 20 ps onwards and is largely absent above 100 ps.

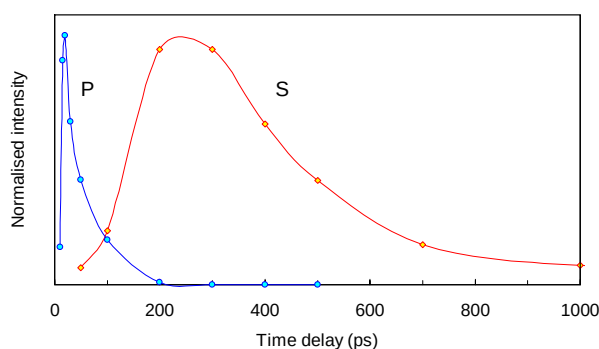


Figure 2. Normalised Raman intensity plots for PMMA and stilbene spectra as a function of Kerr gate time delay (S - stilbene, P - PMMA).

The kinetics of the individual Raman signals from each layer using the full data set is shown in Figure 2. The plot shows that Raman signals from the two layers are well separated in time. An appropriate gate time delay can therefore be used to accomplish an effective separation of the two signals from each other. The large temporal spread of the individual signals from turbid media conveniently relaxes requirements for fast Raman gate speed. In the analysis a situation where the gate opened at around 200 ps and closed at 1000 or 2000 ps following the laser excitation pulse would also provide an effective means for the rejection of the upper layer Raman signal. In fact such a gate would yield a higher signal-to-noise ratio as more of the 'desired' Raman photons would be collected as is evident from Figure 2. This fact is crucially important from a technical point of view as the rather complex optical Kerr gate system can be, in some situations, replaced with a substantially cheaper Pockels cell or gated CCD bringing any potential biomedical applications closer to the point of commercialisation. Other approaches other than Kerr gating could include streak camera and single photon counting detection.

Each experimental condition, however, has to be assessed on its own merits as samples that are thinner, or consisting of more diluted scattering centres will require shorter gating times. In addition, if fluorescence poses a problem then the gate opening time will also have to be optimised with respect to its lifetime and the location of its source within the sample to ensure that fluorescence rejection capability is retained.

To quantify the degree of improvement of Raman signal contrast from individual layers we obtained higher-quality Raman spectra for time delays 20 and 300 ps using longer acquisition time (1200 s per each time delay). The analysis revealed that the ratio of P/S signal was at least five times lower in the spectra with the Kerr gate than that in the spectrum with no gate. In other words, the stilbene spectrum at 300 ps contained at least five times lower relative contribution from the upper PMMA layer than that with no gate. This value is noise limited with the actual improvement likely to be still higher.

To demonstrate the ability to separate a surface thin film signal from an overwhelming substrate Raman signal we performed an

experiment on a thin PET foil placed in direct contact with a stilbene powder sample. This configuration also very closely mimics the retrieval of Raman signal from the very surface of diffusely scattering medium. The measurement yielded the improvement of the PET film-to-stilbene Raman spectrum intensity ratio by a factor of ~ 1200 .

The Raman Kerr shutter used in this study was originally developed to separate Raman signal from fluorescence backgrounds. It is noteworthy that this capacity is still retained in diffusely scattering media although, depending upon the experimental conditions, this performance can be compromised by large temporal spread of Raman signals that can, in some cases, become comparable to the lifetime of fluorescing species. In this case a broader temporal gate might be more effective in recovering sub-surface signals, albeit with poorer depth resolution.

Conclusions

We demonstrate that impulsive Raman excitation (~ 1 ps) followed by fast optical Kerr gating (~ 4 ps) can be used as an effective method to separate Raman signals originating from different depths in heterogeneous diffusely scattering media. The technique was shown to be capable of separating deep layer Raman signals from those of an over-laying matrix, as well as vastly improving the ratio of surface to bulk Raman signal. Both these features are crucial for many biomedical applications where monitoring sub-surface tissue layers normally would require destroying surface tissue or to surface applications where underlying substrate Raman signal interferes with surface Raman spectrum.

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Raman photon migration in turbid media

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Introduction

Although there is an extensive literature on time resolved photon migration in absorption and fluorescence spectroscopies^{1,2)} only a few studies have appeared on Raman photon migration^{3,4,5)}. However, all Raman spectra of turbid materials are acquired under conditions where photon migration is important, so it is necessary to understand how this affects parameters such as sampling depth and temporal response. In previous work, Rayleigh and Raman signals were found to decay over a period of tens to hundreds of picoseconds after the incidence of a picosecond laser pulse on a powdered sample⁴⁾. The Rayleigh signal was shown to decay (approximately) according to $t^{-3/2}$ kinetics, which is consistent with a migration model for the propagation of photons away from the laser focus in an infinite medium. The Raman signal decayed more slowly ($\sim t^{-1/2}$ kinetics). A semi-quantitative explanation for this was given, based on the fact that the probability of generation of a Raman photon is proportional to the time that a laser photon propagates within the powder.

Monte Carlo Modeling

It was clear at an early stage that more sophisticated modeling was required to understand the details of the Raman and Rayleigh temporal response curves, and to use them to interpret data in terms of the structure of layered materials. To this end, we have applied Monte Carlo modeling to predict the temporal kinetics of the Rayleigh and Raman signals under photon migration conditions⁵⁾. The basic parameters for the model are shown in Figure 1 below.

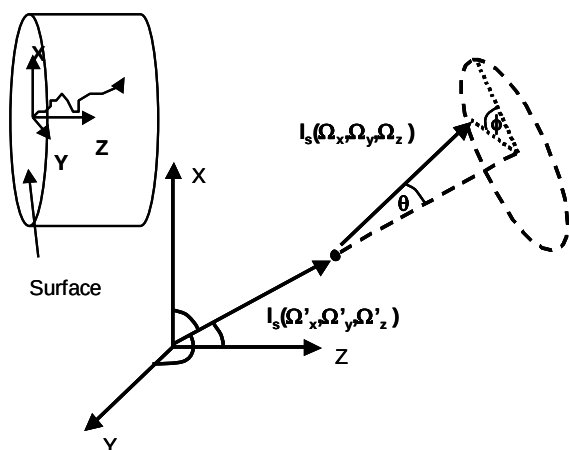


Figure 1. Monte Carlo model for Raman photon migration. The scattering length l_s is assumed constant, ϕ is random and θ can vary either randomly (isotropic scatter) or with a probability distribution that reflects forward-biased scattering.

Initially the laser photons are injected at an origin on the sample surface. The stepwise propagation of each laser photon is modeled, assuming the scattering geometry shown in Figure 1. If the laser photon leaves the sample within a defined region of the surface (termed the collection aperture) then the Rayleigh signal is incremented by one unit at the exit time, (t) . The Raman signal is computed by testing for the generation of a Raman photon each time the laser photon changes direction. If a Raman photon is generated the laser photon is annihilated and

the propagation of the Raman photon through the system is modeled, incrementing a counter if a Raman photon leaves the sample within the collection aperture. Full details of the model are given elsewhere⁵⁾.

Isotropic Diffusion in Infinite Sample

The model was tested using the simple case of propagation within an infinite, isotropic medium. Isotropic diffusion from a point source has a simple analytical solution for the number density at the origin, namely $t^{-3/2}$. In this situation we increment the Rayleigh and Raman counters whenever an appropriate photon is within one scattering length of the origin. Figure 2 shows the results of this computation. As well as giving the expected $t^{-3/2}$ curve for the Rayleigh signal, it confirms that the Raman decay should be much slower, i.e. $t^{-1/2}$.

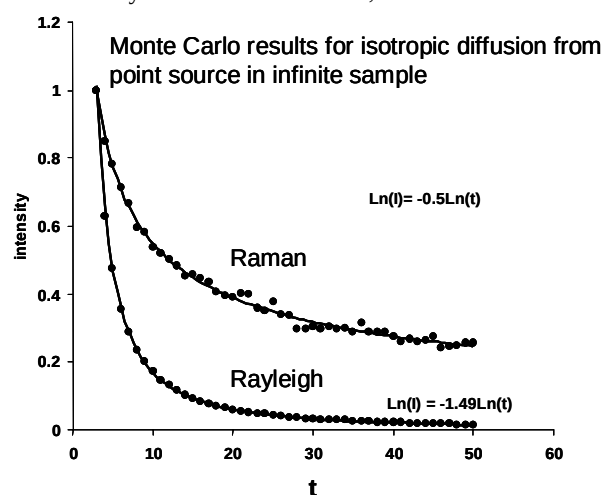


Figure 2. Computed Raman and Rayleigh decays in isotropic medium (t =number of scattering events). The best fits for the temporal exponents are shown.

Scattering in Semi-Infinite Sample

Although the simple model shown in Figure 2 predicts that the Raman decay exponent should differ by c.a. 1 from the Rayleigh exponent, it is clearly unrepresentative of a real experiment on a turbid material, where the laser is focused onto the *surface* of a sample. In addition, when our original data was re-examined it was found that the magnitude of the best fit Rayleigh and Raman decay exponents varied from sample to sample and could be significantly larger than $-3/2$ and $-1/2$, respectively⁵⁾. To refine this model we need to account for the photon loss that occurs at the sample surface. This loss means that the magnitude of the decay exponents is significantly increased in practice, giving faster decays. The exact value of the exponent depends on the size of the collection aperture, the scattering length, and the scattering anisotropy g (i.e. the extent of forward scattering). With the large ($>1\mu\text{m}$) particles used in our original work⁴⁾ the scattering is expected to be highly anisotropic and forward biased ($g\sim 1$).

To show the effect of photon loss, Figure 3 shows the calculated best-fit Rayleigh decay exponents for a semi-infinite sample (still under isotropic scattering conditions, $g=0$). The exponent is the gradient of the linear regression of $\text{Ln}(I)$ against $\text{Ln}(\text{number of scattering events})$. Here the collection aperture is specified by the radius r_2 . Only those photons that leave the

sample within a radius r_2 about the laser injection point are assumed detected (i.e. this is the region that is imaged by the collection lens). Here r_2 is defined in units of l_s .

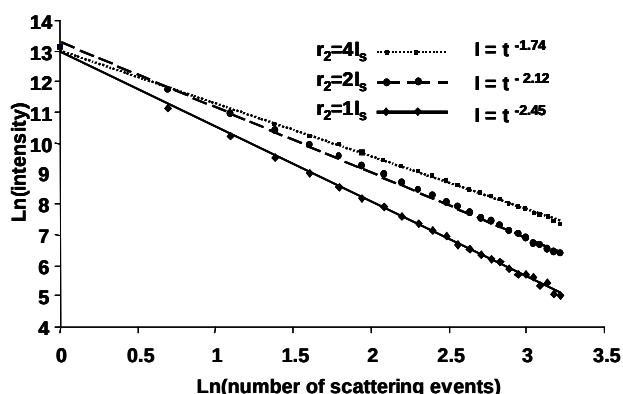


Figure 3. Dependence of Rayleigh decay exponent on size of collection aperture (r_2).

As r_2 decreases the magnitude of the decay exponent increases. The exponent of -2.45 for $r_2=l_s$ agrees well with the analytical result $(-5/2)$ for backscattering from a point source at the surface of a semi-infinite medium, in the diffusion limit⁽⁶⁾. This agreement provides further validation of the model. The decay is predicted to slow significantly as the collection aperture increases, with exponents of -2.1 and -1.7 for $r_2=2$ and $4 l_s$ respectively. This is reasonable since photons that diffuse away from the origin over time are more likely to be emitted within a large aperture than a small one. We also computed the Raman decay exponent as a function of collection aperture, and found that the absolute value of the Raman exponent was always approximately one unit smaller than the Rayleigh exponent, under isotropic scattering. Therefore we conclude that the difference between the Rayleigh and Raman exponents might be invariant with sample geometry and boundary conditions, provided scattering is isotropic.

Anisotropic Scatter and Mean Transport Length

We can calculate the expected temporal decay curves, using the scattering length as a variable parameter, so as to obtain the best fit to the observed data.

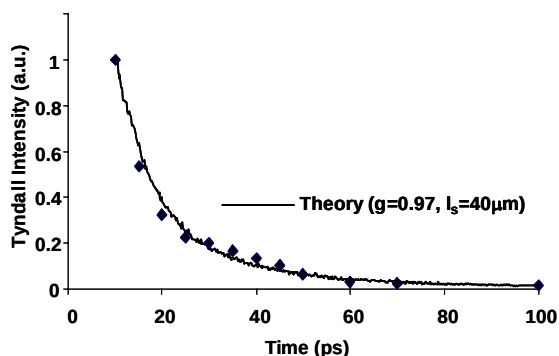


Figure 4. Fit of observed Rayleigh decay points to curve computed for semi-infinite sample on basis of $g=0.97$ and $l_s=40\mu\text{m}$.

Using the experimental data for powdered stilbene⁽⁴⁾, assuming isotropic scatter ($g=0$), we compute a mean scattering length of about $400\mu\text{m}$ ⁽⁵⁾. This is much larger than the particle sizes in the sample ($\sim 10\mu\text{m}$), indicating that the scattering is actually highly anisotropic. In other words we have computed the mean transport length (l_t), the distance over which a photon's direction is randomised through multiple scattering, rather than

l_s (the distance between scattering events). The two lengths are related via $l_t=l_s/(1-g)$.

For large particles we expect $g>0.9$ and hence $l_t>10l_s$. Figure 4 shows that the experimental data for trans stilbene was fitted reasonably well on the basis that $l_s\sim 40\mu\text{m}$, $g\sim 0.97$ and $r_2\sim 50l_s$ ⁽⁵⁾. More work is needed using samples with well-defined scattering lengths to check this model, but the fit is reasonable considering the approximations that have been made.

Conclusion: The Scope for Depth Profiling

One of the important outcomes of this work is the observation that Monte Carlo modelling can be used to compute the average penetration depths of Rayleigh photons, and the average generation depths of Raman photons, as a function of their detection time. For example, Figure 5 shows the average sampling depths computed for both photon types as a function of time (expressed as the total flight path)⁽⁵⁾. Note how the average depth is much shorter than the total flight path.

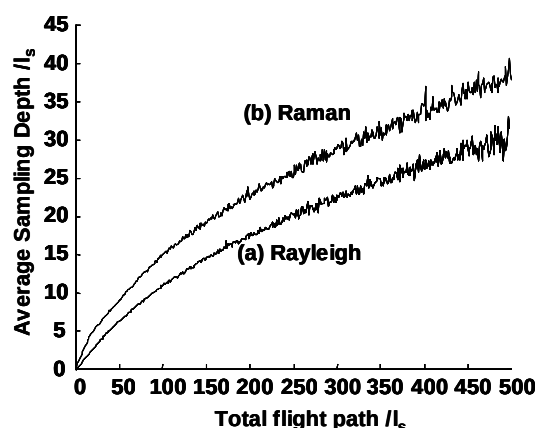


Figure 5. Depth profiling with time resolved photon migration

Figure 5 implies that by selectively varying the detection time we ought to be able to preferentially observe Raman photons that were generated at different depths. Indeed, this is found to be the case and we have recently shown how time-resolved Raman photon migration can be used to depth-profile layered systems⁽⁶⁾.

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Ultrafast reflectivity and polarisation response of noble metals determined from two colour optical pump-probe measurements

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Optical pump-probe measurements using femtosecond lasers have proven to be a very sensitive tool for the investigation of electron and spin dynamics in solids, and also provide excellent spatial resolution. Ultrafast demagnetization¹⁾, ultrafast coherent excitation of magnons^{2,3)} and phonons⁴⁾, ultrafast magnetization reversal⁵⁾, and optical orientation of spins in semiconductors⁶⁾ are examples of phenomena discovered using these techniques. Their characterization capabilities are best illustrated by extensive measurements of the electron-phonon coupling constant in metals⁷⁾ and high T_c superconductors⁸⁾, and of magnetic parameters in nanostructured magnetic materials⁹⁾. However, interpretation of the time-resolved signals has faced several problems. Particularly, in the case of the ultrafast demagnetization process, observed through the magneto-optical Kerr effect (MOKE), there has been debate about various non-magnetic contributions to the signal at short time delays¹⁰⁾. In measurements of ultrafast electron dynamics, observed through the transient reflectivity, concern has arisen that the transient reflectivity is not proportional to the change of the electron temperature as is commonly assumed⁴⁾.

We report results of optical pump-probe experiments in which a white light continuum pulse was used as the probe¹¹⁾. This has allowed us to measure the reflectivity response simultaneously over a wide spectral range. The transient reflectivity of noble metal films has been well studied and understood. On the other hand, because of their favorable transport properties, noble metals are being considered for the fabrication of heat sinks in heat assisted magnetic recording (HAMR) devices. Hence, we chose 30.6 nm and 72 nm Au, and 75 nm Cu films magnetron sputtered on to Si substrates as samples for our study. In addition, we have studied the transient optical polarization response of these samples in order to explore the possibility of optical orientation of electron spins in metal films.

In our measurements we used the frequency doubled output of a Ti:sapphire regenerative amplifier producing 200 fs pulses at a repetition rate of 1 kHz and wavelength of 800 nm. The beam was then split to generate pump and probe parts. The 400 nm pump pulse generated through frequency doubling of the fundamental had energy of 2 μ J. The other part of the fundamental was used to form a white light continuum in a 1 cm water cell. Both beams were p-polarized and focused onto the sample surface to give 200 μ m and 400 μ m diameter spots, for the probe and pump respectively. The spots were carefully overlapped, while being viewed with a CCD camera. The angles of incidence of the pump and probe beams at the sample were 35° and 30° respectively. The pump beam was passed through a delay line and reflected from an optogalvanic mirror just before the sample. The mirror was flipped between two positions at a frequency of 2 kHz so that every second pump pulse was deviated from the sample. The white probe beam was reflected from the sample and dispersed by a grating so that the different spectral components could be detected separately by a linear array detector. A 400 nm filter was placed in front of the detector in order to suppress all side contributions from the pump and original probe beams. Signals with pump on and off were subtracted, normalized, and averaged over a time interval of 10 s. The water cell introduced a chirp within the probe pulse so that red light was delayed by about 2 ps with respect to the blue. Hence, we do not consider here any effects

of the delayed onset of reflectivity signals in different spectral regions but are concerned only with the intrinsic time scales for each component. The signal at different time delays was acquired in a random order so as to remove any slowly varying background.

For measurements of the transient polarization, this detection scheme provided an inadequate signal-to-noise ratio. Hence, we used the output of an optical parametric amplifier (OPA) at a wavelength close to an interband transition as the pump, and the fundamental output of the Ti:sapphire regenerative amplifier at 800 nm as the probe. The latter was p-polarized while a variable retarder in combination with a half wave plate was inserted into the pump beam path in order to make the pump beam circularly polarized. The polarisation could be switched between right and left helicity by rotating the half wave plate by 45 degrees. The reflected probe beam was directed into an optical bridge detector that produced an output signal proportional to the angle of rotation of the probe polarization. The signal was then fed into a lock-in amplifier, with the drive signal to the galvo scanner serving as the reference input. The detector was nulled while its output was viewed using an oscilloscope. A filter at the pump wavelength was placed in front of the detector so as to block any scattered pump light.

An example of the acquired reflectivity spectra for different time delays is shown in Figure 1 for the 30.6 nm Au sample. The spectrum of the white line continuum is shown on the same plot. For very short wavelengths (about 400 nm) the probe was too weak to produce meaningful results, while at very long wavelengths it was so strong that the detectors in the array were saturated. Hence, we will not consider the signal in these latter regions. At negative time delays, the signal is zero over the entire spectral range as expected. At zero time delay, it appears first in the blue region and spans the entire range after approximately 2 ps. At later time delays, the shape of the signal is bipolar with a zero crossing point at about 555 nm for Cu, and 510 nm and 485 nm for the 30.6 nm and 72 nm Au samples. It is interesting to note that the position of the zero crossing point does not stay the same with changing time delay (inset to Figure 1). This point roughly corresponds to the interband transition threshold. However, its precise position depends also upon details of the temperature and wavelength dependence of the complex dielectric function of the sample. As the electron temperature decreases with time delay, the zero crossing point shifts towards shorter wavelengths, which is consistent with calculations in Reference 4. In Reference 12, calculations suggested that the same trend was due to the non-thermal electron subsystem. At present, we are not able to say which interpretation is more relevant to our observation. However, our data may help to identify the correct mechanism if a suitable model for the sample reflectivity is developed, since the spectra at different time delays can be analyzed without invoking a model for the electron dynamics. By averaging the signal over a wavelength range of a few tens of nanometers we can also construct time resolved reflectivity signals for different wavelengths (Figure 2). The signals were fitted to the solution of a two temperature model after assuming proportionality of the transient reflectivity to the electron temperature. This provided values for parameters such as the electron-phonon

coupling constant and the electron-phonon equilibration temperature.

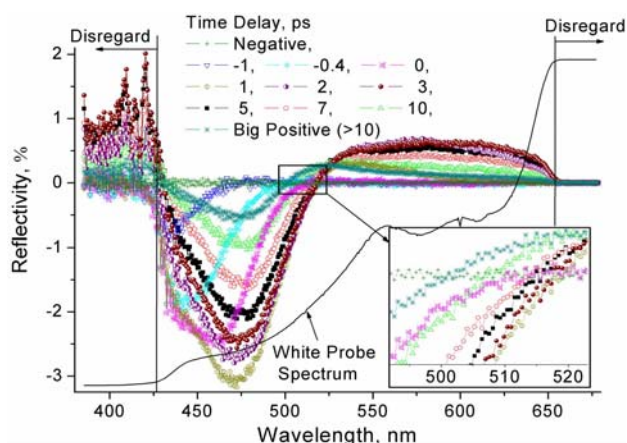


Figure 1. Transient reflectivity spectra are shown for different time delays. The white light continuum spectrum is also shown. The inset shows the position of the zero crossing point for different time delays.

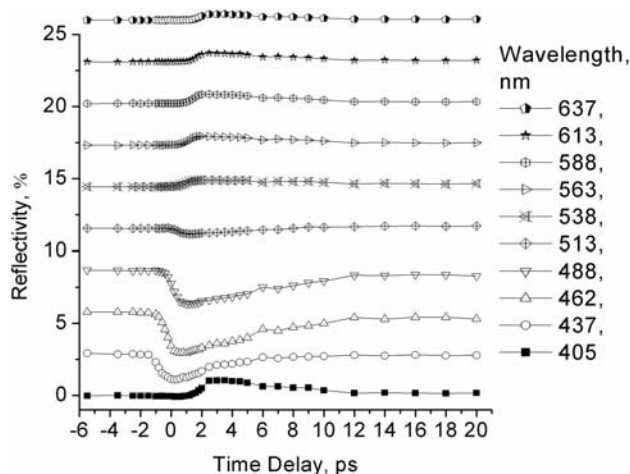


Figure 2. Time resolved reflectivity signals constructed from the spectra in Figure 1 are shown for different probe wavelengths.

These parameter values were found to depend upon the probe wavelength. This emphasizes the importance of developing a proper model for the sample reflectivity function before making any physical interpretation of the time resolved signals, particularly in the vicinity of the interband transition.

An example of the raw time resolved rotation signals is shown in Figure 3 for the 30.6 nm Au sample. The average difference of the signals for the two opposite helicities of the pump is also shown since any breakthrough of the transient reflectivity is expected to cancel out. The latter consisted only of a sharp peak at zero time delay due to the Specular Inverse Faraday Effect (SIFE). No longer lived signal was observed in any of the samples, within the signal-to-noise ratio of the apparatus.

In summary, we have measured the transient reflectivity and polarization response of a Cu sample and two Au samples of different thickness. Using a white light continuum pulse as a probe, we have been able to record reflectivity changes over a range of about 300 nm for each value of the time delay. Such data may allow the dependence of the reflectivity upon the

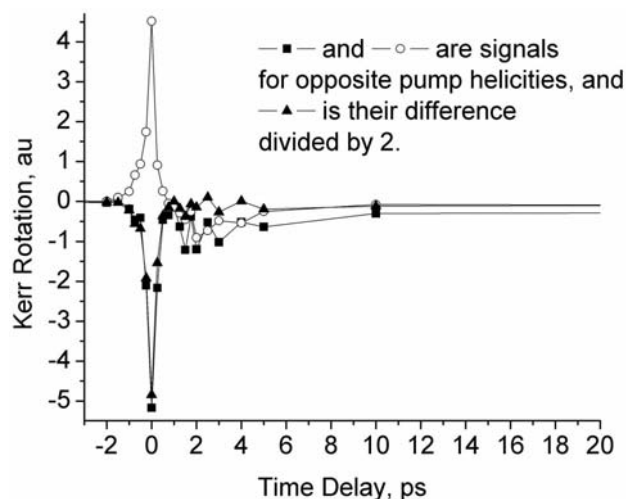


Figure 3. Time resolved Kerr rotation signals are shown for opposite pump helicities. The difference of these signals divided by 2 is also shown.

electron distribution function to be determined and, hence, allow the determination of the latter as a function of the time delay. A SIFE peak was observed in the transient polarization response of the samples, but no longer lived signal characteristic of optical orientation of spin at the Fermi level could be observed.

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Developments in novel methods for investigating excited states of molecules

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(1) Characterisation of Novel Iridium Complexes

Introduction

Six-coordinate iridium complexes have recently generated much interest due to their strong luminescence and long lifetimes. Iridium exhibits strong spin-orbit coupling, that gives rise to spin-forbidden singlet-to-triplet electronic transitions that result in efficient phosphorescence (high quantum yields). These properties make the compounds desirable as phosphors in organic light emitting diodes (OLEDs)^{1,2}. OLEDs with heavy metal complex phosphors are the most efficient OLEDs reported to date³.

Cyclometalated ligands are monoanionic and thus form neutral complexes with iridium (III) that are isoelectronic to cationic ruthenium and osmium complexes, which are widely used in photocatalysis and photoelectrochemistry. Such cyclometalated iridium complexes are therefore of particular interest.

Due to the varied applications of iridium complexes, a full understanding of their excited states is highly desirable, in order that their properties can be tuned. They are therefore potential candidates for developing the technique of time-resolved crystallography of photo-induced species. A series of seven novel cyclometalated iridium compounds were investigated for their suitability for this work. Earlier work⁴ has shown that the crystals are relatively robust upon laser irradiation. In this paper we present the photophysics of the compounds, which is essential information for deciding whether or not the compounds are suitable for the crystallography experiments.

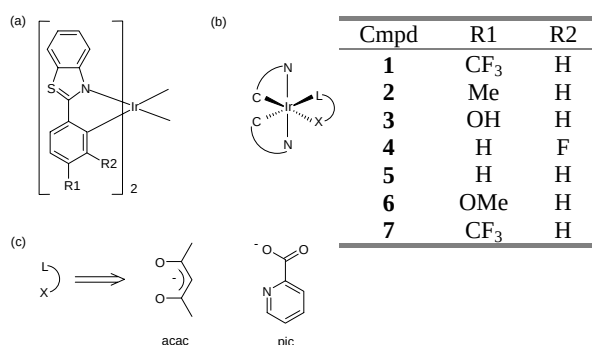


Figure 1. Schematic structural representation of the complexes. The 2-phenylbenzothiazole fragment, with the substituent positions, is shown in part (a), the coordination geometry of the complexes are shown in (b), and the identities of the LX ligands are shown in part (c) (acac for 1–6, and pic for 7).

Results and Discussion

The seven compounds all give absorption spectra that are characteristic of bis cyclometalated complexes (C[^]N)₂Ir(LX).⁴

Two or three intense bands are observed below 350nm, which are assigned to the intraligand ($\pi - \pi^*$) transitions of the phenyl – benzothiazole ligands. Less intense bands are observed above 370nm; these have been assigned to MLCT transitions in similar cyclometalated complexes and are likely to be the same here^{5,6}.

When comparing the positions of MLCT and intraligand peaks, it is observed that relative to the spectrum of **5** (which has no substituents on the ligands), the spectra for all the other compounds show the absorptions are blue shifted, except for **1**, for which they are red shifted. This can be explained by the nature of the substituents of the ligands. **1** has CF₃ groups as the ligand substituents which are electron withdrawing, whilst **2**, **3** and **6** have electron donating substituents. The observed shifts are in line with the electron donating ability of the substituents, such that the peaks in the spectrum are blue-shifted by increasing amounts in the order **2** (-Me), **3** (-OH) and **6** (-OMe substituent). **4** and **7** have electron withdrawing substituents, but **4** has the substituent at the R₂ position and **7** does not have an acac ligand, and these may influence the electronics such that a direct comparison cannot be made.

The solution emission spectra are all very similar, even for **7**, which has a pic ligand rather than an acac ligand. There are two peaks in the range 540nm–615nm, and there is only a small blue shift for the spectrum for **7** relative to the spectra for **1**–**6**. Thus there is little or no acac/pic ligand character in the excited state. A very broad signal in the range 620–670nm can also be observed in the spectra for all the compounds, although it is only clearly defined in **7**. Emission, in agreement with assignments with similar compounds (fac - Ir (C[^]N)₃)⁵ arises from a mixture of MLCT and ³($\pi - \pi^*$) states. The ³($\pi - \pi^*$) contribution to the emission is indicated by the vibronic fine structure of the spectra.

It has been reported with similar materials⁴ that face-to-face $\pi \dots \pi$ interactions of ligands in the solid state cause broad featureless luminescence, which displays a bathochromic shift relative to the solution emission, due to the formation of excimers. The crystal packing of the molecules shows that compounds **1**–**6** all show $\pi - \pi$ interaction to some degree, whereas **7** did not. The emission spectrum for **7** is the best defined: two broad but defined peaks (545 and 595nm) are observed, the peak at 595nm being approximately three times more intense than the peak at 545nm. A very broad peak (635nm) shouldered the peak at 595nm. Thus the spectrum is analogous to the solution spectrum.

The emission spectra obtained at 100K using the laser set-up were the same shape as the spectra obtained at room temperature, and obtained in solution. However, the peaks were centred around different wavelengths. These slight shifts could be due to the wavelength response of the fluorimeter on which the room temperature data was collected, or they could be genuine hypsochromic and bathochromic shifts, due to the

temperature dependence of the transitions responsible for the emission. The excited state lifetimes of all the compounds in the solid state are temperature dependent, with lifetimes in the range of 0.3 ± 0.1 to $2.4 \pm 0.5 \mu\text{s}$ at room temperature and 1.4 ± 0.3 to $4.0 \pm 0.8 \mu\text{s}$ at 100K. The lifetimes for **5** are in agreement with the published values, found in solution⁴). The lifetimes of **1** and **2** are the same at room temperature and at 100K, within experimental error. The fact that the lifetimes are in the microsecond regime lends weight to the assignment of emission as MLCT. The lifetime of **3** was investigated as a function of temperature between 100K and 260K, which showed a small steady decrease in lifetime as temperature increased, within experimental error, with no phase changes visible. Small discrepancies in values are a result of the way the data were collected.

(2) μSR of a laser excited material

Muon spin resonance/rotation/relaxation (μSR) spectroscopy is a technique whereby a (charged) muon can be implanted in a material, and by observation of the decay information on the electronic environment of the muon site may be inferred. In some respects a positively charged muon can be considered as a very light proton, which is generally implanted in bonding regions of high electron density (e.g. double / triple bonds). This is an ideal probe for the excited states of materials which are expected to undergo a change in bonding character in the excited state, such as the three platinum acetylide-based polymers examined in the present study (Figure 2). Such polymers are of application in the area of polymer Light Emitting Diodes⁷), and the characterization of their excited states is critical for the development of efficient light emissive materials.

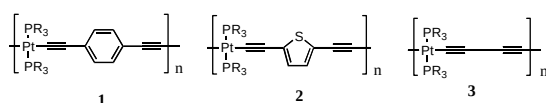


Figure 2. Polymers investigated in this study.

Muon diffusion in unsaturated organic polymers has been studied previously^{8,9}), with the aim of the present experiment being to observe changes in this with respect to laser excitation of the material under study.

The ISIS pulsed muon source provides an ideal environment for time-resolved μSR spectroscopy, with the most intense pulsed muon source in the world. The pulse width of the ISIS muon source is approximately 80ns FWHM, setting the lower limit on time resolved studies, and the muon lifetime is $2.2 \mu\text{s}$, providing a practical upper limit of $20 \mu\text{s}$ on the observation window. The repetition rate is 50Hz, thus samples with lifetimes of the order of $0.1 \mu\text{s}$ to 10ms may be conveniently studied. The platinum acetylide-based polymers of the present study have lifetimes ranging from $30 \mu\text{s}$ - $100 \mu\text{s}$ at a temperature of 10K, and so are ideal for this technique.

For optical pump, μSR probe techniques, a q-switched laser and digital delay generator allows arbitrary phasing of laser pulses to muon pulses within the 50Hz time window. With a 10Hz Nd:YAG ns-pulsed laser, one in five muon pulses is used to observe the excited state of the material, and the remaining four observe the ground state. This configuration ensures that the ground and excited state data are collected under identical conditions in all respects (except for the laser pulse), and thus provide the highest possible confidence that any observed difference is due solely to laser induced effects.

The key element of an optical pump, μSR probe experiment is the alignment of the stopping distances of the muons and photons. Muons are charged particles, and as such exhibit a gaussian distribution about an average stopping depth, whereas

the photon stopping distance is logarithmic. It is clear therefore that matching the stopping depth of a large proportion of the muons with a volume of sample that has a large proportion of light excitation will be non-trivial. In order to reduce the average stopping depth of the muon beam, and thus ensure that muons were stopping as near to the surface as possible, mylar film was placed in front of the sample to act as a "degrader" – essentially acting to reduce the kinetic energy of the muons, while appearing transparent to the excitation photons. The optimal thickness of this degrader was empirically determined by increasing thickness until a significant mylar film μSR spectrum was observed. Due to health and safety requirements, it was not possible to install a dye-laser within the experimental set-up, and so a fixed wavelength for excitation was employed. This is a considerable experimental constraint, as it prevents the selection of an excitation wavelength in order to adjust average photon penetration depth (which is determined by the extinction coefficient of the sample at a given wavelength).

In order to allow a high power pulsed laser beam to impact upon the sample in the muon spectrometer, it was necessary to design and build a special sample holder and optical bench within the DEVA muon spectroscopy instrument. The general design of the optical bench is provided in Figure 3. The laser beam is passed through beam expanding optics to match the muon spot size (approximately 2cm^2), and reflected upwards onto the muon sample holder inside a vacuum sealed cryogenically cooled chamber.

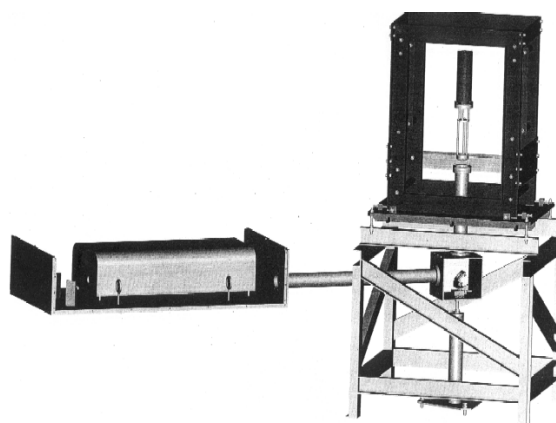


Figure 3. The laser optical bench.

The muon sample holder must be covered with high purity silver at least 1mm thick at any point where muons may strike non-sample areas, in order to allow convenient removal of the sample holder μSR spectrum from the ground state data. The sample holder was mounted at 45° to both the horizontal (muon) beam, and vertical (laser) beam, inside the helium filled cryostat. The sample holder was designed to hold a nominal 2mm thickness of material, as the stopping distance for muons is of the order of 1mm in materials of density $\sim 1\text{g/cm}^3$. The sample holder was fitted with sealing o-rings such that it could be filled with samples that were liquid at room temperature, with the muon/laser "window" being the mylar film "degrader" mentioned previously.

In order to overcome the fixed wavelength (and hence optical penetration depth), a number of experiments were carried out on solutions of the polymer in various solvents (principally di-chloro-methane) in order to decrease the optical absorbance. It was hoped that the muons implanted in the solvent, which was fully saturated, would migrate onto the polymer chains, which are unsaturated, under appropriate temperature and concentration conditions. Unfortunately even at high (room) temperature and maximum (saturated) polymer concentration,

the dominant spectrum was that of the solvent. Samples were therefore prepared either from the powdered polymer, or by evaporation of the polymer solution inside the sample holder.

Initial laser testing indicated that the polymers would withstand the laser at the maximum pulse power ($\sim 200\text{mJ @ } 532\text{nm}$, 2cm^2), although the extinction coefficient of the solid material could only be inferred very roughly from solution UV-vis transmission measurements, which do not take any form of scattering or reflection into account. Calculations of the photon flux and sample volumes indicated a likely maximum excitation of the sample of a few percent, which indicated that high counting statistics would be required.

The μSR spectra of one of the materials did show a small, but statistically significant, difference between laser excited and ground state data, however interpretation of this is yet to be completed. Although the experiment was designed to prevent any systematic errors between laser on and laser off data sets, it is possible that effects due to the laser, but not due to observation of the excited state, (e.g. sample heating) may be the cause of this difference.

In addition to the light-induced data, ground-state μSR spectra of these materials is also of great interest since the results may impart important information about electronic conduction levels, given the highly conjugated nature of the polymers. The data analysis in this regard is yet to be completed.

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Excimer laser surface alloying of titanium with nickel and palladium for increased corrosion resistance

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Introduction

Titanium is highly resistant to corrosion in many media, but its corrosion resistance is low in hot sulphuric acid. However, alloying with palladium,¹⁻³⁾ nickel⁴⁻⁶⁾ or molybdenum⁴⁾ provides substantial improvements. Surface coating and alloying have been of recent interest for increasing the life of titanium foils that are used as electron-transparent windows in the removal of SO₂, NO_x and volatile organic compounds from flue gas by electron beams⁷⁾. The foils undergo corrosion in service in a mixture of ions, radicals and excited species generated in the gas by the beams⁸⁾. Similar damage results in sulphuric acid, a product of irradiation, which was used for accelerated laboratory tests at the operational temperature of the window, 80°C^{7,9)}. In previous work, the surface treatments were accomplished by IBM, IBAD, PSIAD^{9,10)} and HIPPB⁷⁾. However, treatment of full-size windows presents difficulty for vacuum-based techniques. In contrast, the laser alloying, investigated here, has the potential for treatment of large areas. The surface alloying is carried out using a KrF excimer laser, with short pulses of ultra-violet irradiation that minimize thermal penetration.

Experimental

50 µm thick, 99.6% titanium foil was employed for laser treatment. Nickel and palladium layers, respectively about 40 and 310 nm thick, were first deposited by PVD. Laser treatment was carried under the conditions given in Table 1.

Wavelength	248 nm
Pulse Energy	600 mJ
Repetition frequency	2 Hz
Pulse duration	25 ns
Laser focused spot	5 x 5 mm
Energy density	0.4 to 1.1 J cm ⁻²
Number of shots	50
Overlap	50%
Atmosphere	Ar or N ₂ at 2 Bar

Table 1. Parameters for excimer laser treatment.

Immersion tests for up to 50 h were carried out in 0.1 M H₂SO₄ solution at 80°C, with weight changes and open-circuit potentials determined, the latter using a saturated calomel electrode. Specimens were analysed by RBS using He⁺ ions supplied by the Van de Graff accelerator of the University of Paris. Oxygen, nitrogen and carbon contents of near-surface regions were determined by NRA, using 850 keV deuterons. Specimens were also examined by SEM/EDX.

Results and Discussion

Typical potential-time behaviours for laser-alloyed specimens during immersion in H₂SO₄ solution disclosed steady potentials of about - 265 and 500 mV for Ni- and Pd-alloying in argon,

about 495 and 1260 mV higher than for untreated titanium. The potential for nickel treatment applies to fluences above about 0.8 J cm⁻², since potentials fell below - 300 mV at lower fluences; for specimens treated in nitrogen at 0.5 J cm⁻², the potential fell to that of titanium after about 9.2 h immersion due to loss of nickel.

Excimer laser alloying with palladium resulted in weight loss rates of about 0.5 g m⁻² d⁻¹, approximately two orders of magnitude lower than that of untreated titanium. Weight loss rates were generally higher with nickel alloying, about 1 g m⁻² d⁻¹, than with palladium alloying, and the surfaces were depleted of nickel by exposure to the H₂SO₄ solution. By the end of a 50 h period the amount of nickel remaining was sometimes negligible. Eventual loss of all the nickel was followed by rapid corrosion of the underlying titanium. Relatively high weight loss rates for the nickel-treated foils were recorded at a fluence of about 0.5 J cm⁻², with the highest rate being due to depletion of nickel during immersion.

Scanning electron micrographs of the untreated titanium revealed extensive corrosion after immersion for 15 h in H₂SO₄ solution, (Figure 1). Nickel-alloyed surfaces treated at a fluence of 0.8 J cm⁻² disclosed initially numerous fine depressions and raised, nodular, features. The nickel content was significantly higher in the nodules than in the other regions. RBS indicated alloying to a depth of about 200 nm, with little of the original nickel lost in laser treatment. Traces of depressions, but no nodular features, remained after the immersion test. Corrosion of the foil was minor. By this stage, about 17% of the initial nickel remained. A foil treated with a fluence of 0.5 J cm⁻² disclosed few nodular features or depressions of the previous types. Further, immersion in the H₂SO₄ solution resulted in extensive corrosion. According to RBS and EDX analyses, laser-treatment removed most of the deposited nickel, and none was detected after immersion in acid.

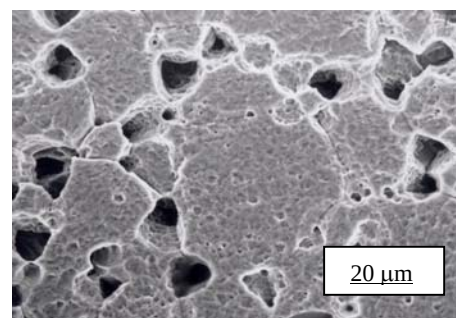


Figure 1. Damage due to corrosion of the untreated titanium foil in H₂SO₄ solution at 80°C.

Foils laser-treated with palladium at the highest fluence of 1.1 J cm⁻² revealed an initial surface decorated by a lace-like pattern of palladium-rich regions, which appear light in scanning electron micrographs, Figure 2(a). The remaining relatively flat areas, were palladium-lean relative to the raised material. Following immersion in H₂SO₄ solution, the pattern of the palladium-rich light regions was still evident, Figure 2(b). However, the flat areas were now enriched in palladium. There

was no significant attack of the titanium at areas most depleted in palladium that now formed islands in the final palladium-rich surface. EDX analysis revealed little difference in the palladium content of surfaces before and after the immersion test. RBS indicated palladium to depths of about 1 μm . The average concentrations of palladium on the initial and final surfaces were about 55 and 70 atomic percent respectively. The amounts of palladium in the surface regions corresponded to 1.2×10^{18} and 0.9×10^{18} palladium atoms cm^{-2} for the laser-alloyed and immersion-tested specimens respectively. The difference is not significant considering the accuracy of the RBS analyses and variability in the initial amount of palladium between specimens. The apparently reduced level of palladium relative to that of the initially coated foil, about 2.0×10^{18} palladium atoms cm^{-2} , may be due to variations in the deposit thickness, difficulty in identifying the precise depth of the final palladium layer, or loss of palladium during alloying. Laser treatment at 0.8 J cm^{-2} produced less effect on the distribution of palladium, with melting leaving occasional islands where the foil was exposed. Any alloying was limited to a depth of the order 100 nm. Following exposure to H_2SO_4 solution, the morphology and composition of the surface region were almost unchanged.

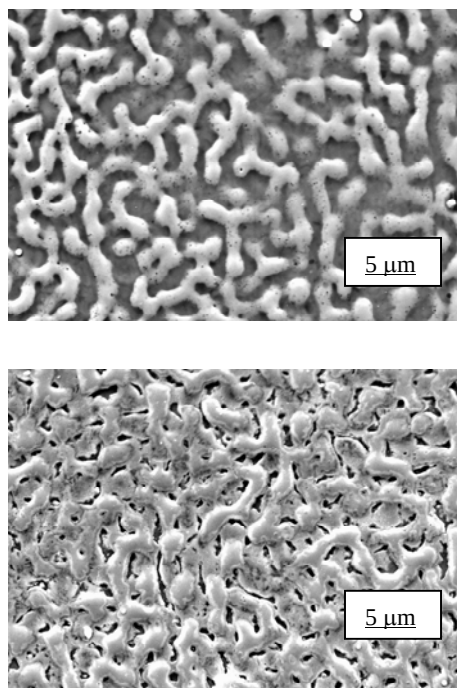


Figure 2. Titanium foil laser surface-alloyed with palladium. (a) Before and (b) after immersion in H_2SO_4 solution at 80°C .

The mechanism of protection of titanium by nickel and palladium is usually attributed to the reduced overpotential for hydrogen generation that results in a shift in the open-circuit potential from the region of corrosion to the region of passivity¹⁻⁶. The potential of the nickel-alloyed foil decreased with reduced alloying element in the original surface and further decreased as the nickel was depleted to levels insufficient to maintain passivity. In the case of palladium coatings, melting and redistribution of the palladium proceeded with limited alloying at low fluence. At increased fluences, alloying was increased, although palladium was distributed non-uniformly on the final surface. Following immersion in the H_2SO_4 solution, palladium enriches at the surface of the alloyed regions.

The nickel and palladium alloying is confined to layers of depth less than about 1 μm . Both nickel and palladium have relatively low solubility in titanium, with the probability of generation of intermetallics, such as Ti_2Ni and Ti_2Pd ¹¹. Further, the

composition of the alloyed layer varies over the melt depth, with influence on stability of phases developed under the rapid cooling conditions of the laser treatment. Thus, alpha, stabilized beta, and martensite phases may co-exist with intermetallics.

The oxygen contents in the surface regions of the laser-treated foils ranged from 0.9×10^{17} to 2.0×10^{17} atoms cm^{-2} , the levels decreasing following immersion in the H_2SO_4 solution by up to about 40%. The carbon and nitrogen levels ranged from 1.3×10^{16} to 1.1×10^{17} atoms cm^{-2} and 1×10^{15} to 1.8×10^{16} atoms cm^{-2} respectively, with negligible dependence upon immersion in the H_2SO_4 solution. Carbon is mainly an adventitious contaminant. The amounts of oxygen and nitrogen were similar to those detected previously in foil coated with palladium, prior to laser treatment. The oxygen detected in the foils after laser alloying and immersion in the H_2SO_4 solution probably arises from oxide films on the titanium foil, and oxygen associated with deposited palladium and nickel.

Conclusions

Excimer laser alloying of titanium foil with palladium and nickel results in major improvement of the corrosion resistance in 0.1 M H_2SO_4 solution at 80°C . The improved behaviour is associated with shifting of the potential to the region of passivity of titanium. Nickel is lost from the surface during immersion in the H_2SO_4 solution, while losses of palladium, which is enriched in the surface regions of the foil, are negligible. Thus, palladium alloying results in extended life of the foils. Low fluences during laser treatment are associated with relatively large losses of the pre-deposited nickel and reduced alloying of palladium. Laser-treated surfaces retain relatively high concentrations of oxygen originating in the rolled surface of the initial titanium foil and the deposited palladium and nickel layers, with some loss of oxygen occurring during subsequent immersion in the H_2SO_4 solution. Nitriding of surfaces treated in nitrogen gas was negligible.

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Two applications of laser-generated acoustic shocks

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Introduction

When a high-power laser beam is focused at a point, the air at the focal point is heated to temperatures of thousands of degrees within several nanoseconds and breaks down. This generates a spark that, in turn, is accompanied by an acoustic shock wave. The laser used to generate the sparks was a Q-switch Surlite III-10 Nd: YAG laser with a 1064 nm wavelength and a power of 800 MJ per pulse. Without focusing, the diameter of the laser beam is 9mm and the intensity of the laser pulse is $2.07 \sim 3.14 \times 10^8 \text{ W/cm}^2$. This intensity is much lower than the threshold of 10^{11} W/cm^2 required to break down the air. A convex lens can be used to focus the beam to a spot of diameter of about 0.3mm so that the light intensity in the focused spot is between 1.88×10^{11} and $2.83 \times 10^{11} \text{ W/cm}^2$. In the experiments reported here, the laser beam was focused using a lens with a focal length of 10cm. Comparisons and analyses of many waveforms has shown that the acoustic pulses associated with the laser-induced sparks are more repeatable and have higher intensity than those from an electrical spark source. A previous article¹⁾ has detailed the acoustical properties of the laser-generated shocks. At 3 cm from the laser-generated spark the peak sound pressure level is 180 dB and the frequency of the main energy content is near 20 kHz. The peak sound pressure level decreases to 150 dB and the main energy frequency decreases to near 10.5 kHz at 20 cm from the spark. This article describes applications of laser-generated shocks to sonic cleaning and to the deduction of bulk parameters from acoustical measurements on thick samples of rigid-porous materials.

Sonic Cleaning

There has been considerable work on the use of sound for debonding and dispersal of particulates. Where the fluid medium involved is air, previous work has emphasized the use of high-intensity low-frequency sound²⁾. This has the advantage that in many industrial applications the source may be positioned at significant distances from the surfaces to be cleaned. For an isolated spherical particle of 100 μm diameter on a surface, a simple force balance between the adhesive force between particle and surface and the oscillating viscous drag due to an incident sound wave suggests that the sound pressure required to detach the particle from the surface decreases dramatically with increasing frequency. In contrast, for a particle of 1 mm diameter, the sound pressure level required to detach the particle is more or less independent of frequency³⁾. This suggests that sonic cleaning of particle-encrusted surfaces in air should be effective when using relatively high audio-frequencies even though this would reduce the distance required between source and surface to be cleaned compared with use of high-power low-frequency sound. Experiments have been conducted using laser-generated acoustic shocks to remove fly ash particles, compacted to various degrees, from a dish that was vertically mounted at a distance of between 10 and 20 cm from the laser-generated sparks. The size distribution of the fly ash particulates is shown in Figure 1. The distribution is asymmetrical and the modal value of longest dimension is 0.75 microns. Figure 2 shows the rate of removal of particulates from the sample holder, for a given initial compaction, as a function of distance from the sparks.

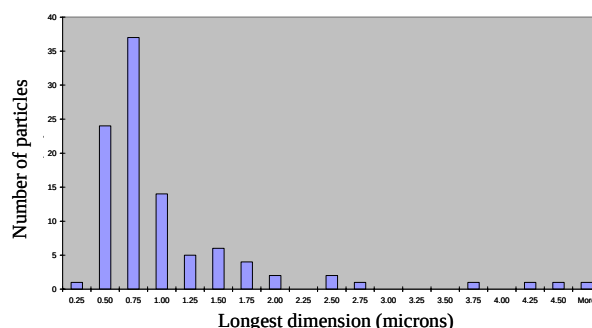


Figure 1. Size distribution of fly-ash particulates.

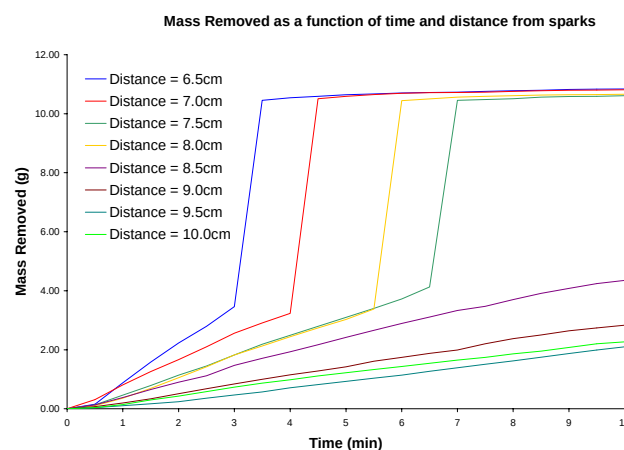


Figure 2. Particulate removal as a function of time and the distance of the sample holder from the laser-generated sparks.

There is a systematic decrease in the rate of removal as the distance increases i.e. the shock intensity decreases. Another noticeable feature is the catastrophic nature of the removal after a certain proportion of particulates have been displaced. Other data show that for the highest initial compaction, the rate of removal was less at the greater distance (lower shock intensity). Shock induced vibrations were measured using accelerometers at five locations: four on the sample holder and one on the supporting table. The greatest induced displacement was at the sensor position on the sample holder in the direction of the incident acoustic shocks. However the induced vibration magnitude was rather small: a peak displacement value of less than 2.5 μm . A mechanical shaker was used to create a similar sinusoidal displacement. However there was no discernible particulate removal with this level of vibration. From these measurements it is concluded that the mechanism of particulate removal is the direct action of the acoustic shocks on the particulates rather than vibration induced in the plate.

Deduction of porosity and tortuosity from acoustical data

The use of ultrasonic methods for characterising fibrous and foam materials is well established^{4, 5}. Such measurements are performed on small thin samples using ultrasonic pulses with central frequency higher than 100 kHz. The small size of pores in foams and fibrous absorbents means that scattering effects will influence only the upper frequencies in the pulse spectrum. However, ultrasonic measurements on materials with large (>1mm) pores, fibres or grains such as porous metals and concrete are not appropriate since scattering effects will dominate. Attenuation at frequencies of the order of 100 kHz restricts measurements to thin (several millimetres) samples and this is a significant limitation for materials with large pores, fibres or grains, since thin samples will not necessarily be representative of the bulk materials. Laser-generated acoustic shocks are useful for an acoustic method of measuring tortuosity (a measure of pore or streamline curvature) and porosity (the ratio of the volume taken up by connected pores to the total volume of the material) of thick samples of rigid porous materials with a mean pore (grain or fibre) size of several millimetres. At sufficient distance from the laser-generated sparks such that the wavefronts may be assumed to be plane, and nonlinear effects can be ignored, the acoustic pulses have a central frequency close to 12 kHz and an approximate bandwidth of between 3 kHz and 20 kHz. In this frequency range inertial rather than viscous effects dominate sound propagation in pores. This allows application of the high frequency limit of an "equivalent fluid" model^{6,7}. Both reflected and transmitted signals are used in the measurements. If the incident pulse duration is shorter than the time of flight through the material, it is possible to separate the pulse reflected from the surface from those due to multiple reflections. If the length of the material sample is 15cm then the first reflected and transmitted pulses can be separated from subsequent ones if incident pulse duration is shorter than 880µs. This condition is valid for the laser-generated pulses used in the experiments reported here. Tortuosity is deduced from the high frequency limit of the phase speed (obtained from transmission data) and porosity is obtained from the high frequency limit of the reflection coefficient once the tortuosity is known. Figure 3 shows the measurement system. Pulses were detected by two pressure-field type ¼" microphones, amplified and captured by a computer-based data acquisition card with a sampling frequency of 1 MHz. A 0.5m long open-ended cylindrical tube was used as a waveguide.

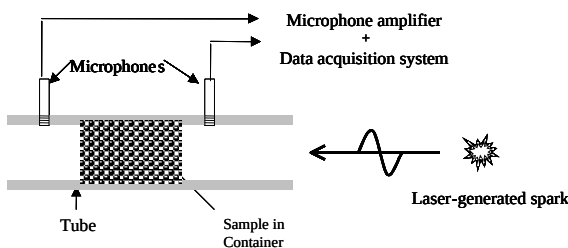


Figure 3. Measurement system for deducing porosity and tortuosity.

Pulses were recorded without a sample inside the tube to determine the speed of sound in air. With the sample material, the incident, reflected and transmitted pulses were recorded. Examples of measured incident, reflected and transmitted pulses in the presence of a 15 cm thick sample of 2.1mm lead shot are shown in Figure 4. The central frequency of the incident signal is close to 11kHz. An FFT procedure has been used to obtain the reflection coefficient amplitude in the frequency domain. The phase information from the FFT analysis was unwrapped to compare the difference between the incident and transmitted pulses. Finally, the difference was converted to the phase speed, using the known distance between the transducers. Three unconsolidated granular materials were tested, including two

types of lead shot and medium (9mm) gravel. Measurements have been carried out also using a 15cm long cylindrical sample of porous aluminium. Since the diameter of this sample was sufficiently close to that of the waveguide tube (5 cm) it was used without the sample holder. Table 1 shows results of these measurements (A) and the values obtained by other methods (R). There is good agreement except for gravel for which still lower frequencies should be used.

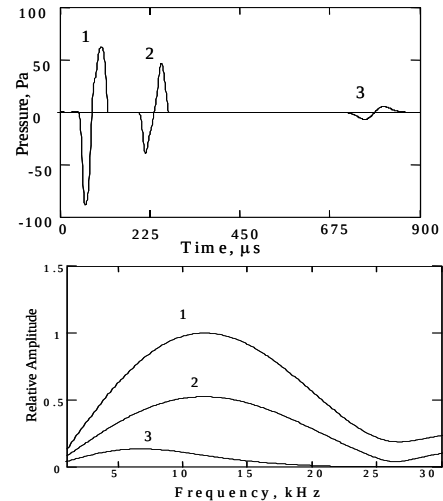


Figure 4. A. Examples of waveforms measured with a 15 cm thick 2.1mm diameter lead shot sample: 1- incident pulse, 2 - reflected pulse, 3 - transmitted pulse. B. Examples of spectra corresponding to the measured waveforms in Figure 2A.

Material	Porosity		Tortuosity	
	A	R	A	R
2.1 mm lead shot	0.41	0.38	1.54	1.56
4 mm lead shot	0.46	0.38	1.46	1.47
Porous aluminium	0.92	0.93	1.03	1.07
9mm gravel	0.56	0.44	1.81	1.55

Table 1. Parameters deduced from acoustical data (A) and from other measurements (R).

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Mixed glass rod amplifier chain – design and implementation

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Introduction

As a part of the Vulcan Petawatt upgrade ¹⁾ there was a requirement for a mixed glass rod amplifier chain. The two glasses used were Neodymium doped Phosphate and Neodymium doped Silicate glass. The two glass types have different line centre gain values, hence a correct combination of two different glasses will provide an overall increase in the gain bandwidth of the Vulcan Petawatt chain. The current, purely phosphate amplifier chain had a gain bandwidth of 2.5 nm, this is not sufficient to support the sub 500 fs pulse duration required to achieve Petawatt regime intensities.

Modelling

In order to determine what ratio of phosphate to silicate glass would be needed in the amplifier chain a numerical model was developed using the PV wave code ²⁾. The code generates the fluorescence curves (see Figures 1 & 2 for the actual curves)³⁾ for the different glass types by summing two or more Gaussian curves with differing properties. A factor in the code, GIR, represented the amount of gain provided by each type of glass. A GIR factor of 1.0 represents a purely phosphate chain where a GIR factor of 0.0 represents a purely Silicate chain. A GIR factor of 0.5 would represent half the overall system gain being provided by each types of glass (see Figure 3).

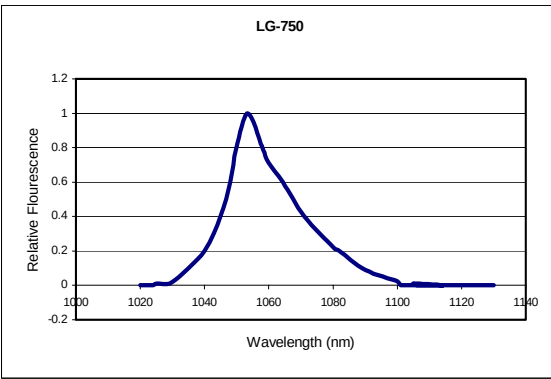


Figure 1. Fluorescence curve for LG750 phosphate glass.

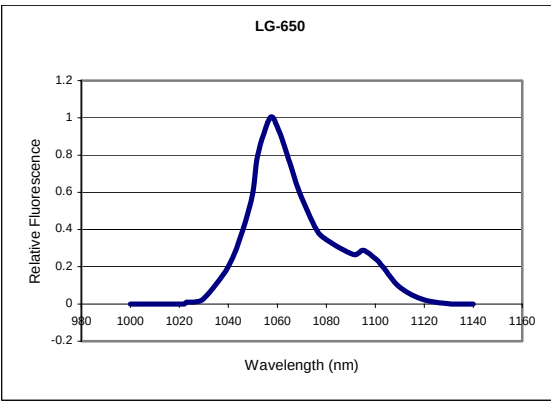


Figure 2. Fluorescence curve for LG650 silicate glass.

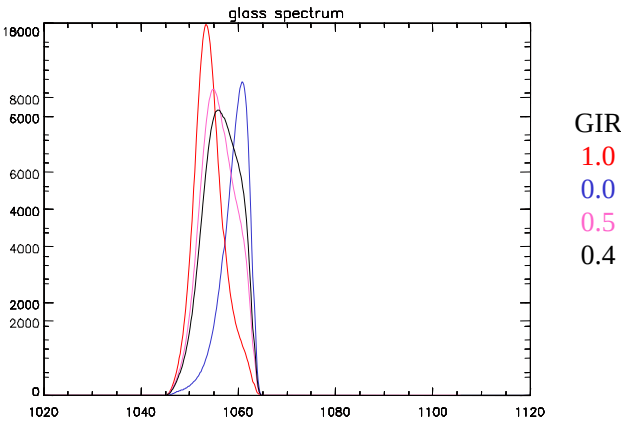


Figure 3. Gain bandwidth for mixed glass chains.

From Figure 3 it can be seen that the purely phosphate chain has a higher gain than that composed entirely of silicate glass. This is because for the same pumping geometries and voltage, silicate glass produces much lower line centre gain ⁴⁾ (see Figure 4). In order to produce the same output energy with a silicate chain more amplifiers, or higher pump voltages are required. However this data is somewhat deceptive as the line centre gain for Nd doped silicate glass is 1060nm.

Rod size (mm)	Pump Energy kV	Phosphate 1053	Phosphate 1064	Silicate 1053	Silicate 1064
9	1.8	30	11	5.5	11
	1.6	20	8	4.47	8
16	2.2	23	9	4.8	9
	2.0	19	6.7	3.9	6.7
	1.8	17.5	6.5	3.5	6.5
	1.6	13.3	4.25	2.8	4.25
25	2.2	13.5	6.25	3.7	6.25
	1.9	8.75	5.3	3.3	5.3
	1.7	6.25	4.75	3	4.75

Figure 4. Rod amplifier gain characteristics.

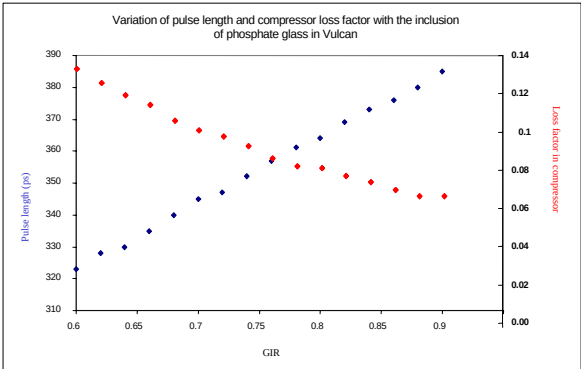


Figure 5. Pulse length variation and loss in compressor for inclusion of silicate glass.

From running the model it becomes apparent that with the inclusion of more silicate glass the pulse duration of the laser decreases. However there is a further effect to consider, the Petawatt compressor has a finite bandwidth that it can support, thus energy then becomes lost in the compressor, effectively reducing the on target intensity. Figure 5 illustrates this effect. A compromise between pulse length reduction and loss factor appears to occur at a GIR value of 0.76. This is based on a 16nm super Gaussian input spectrum.

Amplifier selection

As silicate amplifiers are added to the overall chain design, the GIR value changes by discrete amounts. It is therefore possible to add the silicate amplifiers as rod amplifiers at the start of the amplifier chain. The Vulcan disc amplifiers use phosphate glass and were not considered for replacement by silicate glass. This is because it is far more economical and practical to replace the phosphate rod amplifiers. A purely silicate rod chain and phosphate disc chain would produce a GIR value of 0.5. Figure 6 illustrates the options for different combinations of phosphate and silicate rod amplifier chain designs.

The final design implemented incorporated a single passed silicate 9mm amplifier, a double passed 16mm silicate amplifier and single passed 25mm and 45mm phosphate amplifiers. This, in conjunction with the existing phosphate disc chain, comprising; double passed 108mm disc amplifier, single passed 150mm disc amplifier and 3 single passed 208mm disc amplifiers, produces a GIR of 0.75.

Implementation

The requirement for the mixed glass chain was that it did not compromise laser operations to either target area East or West. It was decided to build a stand alone silicate chain which would

then feed into the existing phosphate chain before the 25mm amplifier stage (see Figure 7). The beam size through the first stage of the silicate chain is a 6mm collimated beam.

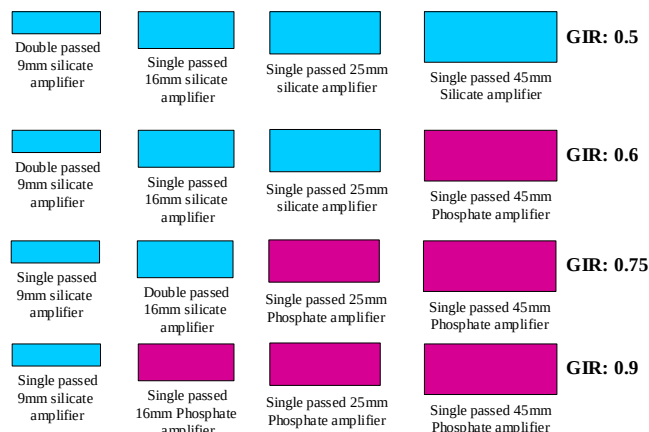


Figure 6. Mixed glass amplifier chain options.

The design for the silicate chain includes a DC faraday isolator after the single passed silicate 9mm amplifier. A Vacuum Spatial Filter (VSF) then provides image relaying to the 16mm amplifier and expands the beam from 6mm to 10 mm. Optical pulses are directed either into the silicate chain or phosphate chain by the use of polarising beam splitting cubes and a wave plate. Pulses are then re-injected into the phosphate chain immediately before the 10-20mm expanding VSF, by the use of a polarising beam splitting cube.

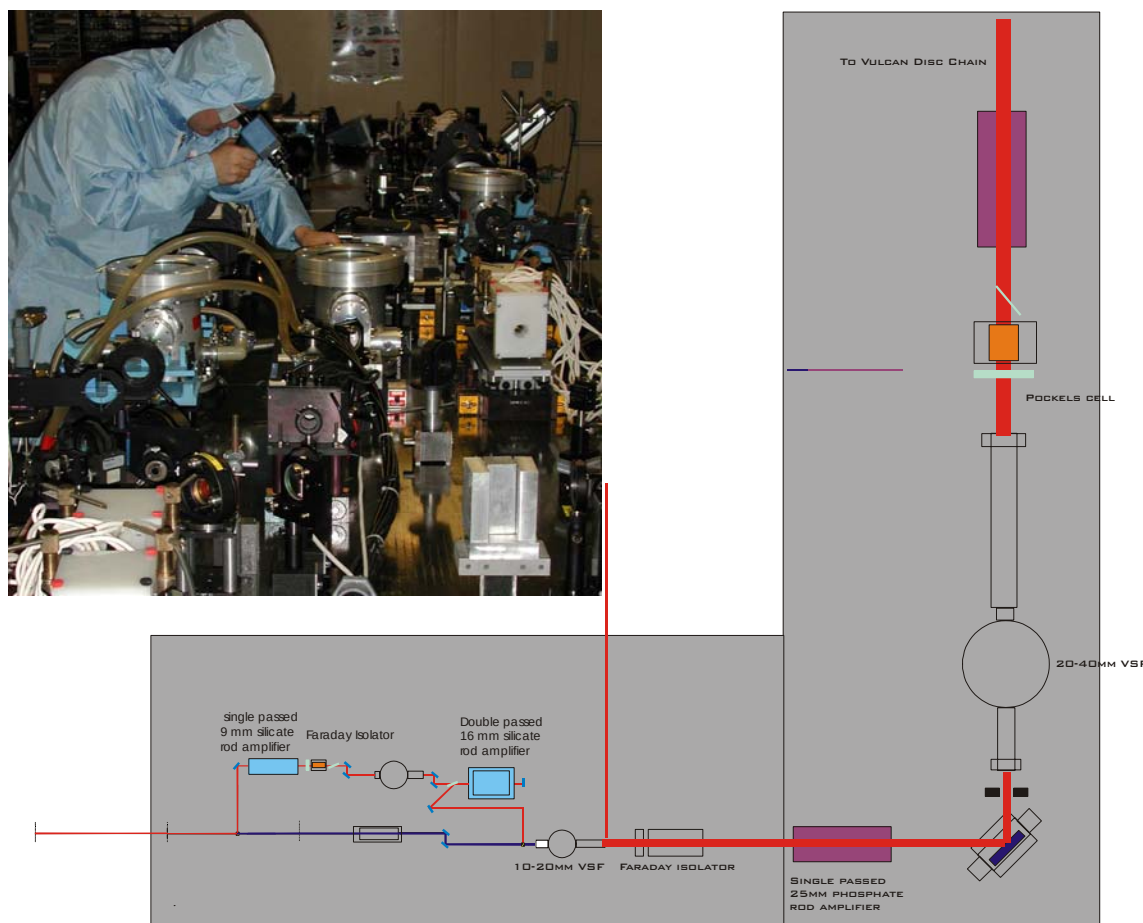


Figure 7. Mixed glass amplifier chain implementation.

Results

High energy disc shots were fired using the purely phosphate chain and then with the additional silicate amplifiers. A 13nm top hat spectrum was injected into the amplifier chain from the OPCPA front end ⁵⁾. This resulted in a considerable improvement to the bandwidth at the output of the laser chain. Figure 8 shows a 2.8nm FWHM spectral bandwidth from the phosphate chain, where figure 9 shows a 5.5nm FWHM spectral bandwidth from the use of a mixed glass rod chain.

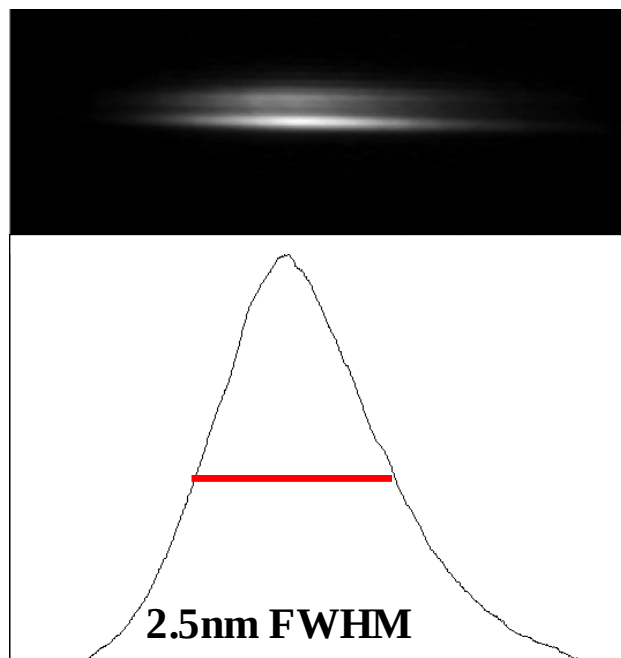


Figure 8. 2.5nm Bandwidth from purely phosphate chain.

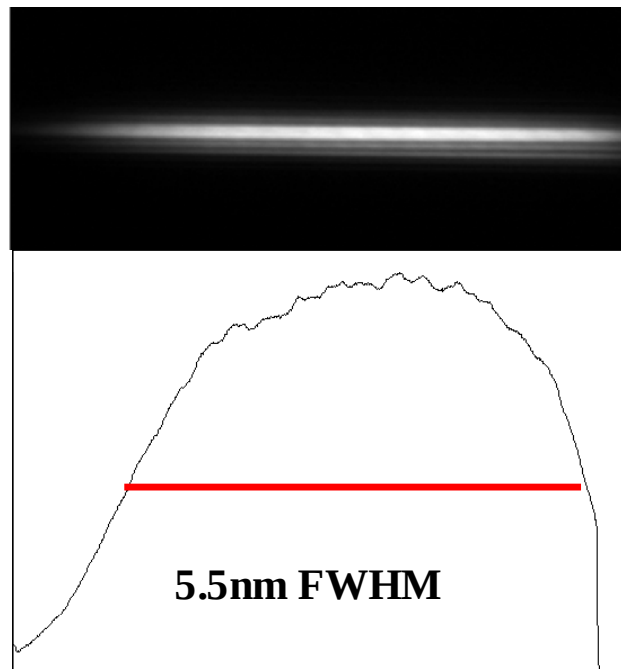


Figure 9. 5.5nm Bandwidth from mixed glass chain.

The Phosphate chain strongly gain narrows to 1053.5 nm, the line centre gain of the phosphate glass. The mixed glass chain produces a line centre gain at 1054.5nm as a result of the additional gain towards the longer wavelengths from the silicate.

Conclusions

It has been demonstrated that by the use of a mixed phosphate and silicate glass rod amplifier chain the bandwidth of amplified pulses for the Petawatt facility can be increased from 2.8nm to 5.5nm. 5.5 nm is a sufficiently broad bandwidth to support the sub 500fs pulse duration required by the Petawatt facility.

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Retro energy measurement on Vulcan Petawatt beam line – a preliminary study

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The Vulcan Petawatt beam line has been operational to the user community for a number of different experiments. A preliminary investigation into the amount of energy propagating back from targets down the Vulcan Petawatt beam line on full energy shots has been made.

Measurements of the energy returning back down the laser chain were made in Laser area 4 which houses the three 208mm disc amplifiers and the input to the expanding vacuum spatial filter (VSF) which is immediately before the Compressor, see Figure 1. A 3550mm focal length lens was placed behind the final high reflective turning mirror before the VSF. Any beam returning from the interaction chamber would propagate back down the amplifier chain but a small percentage would “leak” through the back of the final turning mirror and be collected by the lens. The transmission through the turning mirror was measured to be 0.001%.

Initial measurements were made using Kodak linagraph direct print paper, which is commonly used for laser burn alignment. This was chosen as an initial method of determining the returning energy as the fluence required to create an image on the paper is well characterised. From experience a 1.0J rod amplifier shot in a 40mm beam produces a good quality beam image on the paper. This equates to a fluence of $140\text{mJ}/\text{cm}^2$. Burn paper was placed in the focussing beam and moved closer to the focus of the lens on successive full energy, 500 J, laser shots. A burn was finally produced with the paper close to focus, the beam size was measured to be 250 microns, see Figure 2. Assuming a $140\text{mJ}/\text{cm}^2$ fluence the energy required to produce this burn would be 70 micro joules. Given the transmission of the high reflecting mirror this indicates 70 millijoules returning down the laser chain. The petawatt compressor has a throughput of about 60%, so this would indicate as little as 114 mJ returning from the target. From 500 Joules out of the laser chain less than 0.03 % returns back down.

As these measurements were made the other side of the spatial filter pinhole to that of the target, the energy measured only includes retro energy which is on axis to the laser beam. This energy also represents the maximum possible retro energy from the target. Some components of the energy measured may have been retro-reflected from other sources such as the diffraction grating in the compressor or other lenses in the spatial filter.

The targets used in the initial measurements were solid targets.

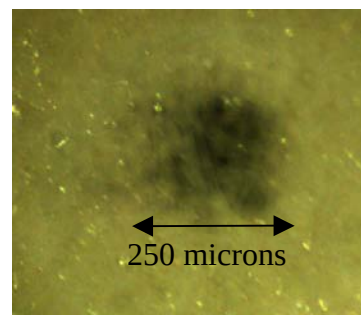


Figure 2. Retro energy burn.

A study into how much energy returns when gas jets were the target was also made. Initial measurements showed the energy detected at the same point was comparable to that of solid targets. A CCD camera was placed at this point so that the actual image could be captured on the shot, see Figure 3. During the experiment several shots were fired with a much higher density gas jet. These shots increased the retro reflected energy, to around 0.1% of the 500 J laser output, Figure 4.

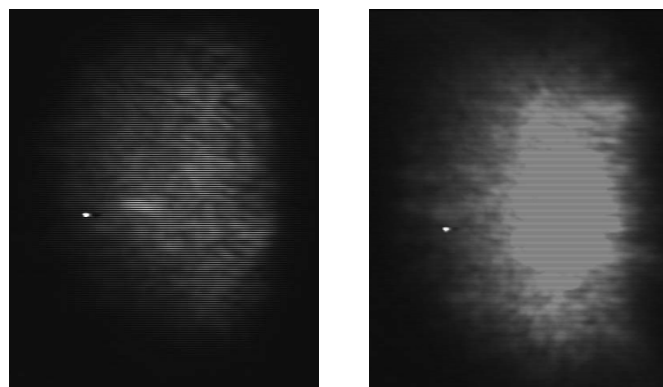


Figure 3 and 4. Low and high density gas jet retro energy.

Initial measurements of the energy retro reflected from target indicate that from solid targets <0.03% of the incident energy is retro reflected. This is comparable for standard gas jet targets, however when high density gas jets were used this was seen to increase. Future measurements will hope to finesse the method of measuring the retro energy.

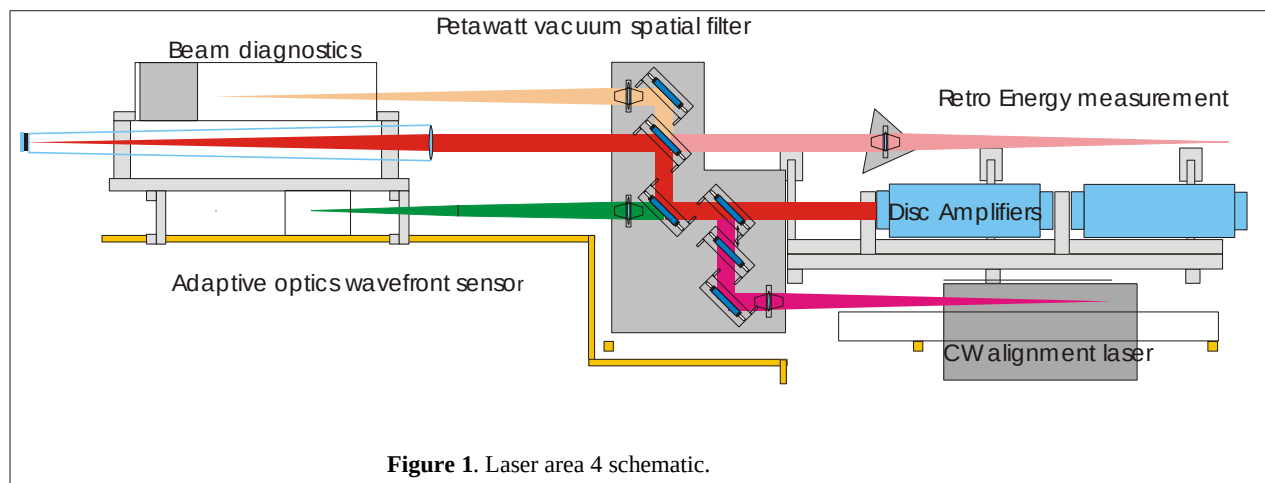


Figure 1. Laser area 4 schematic.

Vulcan 9mm pre-amplifier upgrade

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The Vulcan laser pre-amplifier stage utilises five nine-millimetre neodymium/glass rod amplifiers, with some of them in double pass configuration to provide the required early beam intensities. Apart from pumping the main beam-amplifying network these amplifiers are used extensively to provide laser pulses for beam timing and alignment, for which they are able to run at a relatively high repetition rate of 0.1Hz. This requirement makes these amplifiers the most worked in the system, and the high gain delivered demands good stability to provide consistent output energies.

Over a given period, statistics on laser operations showed a gradual increase in the number of failed laser shots that could be attributed to deviation in the 9mm pre-amplifier stages. This problem was addressed on many occasions and corrective electrical maintenance of the unsupported and obsolescent power equipment only slightly improved the overall performance.

The eventual provision of a sustainability budget presented an opportunity to acquire replacement amplifiers that would re-establish laser output stability. The protracted overall cost of this exercise required for tenders to be invited from manufacturers Euro-wide, and a specification was drawn up and issued for this purpose. The main criteria drawn up in the specification were:

- Compatibility with the existing 9mm amplifier heads
- Stand alone control system which could be integrated into the Vulcan main control system
- Diagnostic of power supply performance
- Ease of maintenance

The UK company Innolas (UK) Ltd were awarded the contract to initially supply one laser head, power unit and control computer for acceptance testing. After acceptance a further five power units and control system to integrate with the Vulcan central control computer would be delivered.

To make this upgrade transparent to the laser operations programme, the delivery dates were set to coincide with a scheduled laser shutdown during which the laser room air

conditioning plant was to be replaced. This worked very well with acceptance testing of the first delivery being carried out in the off line clean environment of the laser amplifier test facility. A design engineer from Innolas was in attendance throughout to provide guidance on the operation of the control program, the main features of which are shown in Figure 1, and to make any necessary changes revealed at this stage.

During the period between acceptance tests and installation of the second delivery, software for the Vulcan central control computer was written, with only limited testing possible off-line. Simulation of a complex control network as used on Vulcan may be possible, but the vagaries of the electrically hostile environment would be difficult and costly to simulate. Throughout the commissioning stage of installation the design engineer from Innolas was again in attendance to assist with integration of the control computers. A mutual understanding and co-operation between the supplier and customer is an important feature in replacement installation projects, and something from which everyone involved benefited.



Figure 2. Two of the Innolas 9mm amplifier power supplies installed in Vulcan.

Two of the Innolas power supplies are shown in Figure 2 after being installed in the Vulcan laser area. After a smooth period of installation and testing the results have thus far been most rewarding. The project has been successful and the essential level of stability expected at the pre-amplification stage has been achieved.



Figure 1. The computer interface used for the control of the 9mm pre-amplifiers.

Vulcan infrastructure refurbishment – air conditioning, nitrogen and cooling water

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Introduction

Vulcan has been operational for some 25 years now. It has been expanded and had additional capabilities added but some of the infrastructure was original and beginning to show its age.

The servicing contractor reported that they were concerned over the serviceability, parts availability and application of the Vulcan laser area air conditioning system. The majority of critical spare parts for the air conditioning units were now obsolete and as failures occurred units were being cannibalised to keep other units going. Some units were unserviceable and others were being left non-operational. Vulcan operations were in danger of being compromised, with close control of the environment not being achieved. The condensers on the compressors were scaling up and were dependant on the site tower water system, which itself is showing signs of age. The efficiency of these systems is also not up to modern standards.

Parts of the nitrogen distribution system were also fairly old. Plastic pipes were showing signs of ultra-violet embrittlement. Also the system had been altered, repaired and added to over many years such that the circuitry was unknown and operationally non-optimal.

Similarly the water cooling system was in need of new plant, refurbishment and rationalisation.

These types of problems were not unique to the CLF and a successful CCLRC bid to OST recognised this historical underfunding of facilities' infrastructure. This article explains the work carried out in early 2004 under the first year of this funding.

Air conditioning

When specifying the new air conditioning system a number of factors were taken into account. The main items addressed were: current heat loads, airflow distribution, access and maintenance of the units, changing to air cooled condensers, humidification requirements, reliability of equipment, parts availability, equipment efficiency, filtration requirements and any future expansion or change of use.

The heat loads (to air) in the laser areas were assessed to be in the region of 51kW. A temperature stability of $20^{\circ} \pm 1^{\circ} \text{C}$ and a cleanliness of class 10,000 were specified.

The final work package involved the stripping out and removal of the existing air conditioning equipment followed by the installation of 6-off close control air conditioning units (2 units per area) and associated roof mounted condensing units (total sensible cooling capacity of 78kW). Also installed were 31-off fan filter units (15 units LA1, 6 units LA2, 10 units LA3) and associated speed controllers etc. The total cost for the work was ~£150k. See Figure 1 for a schematic of the new system and Figure 2 for a photo of the new air conditioning units.

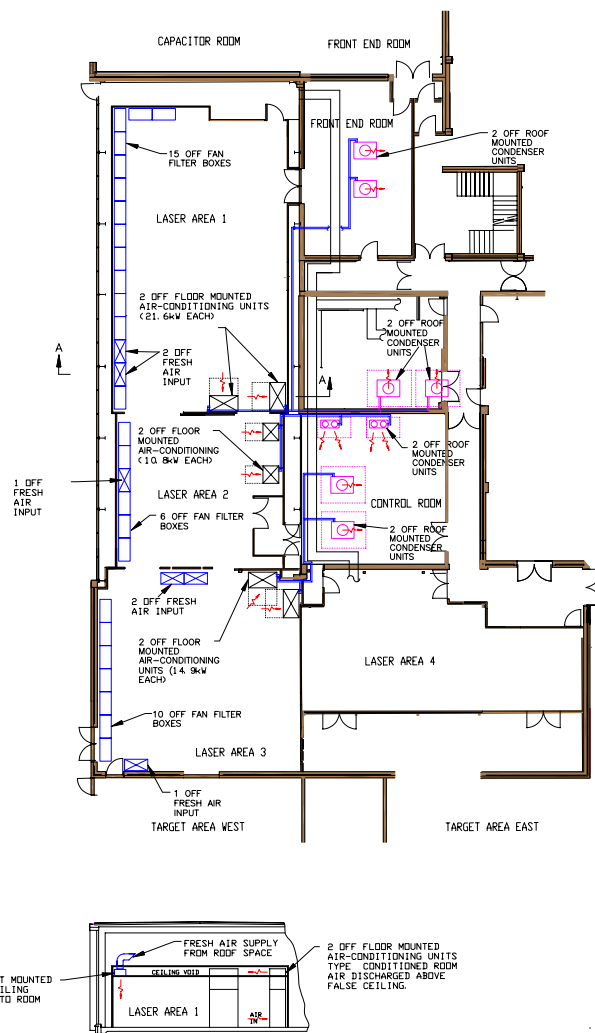


Figure 1. Schematic of new air conditioning system.



Figure 2. Photo of new air conditioning units after installation.

Nitrogen

The nitrogen system needs to supply dry, clean nitrogen around the laser area for purging amplifiers, VSF let up, air tools and pneumatically operated mirror slides, gate valves and shutters. It has been designed to simplify the circuitry, and includes area isolation valves, flow meters and regulators, replaces degrading plastic pipework with chemically cleaned, welded stainless steel pipes and meets the current requirements in each of the areas. The system supplies clean nitrogen at 80 psi. The amplifier purging has two modes, a 5l/min flow during normal hours and a 2l/min flow rate during silent hours and is fed directly from the storage tank. The total cost of the upgrade was ~ £20k. Figure 3 shows a schematic of the new system including the Vulcan Petawatt circuitry previously installed.

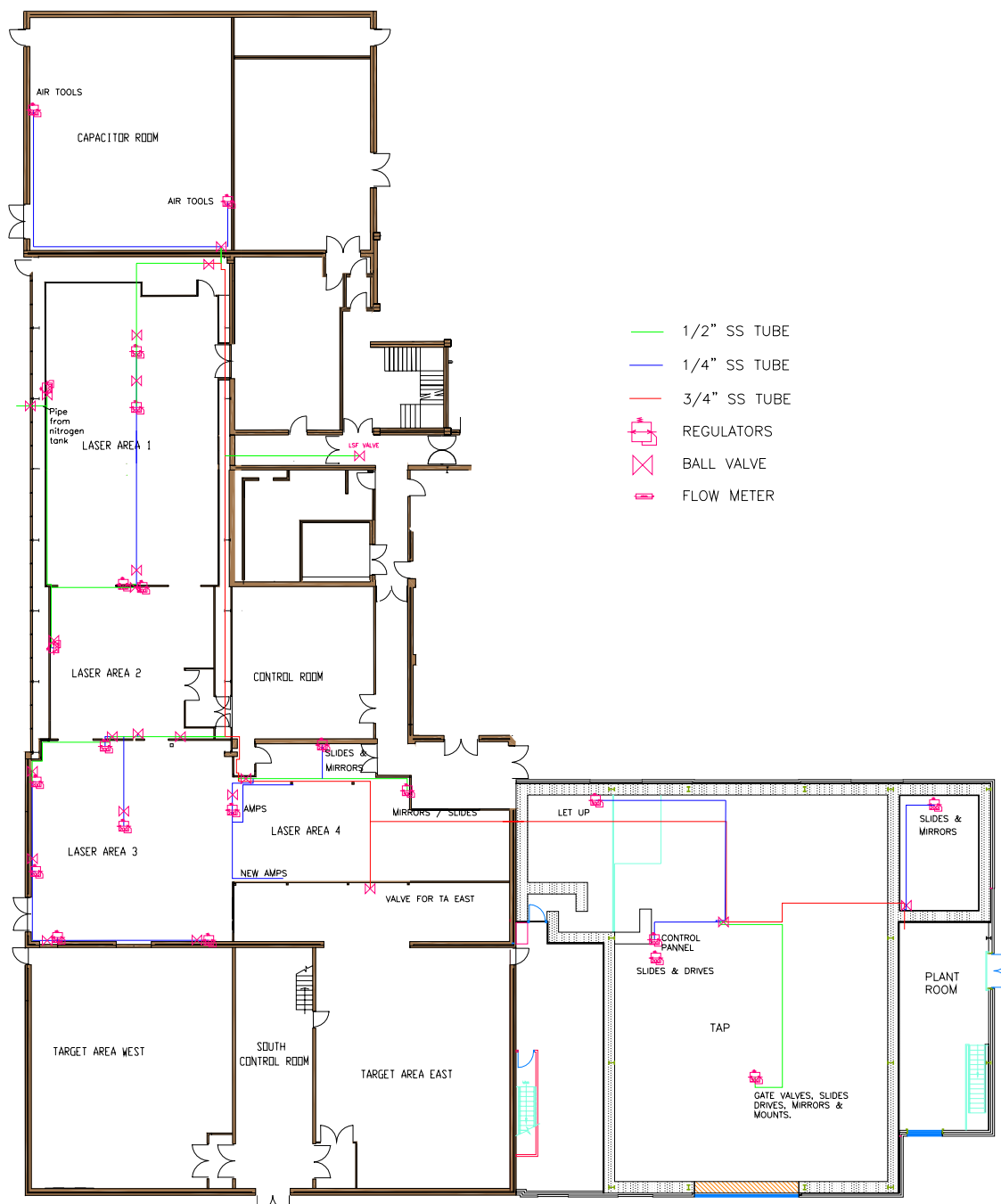


Figure 3. Schematic of new nitrogen system.

Cooling water

Cooling water is needed in the laser areas to cool the rod amplifiers and various oscillators. The final design for the water cooling system was to remove the old water refrigeration system and install a new 9 kW chiller with an overhead header tank of 60 litres capacity. The tank has a low level alarm at 10% loss which shuts off the water system's valves and pumps. The chilled water is fed to a heat exchanger from which 3 cooling circuits have been installed. The first circuit serves the Quantel amplifiers, and operates at 1.5 bar and 15 l/min flow.

The second circuit serves the 9mm amplifiers in 2 locations, 3 in series in LA1 and 2 in series in LA2, and operates at 3 bar and 25 l/min flow. The third circuit serves the ISI and 2 SLM oscillators. It operates at 2 bar and 15 l/min. The total cost of the upgrade was ~£20k. Figure 4 shows a schematic of the new water cooling system.

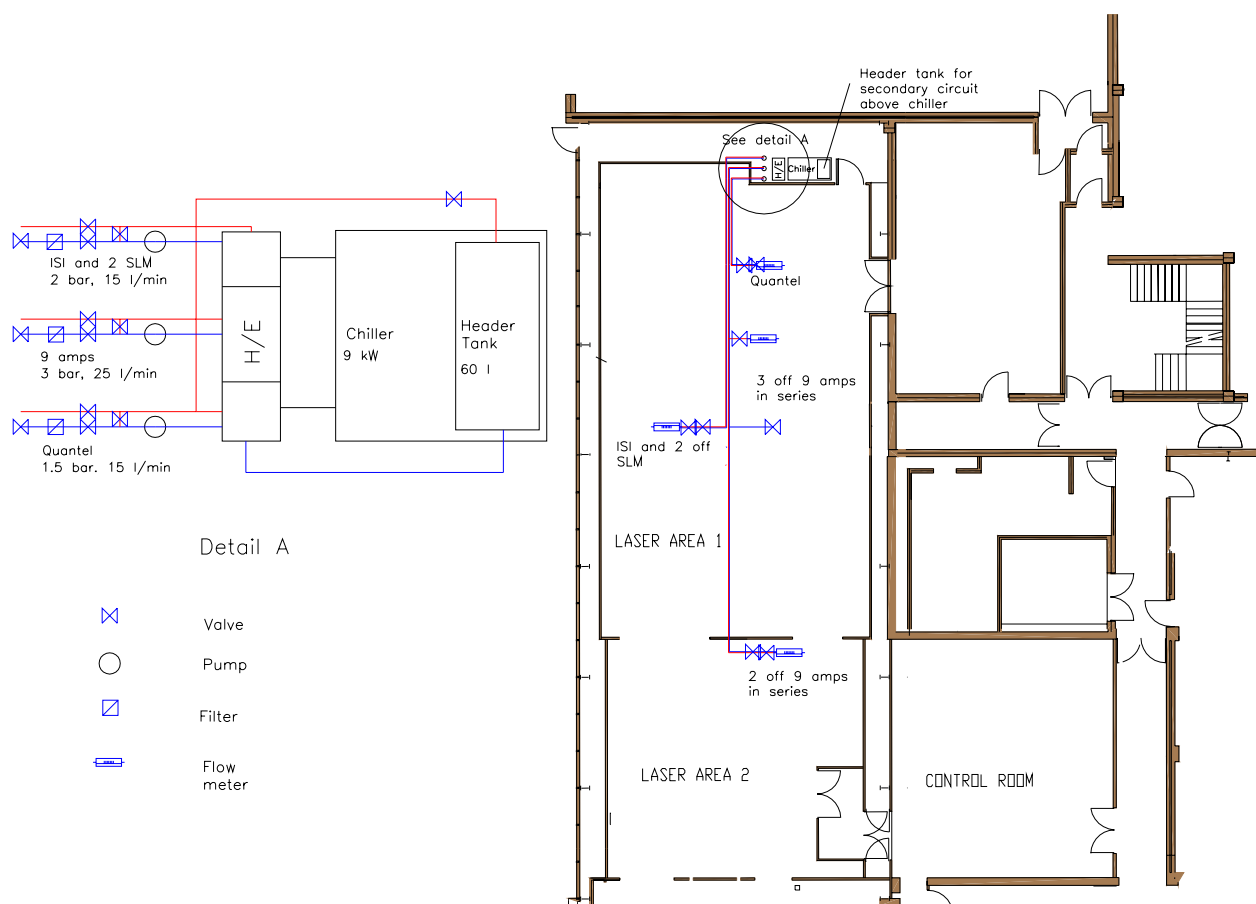


Figure 4. Schematic of new cooling water system.

Summary

A much needed injection of funding has enabled the ageing air conditioning, nitrogen and water cooling systems for the Vulcan laser to have been replaced with purpose designed, modern equipment that will enable Vulcan to continue operations into the future.

Nanosecond pulse square pulse distortion (SPD) correction (for large-scale OPCPA trials)

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Introduction

Previous trials of large scale OPCPA experiments using Vulcan produced encouraging results but were hampered in producing the required amplified spectral profile – spectral narrowing of a potential bandwidth of 40 nm was shown to result from the far from ideal temporal shape¹⁾ of the beam-7 pump pulse on Vulcan. This pump pulse is generated by a long (~20ns) pulsed (SLM) laser and a nominal square pulse of tens of microjoules and nanosecond duration is ‘switched out’ for further amplification by the Vulcan long pulse switchout, VLPS. In this report we tried to address two aspects of this problem – a ‘double pulse transmission’ on the VLPS and more importantly, gain saturation in the Vulcan disc amplifiers that increased the leading edge intensity relative to the trailing edge.

Improved impedance matching

This first problem was addressed using appropriate 50 ohm matched URM 67 cables with HN connectors between the VPLS driver unit and its pockel cells - these had been changed on previous experiments in an attempt to try and shape the pulse profile.

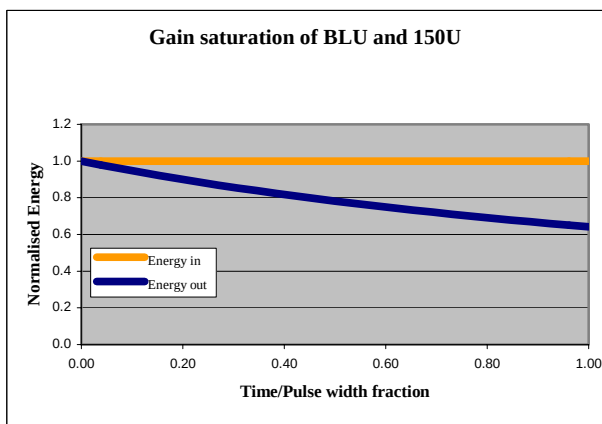


Figure 1(a). Modeling of SPD distortion due to gain saturation.

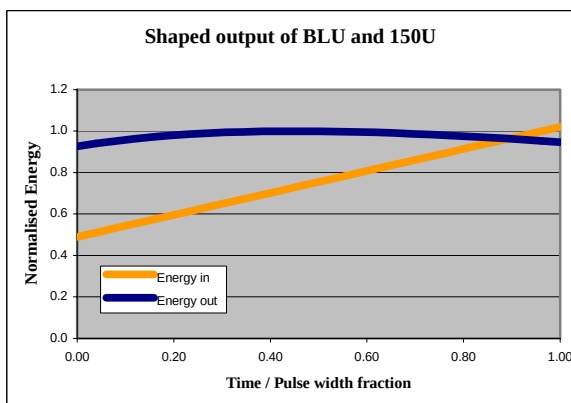


Figure 1(b). Near 100% SPD correction using a linear sloped input.

Modeling

Vulcan produces ‘corner’ energies after the rod amplifiers which do not show any saturation behaviour. We therefore modeled the saturation process in the disc amplifiers using some simple time slice modeling in Excel with the standard time independent Fanz-Nodvik²⁾ equation :-

$$E_{out} = E_{sat} \ln \{ 1 + [\exp(\frac{E_{out}}{E_{sat}}) - 1] \exp(g_0 l) \}$$

where E_{sat} is that saturation fluence, E_{in} energy in and g_0 the small signal gain.

Using established saturation fluences of 4 Jcm^{-2} for Nd doped phosphate glass and an effective diameter of 135 mm resulting in a saturation energy of 572J, time dependent ‘corner’ gains for the double pass BLU and the final 150 mm amplifier of beam-7 predicted square pulse distortion (SPD). Figure 1(a) shows the outputs achieved for a square input pulse – they were similar to those observed in the previous experiments. To try and correct for this distortion, the input pulse was then changed to a trial pulse with a linear slope. - Figure 1(b) shows that this would result in a substantial correction to the output profile, remaining distortions being only ~10%.

Fast Pockel cell and Driver

Figure 2 shows a typical temporal transmission profile of a fast pockel cell located between crossed polarisers – the output profile has the usual voltage dependent transmission $T = \sin^2(\pi V / 2)$ behaviour, V being the half-wave voltage, required to produce a half-wave rotation equivalent to a π phase-shift. This half-wave voltage is typically ~6KV for a dual cell pockel cell. It shows that a ‘linear ramp’ in the optical output of a fast pockel cell could be achieved at operation of 50% of half-wave voltage with only a factor of 0.5 in loss in throughput. The SLM lasers produce enough output to be able to cope with this attenuation. The requirement for SPD correction on beam-7 would need an optical ‘ramp’ from 0 to half-wave voltage during 1 ns matching that required as an input in Figure 1(b).

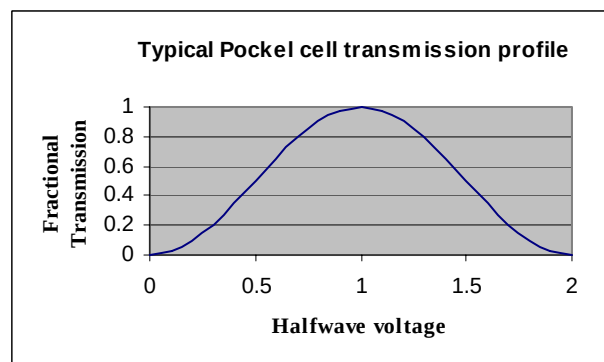


Figure 2. Transmission profile of a pockel cell system.

Fast shaping pockel cell installation and characterisation

An appropriate Kentech fast 6.4 KV driver and a Leysop 8 mm diameter aperture pockel cell system was incorporated to provide the necessary slope and synchronised to the VLPS on the outer track immediately after the SLM lasers. The arrangement is shown in Figure 3 where a horizontally polarized output is required to pass through the outer track polarizer - rotation of the wave-plate immediately before the pulse shaping pockel cell as well as the ability to turn off the driver enabled operation without the shaper if required.

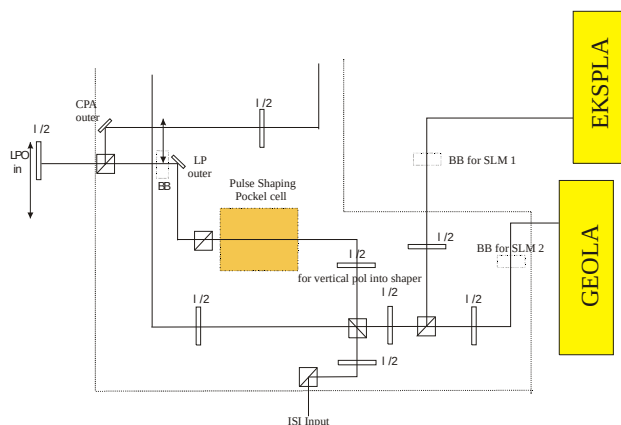


Figure 3. Arrangement on outer track of ‘shaping’ fast pockel cell.

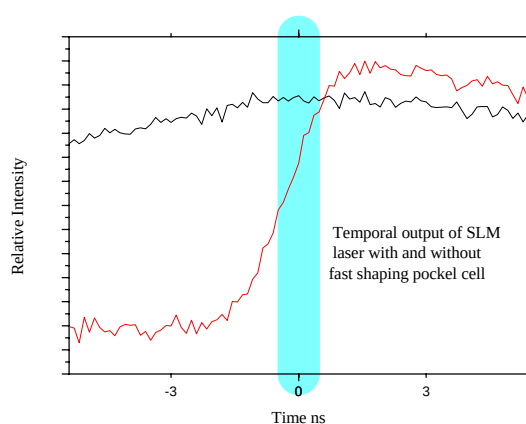


Figure 4. Temporal profile of square unshaped ~20ns SLM pulse and selected (shaded) shaped 1 ns pulse using the VLPS on the outer track.

Figure 4 shows the temporal profile of the normal SLM output and that achieved after the shaping fast pockel cell. These traces were obtained using a ~2GHz InGaAs PIN detector coupled to a 5 GHz scope. The shaded region of 1 ns duration, matches the slope required in Figure 1(b) to correct for the SPD on beam-7. The graph also illustrates the ability to change the slope and transmission of the shaped pulse through the VLPS by changing their relative delays. This relative delay was optimized during experimental runs using a dedicated DG535 pulse generator for triggering the fast shaping pockel cell. Enough energy from the SLM was available to run the shaper at lower transmission, with a dip in the linear rise if required.

Final amplified temporal profiles

Results obtained on beam 7 showed excellent SPD correction. Figure 5 shows streak camera profiles obtained at 300J and 150J using a 1 ns pulse from the VLPS - high pixel numbers corresponding to earlier times. The streaks, corrected for phosphor ‘degradation’ on both ends of the streak axis, show how gain saturation corrects for the slope imposed by the fast

shaping pockel cell on the SLM laser output. There was some evidence on high energy shots of a ‘dip’ in the temporal profile – this was attributed to some residual mismatch between the VLPS and its driver unit and was partially compensated for when a 0.8 ns pulse width was selected from the VLPS for optimum OPCPA pumping. The resultant amplified square temporal pulse profile enabled a broader amplified bandwidth and hence a shorter pulse after compression in the large-scale OPCPA experiments to be achieved.

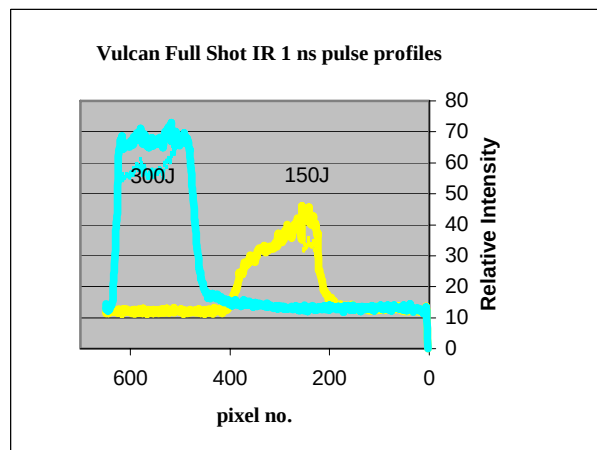


Figure 5. Streak camera temporal profiles of beam-7 outputs.

Conclusions

We have shown that suitable corrections for SPD can be made using a fast ‘shaping’ pockel cell. The optical ramp produced with these fast pockel cells can be sufficiently varied in conjunction with the VLPS to enable relatively easy optimization of the amplified output. Slower optical ramps could be produced by rotation of the waveplate before the shaper – faster ramps using the appropriate driver. Where finer pulse shaping is required, the suitability of fiber based modulator systems requiring lower drive voltages from Arbitrary Waveform Generators are currently being investigated.

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Improvements to the Astra laser system in 2003 - 2004

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Introduction

A number of improvements to the Astra system have been carried out over the past year. These were aimed at improving the beam quality, reducing the level of prepulse and increasing the energy available on target. The changes involved a redesign of the third amplifier and of the optics at its output, so the opportunity was taken of incorporating improved near- and far-field diagnostics and continuous energy monitoring. In addition, a new higher-power CW diode laser that is more easily detected in the target area was installed, and the attenuator mirrors for low-power operation were mounted on a new slide that has far better repeatability. The new layout is shown in Figure 1. Some of the developments have been delayed for technical reasons; it is expected that these will be completed in the coming year.

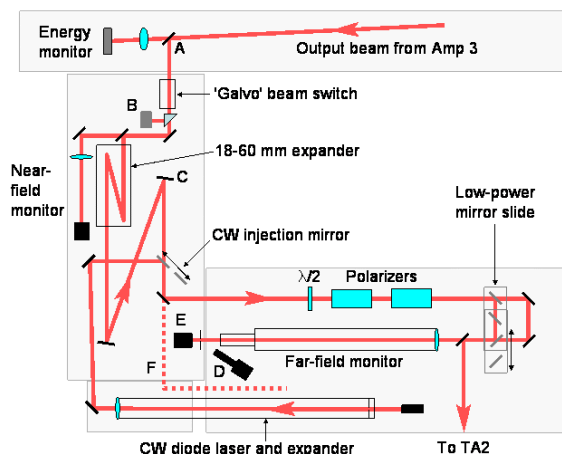


Figure 1. Revised layout of Astra Amp 3 output.

Amplifier 3 output monitors and beam control

Figure 1 shows the beam path between the final pass of the Ti:sapphire crystal and the shutter leading to TA2. The steering mirror at A, placed before the beam switch, allows continuous monitoring of the output energy, which was not possible with the old layout. The galvo beam switch is the same device as before, which either deflects the beam via a prism into a beam dump at B, or allows it to pass on to the new beam expanding telescope. The fraction of the beam transmitted through the expander input mirror is used to monitor the beam profile at a plane equivalent to the input aperture of the expander.

The beam diameter in Amp 3 before the reconfiguration was 16 mm, and this was expanded to the 60 mm required for TA2 in a custom-made off-axis beam expander. With the change of beam diameter to 18 mm, the expanded beam would be 67.5 mm, which is too large for the downstream optics, so a new beam expander was purchased. The new expander is very similar to the old one, with a dielectric-coated spherical primary and a gold-coated off-axis paraboloidal secondary.

The expanded beam follows a dog-leg via mirror C, which will be replaced with an adaptive optic in the near future. The wavefront sensor needed to control the AO will be constructed in the path shown with a dashed line at F. The new CW diode beam is expanded to 60 mm and injected via a sliding mirror as shown. This beam has a power of 90 mW, and is used both for alignment in the target area and for measuring the transmission of the compressor to determine whether the gratings require

cleaning. Following the waveplate and polarizers is the new low-power mirror slide, and an improved far-field monitor based on a 70 mm astronomical telescope. The far-field monitor has two cameras D and E, which give wide- and narrow-field views respectively, allowing easy setup and adjustment.

Large-aperture Pockels cell

Astra's main prepulse monitor, which measures the prepulse after amplifier 2, shows several pulses at times up to a few tens of nanoseconds before the main pulse. These prepulses are typically at the level of 10^{-7} to 10^{-8} of the main pulse, and are known to be caused by scattering from the anti-reflection coatings of the Amp 2 TiS crystal. To suppress these prepulses, a 20 mm aperture Pockels cell was obtained and placed in the Amp 2 output beam after the expander. After the installation of the cell the prepulses were no longer detectable, implying at least a factor of 100 reduction. The extinction of the main pulse by the crossed polarizers was measured as 1000x, and the same factor should apply to the prepulses. Unfortunately, the intensity at that point was very close to the damage threshold for the KDP used in the cell, and after a short time of operation the entrance face of the first crystal was found to have laser damage. The optical layout will be modified so that the Pockels cell is positioned after the 50% beamsplitter that sends the beam to TA1; this will halve the intensity at the Pockels cell, and should prevent it from being damaged again.

Vacuum Spatial Filtering

The long propagation paths in Astra allow unavoidable phase errors to grow into amplitude modulations, which can damage optics unless the energy is restricted. To reduce this effect and improve the near field of the beam, image-relaying spatial filters have been installed: one at the output of Amp 2 and two more within the multi-pass Amp 3 itself. The first of these replaces the Galilean-type beam expander used previously. It expands the beam from approximately 5 mm to 20 mm, after which it is apodized to 18 mm by a 'hairy hole' type aperture. The 18 mm beam is suitable for Target Area 1 as well as being optimum for input to Amp 3.

The new configuration of Amp 3 has one Vacuum Spatial Filter (VSF) after the first pass of the Ti:sapphire crystal and one after the third pass (the VSFs are not shown in the Figure 1). Due to thermal lensing, the TiS crystal is itself a weak positive lens of about 17 metres focal length when pumped. The symmetry of the system means that the sequence of crystal-VSF-crystal is afocal, so the collimated input beam is again collimated after the second pass of the TiS. The same is true for the third and fourth passes of the crystal and the second VSF. The diameter of the 800 nm beam is thus 18 mm at each pass of the TiS crystal, allowing maximum energy extraction from the pumped region, which is also 18 mm in diameter.

The lenses used are custom-designed air-spaced achromats with minimum variation of focal length between 750 nm and 850 nm. The two focal lengths are 330 mm and 1300 mm; the latter is used both as the second lens of the beam-expanding VSF and at either end of the Amp 3 VSFs. The lenses were not used as the windows of the VSF tubes, because the focal length of the Amp 3 TiS crystal is not known exactly. The lenses are placed external to the VSF windows so they can be moved axially to the positions that give correct beam collimation in the amplifier. The pinhole sizes are 1 mm in the first two VSFs and 1.3 mm in the final one. All three VSFs are pumped to a pressure of around 3×10^{-2} mbar by a single oil-free pump.

RF plasma cleaning of compression gratings for intense femtosecond pulses

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Introduction

Many developers of high repetition-rate, intense femtosecond lasers have reported a significant reduction of compressor grating efficiency even after only brief periods of exposure to intense laser pulses. Commercial compressor gratings have efficiencies greater than 90% when new. Thus a typical double-pass compressor can have a maximum efficiency better than 65%. After only weeks of use, however, grating efficiency can drop below 80% thus reducing the overall efficiency of the compressor to around 40%.

The reduced efficiency is due to the build-up of a dark absorbing layer on grating surfaces. This occurs most significantly on the last grating in the optical chain at which the pulse is shortest and most intense. Typically the level of irradiance at this grating is in the region of $10^{11} - 10^{12} \text{ Wcm}^{-2}$. This is quite sufficient to photo-dissociate vacuum pump oil and organic molecules adsorbed on the grating surface and to thus form an absorbing layer of carbon.

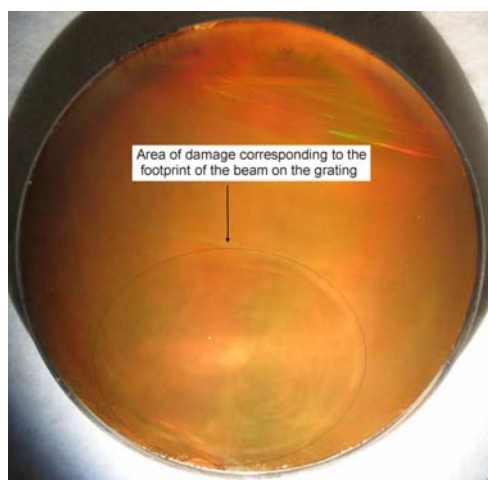


Figure 1. Damaged 1480 lines/mm LLNL grating (150 mm diameter).

Compressor gratings can cost between thousands and tens of thousands of pounds largely depending on size. The cost of their replacement, plus the work involved in regularly fitting and aligning new gratings, can be a significant overhead on the running costs of a high power laser facility.

A promising technique which has been shown capable of cleaning gratings and to extend their working life is Radio Frequency (RF) plasma cleaning. This is an established technique in many ultra-clean manufacturing environments, like the microprocessor industry for example, where it has several advantages over other cleaning techniques. Primarily it avoids the use of toxic, hazardous or corrosive solvents and can be carried out in situ as part of the manufacturing process. In plasma cleaning, surfaces are exposed to a gas discharge maintained by a 13.56 MHz radio frequency source. A gas mixture comprising Ar and O_2 is often favoured because this promotes surface cleaning via a combination of ion bombardment and chemical reaction between oxygen ions and adsorbed organics.

We verified the cleaning process initially by cleaning an old grating in an RF plasma discharge rig used for cleaning silicon chips. The gratings, with an average efficiency of 73%, were exposed for a total of 12 minutes to a 150 W O_2 plasma

discharge at a pressure of 100 μTorr and a flow rate of 35 standard cubic centimeters per minute (sccm). The measured efficiency after cleaning increased to 84% with no visible damage to the grating surface.

For our application cleaning is best carried out inside the compressor vessel since this avoids removal of gratings for cleaning and the need to realign them afterwards. The RF cleaning apparatus used in the Astra laser compressor is shown in Figure 2.

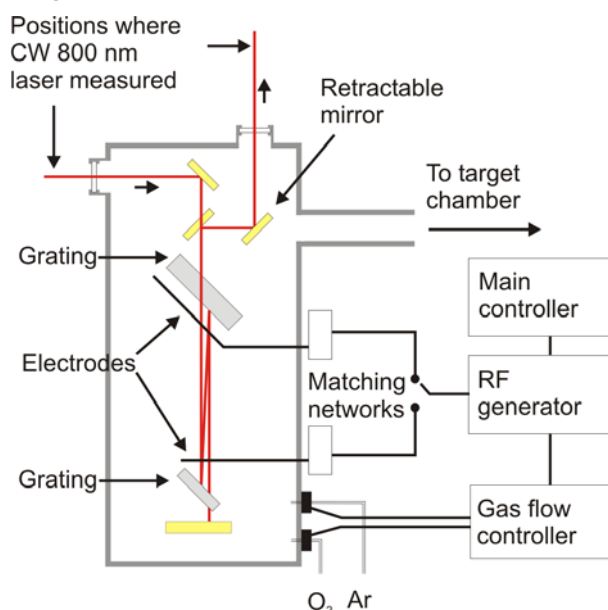


Figure 2. Arrangement of RF plasma discharge apparatus used to clean gratings in situ.

The RF power is provided by an ENI RF generator controlled by an ENI RF controller RFC-5MW. The RF power can be switched between two matching networks (ENI Matchworks 5D) which deliver the RF power inside the chamber to either of two aluminium electrodes placed directly in front of each grating, see Figure 3. The flow of Ar and O_2 is controlled by two MKS Instruments *Mass-Flo* controllers in the gas lines which are in turn controlled by an MKS Instruments mass flow controller (PR4000).

After installing and testing the RF plasma discharge, new Jobin Yvon 1480 lines/mm gold coated gratings were installed in the compressor. The efficiency of these gratings was $\geq 90\%$ and the measured transmission through the compressor which includes losses at the anti-reflection coated input window and gold coated mirrors was 67%.

The efficiency of the compressor transmission was monitored at intervals during experimental runs by comparing the power of a plane-polarized 805 nm CW diode-laser (Power Technologies Inc. PPM90) at the input and output of the compressor, Figure 2. When the compressor efficiency dropped by 5 to 10% an RF plasma clean was carried out. Cleaning occurred at a backing pressure of about 10^{-2} mbar. The O_2 and Ar gas flows were set at 5 sccm and 30 sccm respectively. The RF power used was 75 W. The cleaning process was carried out while monitoring the transmitted diode-laser power until no further increase was observed. This was normally for periods not exceeding 5 minutes for discharge at each electrode.

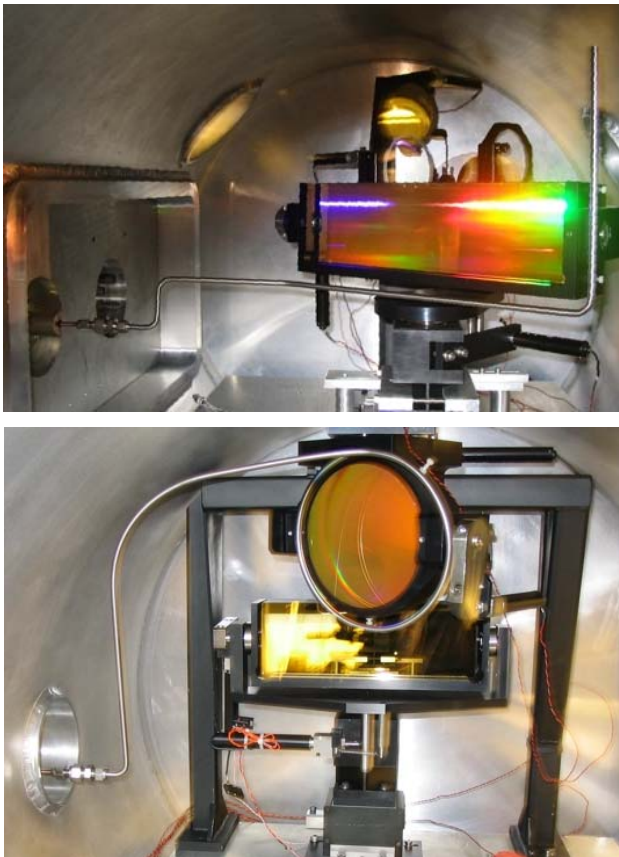


Figure 3. Pictures of the gratings inside the compressor showing aluminium electrodes.

Efficiencies measured during two recent periods of use of the compressor are plotted in Figure 4. Apart from a very slight decline in transmission over time, the use of RF cleaning has enabled us to keep the efficiency at or above 60 %.

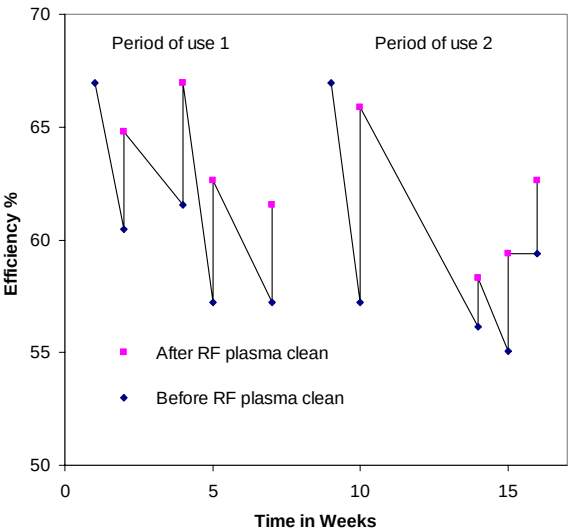
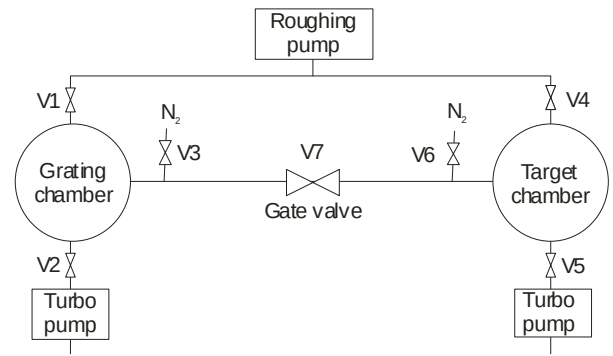


Figure 4. Plot of the transmission efficiency of the grating compressor showing the measured efficiencies before and after cleaning on each occasion the RF plasma discharge was used.

A PLC based vacuum system controller has been developed so that the compressor and target chamber vacuum systems can be switched quickly between three modes of operation: normal mode (10^{-5} mbar, both chambers), gas jet mode (10^{-3} mbar in both chambers for gas jet experiments) and RF clean mode (10^{-2} mbar in the compressor only). The modes of operation are described and illustrated below.



Normal mode	<u>Grating chamber</u>
	Roughs down from atmosphere via V1 and switches to turbo pumping via V2
	<u>Gate valve</u>
Gas jet mode	<u>Grating chamber</u>
	Only rough pumped via V1. On switching from normal mode chamber is let up to roughing pressure via V3 & then rough pumped via V1
	<u>Gate valve</u>
RF clean mode	<u>Grating chamber</u>
	Only rough pumped via V1. On switching from normal mode chamber is let up to roughing pressure via V3 & then rough pumped via V1
	<u>Gate valve</u>

Table 1. Diagram and Table showing modes of operation.

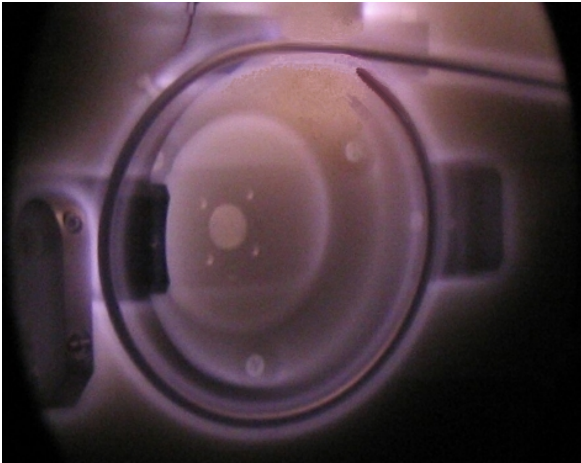


Figure 5. RF glow discharge in O₂ : Ar gas mix in the compressor chamber.

Acknowledgements: Mikhail Kalachnikov and Elena Gubbini at MBI, Berlin and Frank Eggenstien at BESSY, Berlin for discussions and information on RF plasma cleaning of gratings. Slava Djakov for cleaning gratings in an RF plasma discharge plant in the Central Microstructure Facility at RAL. Staff at Scientific Vacuum Systems Ltd., Finchampstead, UK for their assistance and for installing the RF plasma system at RAL.

The Astra “Gemini” Project

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Introduction

In March 2004 the CCLRC announced a £3 million project to upgrade the Astra Titanium Sapphire Laser Facility at the CLF. The upgrade project, named the Astra “Gemini” Project will see Astra transformed from a single beam, 10 TW system into a dual beam facility, with each beam delivering a power of 0.5 PW.

The dual beam nature will make it internationally unique and will enable a far greater range of experiments to be performed than compared to the single beam facilities being developed elsewhere. Each beam will be independently configurable and focusable to $\sim 10^{22} \text{ Wcm}^{-2}$, approximately 1 order of magnitude higher than the Vulcan PetaWatt, currently the highest intensity laser world wide, and almost 3 orders of magnitude above the current operating point of Astra.

A crucial aspect of the design is that the system will be capable of firing approximately once every minute, offering a completely new experimental approach to ultra high intensity physics research. This performance will easily differentiate the Astra Facility from large-scale systems around the world and will reinforce the position of the CLF as one of the world’s leading providers of state of the art laser facilities.

Central to the proposal is the exploitation of a natural synergy within the CLF, in that it has expertise both in Ti:S technology (Astra) and Nd:glass technology (Vulcan) through operating and developing these two facilities. The technology developed to support the Vulcan programme over the years is exactly that required to enhance the Astra facility in the manner outlined. The CLF is one of only a few organisations world-wide where such a technology transfer could occur entirely within its own domain. This is a compelling argument that is at the heart of this project – a unique combination of need, circumstances and capability, which together permit the development of a truly leading facility.

Methodology

The project will require the expansion of the existing facility, the development of new laser systems, the development of a new interaction facility and the development of new target handling capability, including radioactive and activated component handling. A new mezzanine area will be constructed above the ceiling of the existing Astra facility to house all of the pulsed power, vacuum and electrical / mechanical infrastructure required, providing complete environmental isolation with respect to the new laser and target area. The mezzanine will also house the radioactive handling area and provide storage space for ancillary equipment.

The development requires the expansion of the two current Astra laser bays into a third area and operation into a new, third target area. The space needed is already occupied by the CLF and no new buildings are specifically required. There will be a re-organisation of the existing Astra floor plan and some internal building modifications. A third target area control room will also be provided in addition to an access-restricted radio-isotope handling area and storage facilities. Furthermore, the Target area will benefit from a dedicated diagnostics area that is located outside of the radiological shielding but having direct and configurable line of sight access to the interaction point. (See Figure 2).

Laser Development

The proposed scheme is shown in Figure 1.

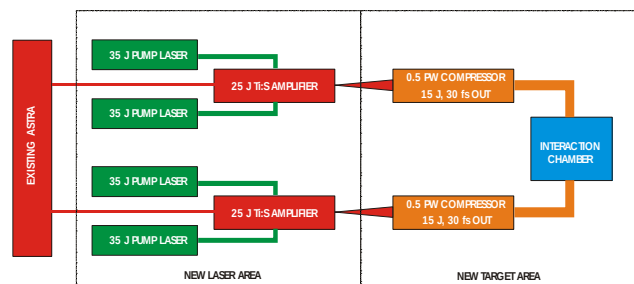


Figure 1. Schematic layout of the upgraded facility.

Four 45 mm diameter pump lasers will be constructed using Nd:glass rod technology in the new laser area. This technology is well known and understood, and the CLF has many years experience in using it on the Vulcan system. The pump lasers will be designed to operate at approximately 1 shot every minute, using techniques for thermal bi-refrignence management and the deployment of adaptive optics, of which the CLF has particular expertise. Each pump laser will produce a 35 J, 10 ns optical pulse at a wavelength of 527 nm. These pump lasers will operate in pairs to provide up to 70 J of pump energy per pair. Each pair will be used to pump two independent 70 mm diameter Ti:S amplifiers, one pump pair per amplifier, also located in the new laser area.

A pulse from the existing Astra system will seed each amplifier, which will also incorporate a large aperture adaptive mirror. From the 70 J pump energy per amplifier, approximately 25 – 30 J will be extracted by each seed pulse. The two beams will then propagate through vacuum spatial filters to two compressors located above the new interaction facility described below. The two beams will be delivered to the interaction chamber vertically and turned horizontal inside the interaction chamber.

Locating the compressors above the interaction chamber has the dual advantage of both maximising the use of available space and offering independent polarisation control of the interacting beams when turned horizontal. It also has the benefit of allowing unhindered 360 degree access to the interaction point. Temporal compression will produce two 15 J, 30 fs pulses, carrying 0.5 PW of power each. They will, of course, be synchronised and because of the use of the adaptive mirrors in the amplifiers, they will be virtually diffraction limited. Using $\sim F\#2$ off axis parabolic focusing inside an interaction chamber, optical intensities of $\sim 10^{22} \text{ Wcm}^{-2}$ in each beam are anticipated.

An important parameter for some of the anticipated science is optical pulse contrast. Currently on Astra the Pulse Peak : ASE ratio is $\sim 10^6 : 1$ which is insufficient to prevent target breakdown well ahead of the arrival of the main pulse. Therefore a new system for temporal “pulse cleaning” utilising an ultra-fast self gating technique very recently developed in the CLF will be installed in the existing amplifier chain. We anticipate a contrast increase to $10^{10} : 1$ which will be sufficient to prevent to prevent early target breakdown. Experiments to verify this are underway.

In addition to the dual beam system described above, there will be considerable scope for additional development of the facility not covered by this project. For example, the pump lasers could easily be re-configured to act as drivers for an *Optical Parametric Chirped Pulse Amplification (OPCPA)* scheme, an ultra-broad band amplification technique pioneered within the CLF. Initial modelling suggests that a 10 fs, 4 J, 400 TW optical pulse could be produced using one pair of pump lasers. Another later stage, low cost, development could be synchronised provision of the raw energy of the pump lasers in a “long pulse” mode – one pump pair could, for example, produce a few ns, 100 J optical pulse in one beamline synchronised to the other beamline running in 0.5 PW mode.

Interaction Facility

The proposal will require the development of a new interaction facility. Building space already exists and this will be refurbished to create a new target area to house this new interaction facility. The expected intensities coupled with the repetition rate of the system mean that the radiological impact is significant and extensive radiation shielding will be required. By drawing on the experience of operating the Vulcan PW facility, and subsequent radiation measurements obtained from it, an optimised shielding design has been established in consultation with the RAL Radiation Protection Advisor. It is envisaged that the interaction facility itself will be a large high density concrete “bunker” with ~1 m thick walls and a ~0.3 m thick concrete roof, housed within the confines of the new

target area. This bunker will have approximate internal dimensions of 7 m x 7 m, at the centre of which will be a new interaction chamber. This chamber has been designed to accommodate as many experimental configurations as is practical, drawing on experience and experimental expertise within the CLF. Experimental diagnostic compatibility will be retained with both the existing Astra and Vulcan systems. This approach will provide the user community with a high degree of experimental flexibility, generally free from the burdensome constraint of localised shielding. Dedicated space will also be provided outside this bunker, but within the target area, to enable the deployment of time of flight systems and sensitive diagnostics that will benefit from the radiation shielding with line of sight access to the interaction point.

Remote target loading and manipulation will be needed, in addition to the provision of a restricted radio-isotope handling area to deal with longer lived radioactive isotopes that will be produced and to enable radioactive measurements to be performed. It is anticipated that no user of the facility will be required to be classified as a radiation worker.

A conceptual design of the new facility is shown below in Figure 2. The development is designed to be transparent to the existing Astra programme with no reduction in its current level of operation anticipated during the new facility construction. The new facility is due to be online to users in summer 2007.

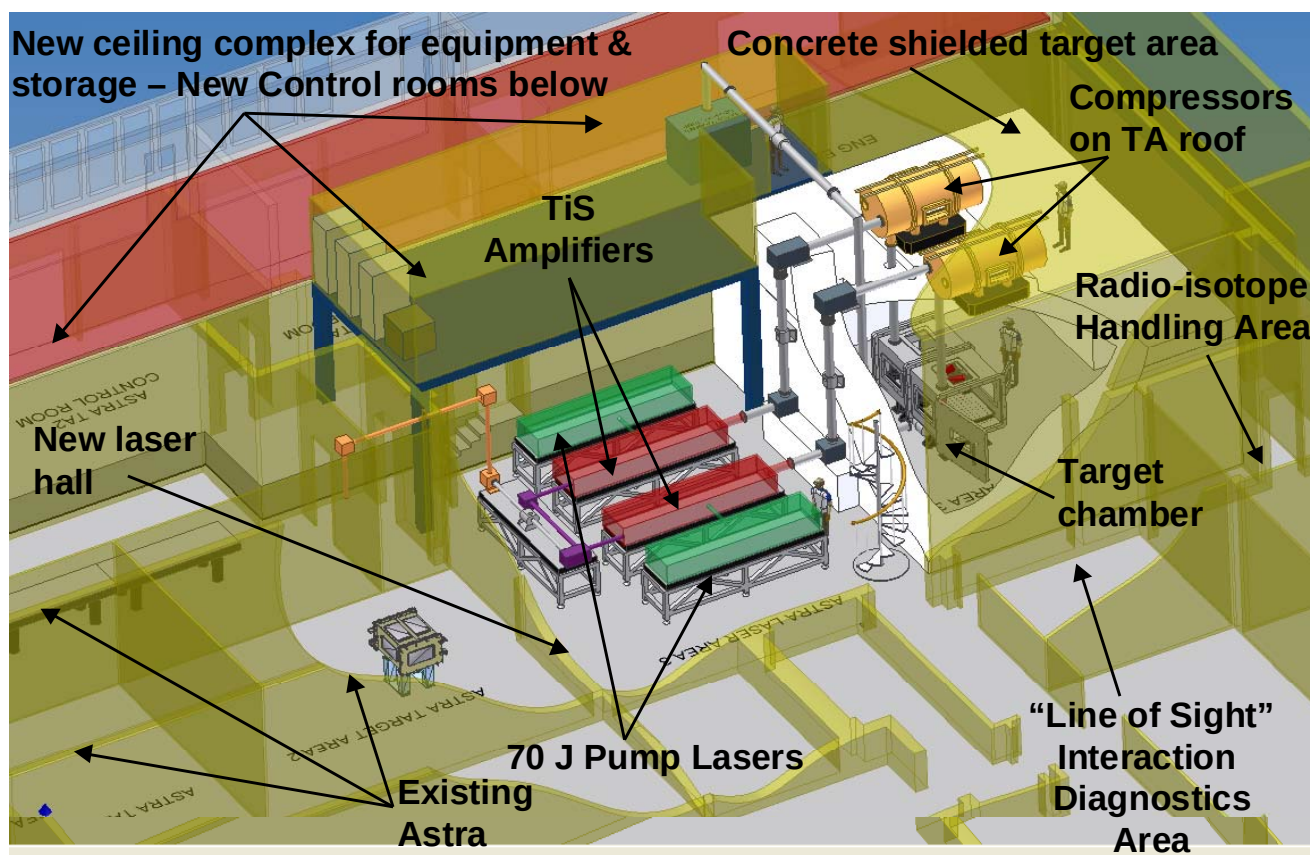


Figure 2. Conceptual Design of the Astra Gemini Project.

Novel detectors for near infra-red time resolved absorption spectroscopy and time resolved single photon/electron imaging

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Introduction

The Central Laser Facility and Instrument Department are working together to develop innovative sensors and sensor applications for imaging and spectroscopy. This fruitful collaboration has led to three novel generic sensor concepts that have received seed funding through CCLRC's Centre for Instrumentation (Cfi) development fund.

The first of these is a unique high sensitivity near IR linear array for ultrafast spectroscopy that will be commissioned by the end of 2004. The near IR apparatus will provide a new method to probe the fast photo-dynamics of important molecular species such as free radicals, solvated electrons and large conjugated molecules of importance in biological function, molecular electronics, chemical catalysis, polymerisation and solid state physics.

The second and third developments are based on novel monolithic active pixel sensor (MAPS) architectures. These use CMOS technology with integrated signal processing circuitry on chip. One is the so called OPIC (On Pixel Intelligence CMOS) sensor that has potential for ultra-high rate single event counting many orders of magnitude faster than possible with current state of the art sensors and with a unique ability to output a time stamped and digitized signal. The OPIC sensor could have applications in X-Ray, low energy photon, ion and electron spectroscopy and imaging. This should provide many new opportunities in ultrafast time resolved, time of flight and time correlation measurements. The third sensor is the tweezers sensor that has the potential to revolutionise the force feedback method employed in optical tweezers. This is described in a separate report in this section¹⁾.

The proposed near infrared ultrafast spectrometer

A schematic of the proposed spectrometer is shown in Figure 1. This spectrometer will provide unique opportunities to develop new transient absorption capability covering the 1000–1700 nm wavelength region for investigations on the ultrafast reactions of a variety of molecular species such as free radicals. Few studies of this type have been carried out previously because of the lack of suitable fast readout array sensors.

The new NIR ultrafast spectrometer will use commercial (Xenix) InGaAs 256 element arrays, 500 μm tall, with 50 μm pitch, wire bonded to an 128 channel XDAS module. Two strips were connected together into each of the 128 channels of the XDAS-10 to give a 128 channel detector with a 100 μm pitch. The arrays are readout by the existing commercialised Xstrip readout system. The Xstrip readout chip (or X2) is a 128 channel charge integrating system designed for readout of photodiodes. It has advantages over scanned systems as it has better noise and dynamic range as well as parallel storage of integrated charge. The latter feature gives less dead time, faster operation, synchronous acquisition over the array as well as flexible readout. This fast readout provides the means to signal normalise and discriminate on a shot by shot basis that in ultrafast spectroscopy is essential for optimum signal to noise.

As an example of the science that the new array might enable, it would make it possible to study, for the first time, the ultrafast excited state dynamics and charge transfer characteristics of

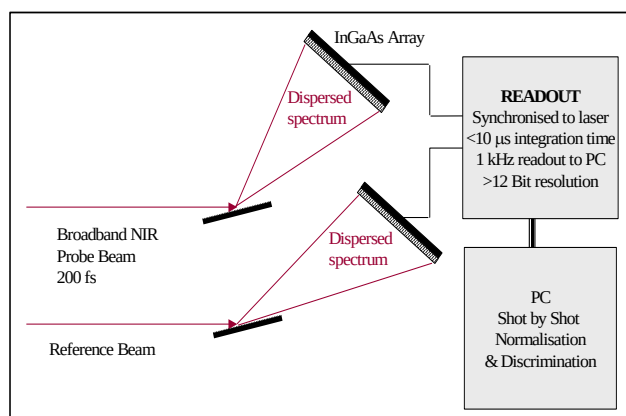


Figure 1. Schematic of NIR transient absorption detection scheme. Approximate laser probe specifications. 1 kHz repetition rate, tuning range 800–1700 nm, energy ~ 0.1 nJ per 20 nm, pulse length ~ 150 fs.

long chain carotenoids, having absorption max > 1000 nm. For example; the most well known β -carotene radical cation absorption maximum is at 1050 nm. This type of radical species can be generated via judicious photochemistry or photoionisation. Other examples include canthaxanthin (in carrots), and lycopene (red of tomatoes). Both are believed to prevent cancer but the latter also to prevent heart disease, ageing and macular degeneration. The chemistry of these processes remains little understood. Other molecular systems include radical ions of multi-ring benzenoid compounds with relevance to molecular switches and light limiters. The linear InGaAs detector provides a useful non cryogenic solution to permit these experiments and broaden the CLF applications and users.

The OPIC sensor for time resolved photon/electron imaging

The Cfi funding in 2003/4 enabled a paper design for a new MAPS for fast readout of single events with digital readout of amplitude and time stamp for photon/electron imaging applications²⁾. The robust nature of MAPS technology brings potential for direct electron event detection that would in some applications remove the need for delicate image intensifiers. The OPIC sensor could dramatically reduce data overheads and would be beneficial to many applications, such as photon counting streak cameras, image intensifiers, ion and electron imaging intensifiers, direct electron imaging and time of flight, charged particle tomography and electron microscopy. These techniques find wide use in a broad range of applications, including analytical instrumentation, military, medical, space science, high energy physics and spectroscopy.

Within CCLRC there is also a rapidly growing interest in the development of kHz – MHz laser and accelerator based studies utilising time resolved pump probe studies that detect photons across the electromagnetic spectrum from IR to X-Rays as well as electrons, ions and other more exotic particles. These studies range from time resolved X-Ray diffraction measurements on the structural dynamics of biomolecules to the gas photochemistry of the ions and molecules found in interstellar space.

To provide high signal to noise possible and make best use of these valuable resources the measurements will require novel detector formats that enable powerful correlation techniques to be used to extract signals from noise in the fastest way possible.

To achieve this goal high count rate single electron and photon resolved imaging correlated to the pulse structure of the light source is generally highly desirable. This poses a fundamental challenge since there is a requirement to capture events at high frame rates and accurate time stamping well beyond what is possible with slow readout CCD (or CID) sensor technology currently employed. The OPIC sensor has the potential to circumvent the readout problem by employing an on pixel “look at me” architecture that triggers and reads out only at the detection of an event thereby minimising data overheads. This mode of operation provides a potential for orders of magnitude increase in single event counting rate capability over CCD’s. Each pixel could also incorporate an analogue to digital converter and be able to time stamp an event with an accuracy of a few tens of nanoseconds. These new multi-parameter features would enable time correlation with light sources operating at repetition rates in excess of 10 MHz and through the analysis of the analogue signal to give information on parameters such as photon event intensity and X-Ray or electron energy.

Figure 2 shows just one design circuit for a single pixel with “look at me” event counting, time stamping and analogue readout capability. Operating this circuit with a 40 MHz master clock would allow readout cycles at around 150 kHz with a short dead-time between each cycle. At the start of each cycle the photodiode sensor is reset to zero charge. Behind each pixel is a voltage comparator that generates a “hit” when an event exceeds an externally set threshold charge on the sensor element. This latches the time stamp register to the digital value corresponding to the time of the event. The same type of logic could also be used to provide a digital value corresponding to the amplitude of the signal. The corresponding value would be stored in the amplitude register. At the end of each cycle the selective readout block controls that only pixels with a hit are read out, thus reducing the data overhead. At the readout stage the pixel identifier and the timing information can be correlated with an external source such as a pulsed laser.

There are different forms that the OPIC sensor can take, for example additional registers would enable simultaneous measurement of amplitude and timing within one cycle. Also

since the sensor is based on MAPS technology it could be adapted to very large format arrays, faster readout, higher bit resolution or higher timing resolution for applications in future pump probe facilities. The paper design has been completed and a patent application has been filed²⁾.

Conclusion

The motivation for the development of novel time resolved imaging and spectroscopic techniques is often to satisfy the demands of the scientific community. This has spurred R&D into new light sources and spectroscopic methods that show huge promise for new scientific studies spanning all fields of science. As time resolved pump probe spectroscopy and imaging emerge with increasing strategic importance to the CCLRC it will be necessary to review how the best use can be made of its advanced light and particle sources. This report highlighted two novel detector array formats specifically designed for time resolved studies that use the expertise found within CCLRC. The NIR ultrafast spectrometer opens up new spectral windows utilising the fast readout capability of XSTRIP technology to provide the highest signal to noise possible. The paper design of the OPIC sensor highlights the potential of MAPS based technology to revolutionise time resolved pump probe spectroscopy by enabling virtually noise free, energy and spatially resolved imaging of photons and electrons that are correlated to external light or electron sources to an accuracy of the order of a few tens of ns providing the means to differentiate small signals on large backgrounds that is not possible at present.

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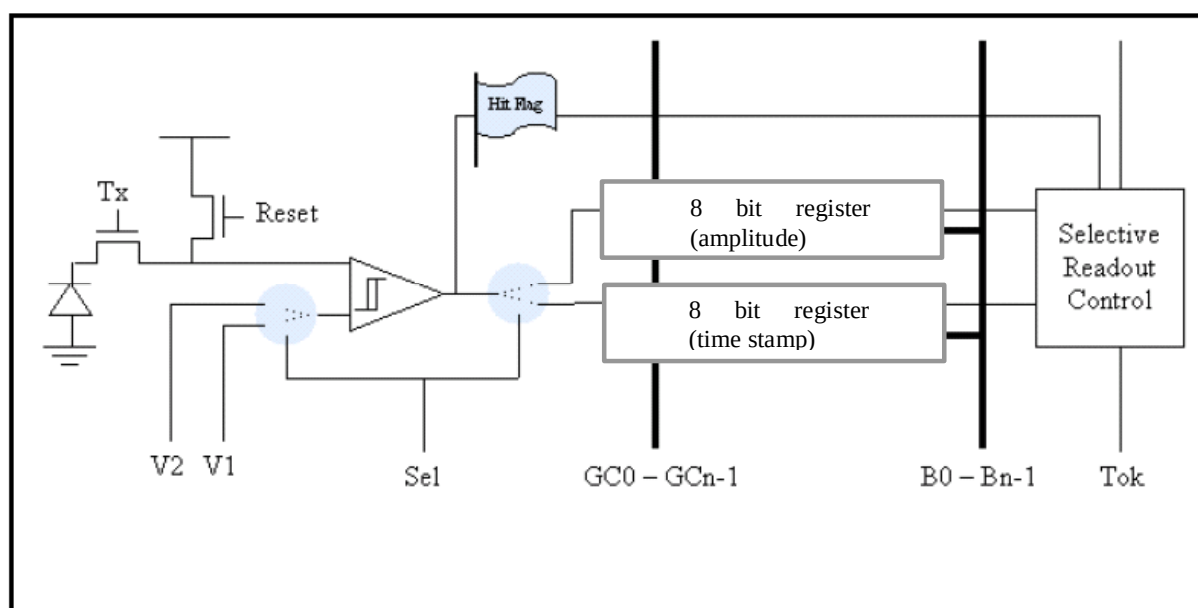


Figure 2. One example of the circuitry for an OPIC sensor.

PIRATE: increased tunability and sensitivity

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Introduction

The Picosecond IR Absorption and Transient Excitation (PIRATE) facility within the CLF Ultrafast Spectroscopy Laboratory provides both narrow and broadband ultrafast light sources, and supercritical fluid apparatus, coupled with the IR array detectors to provide a world class facility. A major achievement of this project was the development of the high sensitivity broadband femtosecond time resolved IR, TRIR, spectrometer. The TRIR system is complementary to the TR³ technique which together provide a unique capability to visualise short timescale solution phase molecular dynamics of scientific relevance across many fields of research.

Increasing tunability

Nearly all our TRIR experiments to date have used the high power second (~400 nm) and third (~266 nm) harmonics of the regenerative amplifier as a photo-excitation pump source. The reason for this was that the stability of the mid IR source and therefore the TRIR sensitivity was critically dependent on the stability of the regenerative amplifier output. In particular inherent thermal instabilities in the two-pass Super-Spitfire amplifier stage introduced unacceptable spectral and intensity instability in the mid IR probe beam making it unusable. To avoid this the amplifier gain needed to be kept at a lower level resulting in the lower pulse energy available on the output. This leaves insufficient pulse energy to drive the existing power-hungry optical parametric amplifier (OPA) on the pump side, which was optimised for ps operation. To resolve this problem we built a simple OPA optimised for the femtosecond pump and with much lower threshold operation.

The key motivation to broaden the pump wavelength tuning range was to gain full flexibility in photo-exciting specific electronic states. Control of pump photon quanta is also critical in the interpretation of TRIR spectral changes observed in the first few picoseconds after photo-excitation. At early times spectral changes are often dominated by vibrational relaxation and energy dissipation away from the initial Frank-Condon state and this can obscure subtle structural changes occurring on the same timescale. Variation of the pump photon quanta allows systematic control of excess energy imparted to the molecule and this aids in the deconvolution of the relative contributions from intramolecular vibrational relaxation dynamics relative to true changes in electronic state.

Development of low threshold OPA

To resolve the OPA problem we built a dedicated femtosecond OPA based on a simple adaptation of the efficient design we had previously built for a 40 kHz amplifier¹⁾. This simple robust, extremely low threshold OPA sits alongside the picosecond OPA to provide dedicated femtosecond and picosecond systems for rapid change over.

Enhancement of the TRIR apparatus to operate with low pump energy

The general performance of the TRIR apparatus was also improved by replacing the spherical focusing mirror and CaF₂ lens collection system with short focus gold reflective off axis paraboloid mirrors to create a sample interaction region of less than 100 μm diameter. This reduced pump beam power requirements by at least four fold, without compromising TRIR signal to noise.

Scientific investigations

The upgrade of the apparatus has supported a number of investigations.

A. Vlček has carried out an extensive time resolved IR experimental and theoretical study of the nature and dynamics of low-lying excited states of group 6 metal pentacarbonyl derivatives that play an important role in the development of our understanding of organometallic photophysics and photochemistry. Picosecond TRIR spectra were measured after 400 and 500 nm excitation. The differences in the spectral dynamics revealed a rich early time behaviour due to vibrational relaxation²⁾. It was shown that both the relaxation dynamics and the extent of ultrafast ligand dissociation vs. excited-state relaxation depend on the pump wavelength.

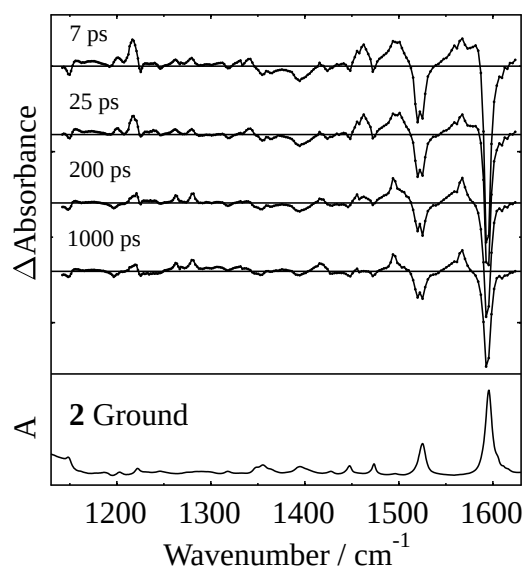


Figure 1. TRIR spectra of a rhenium complex with a pendant azacrown ether, covering the fingerprint region and showing inter-converting excited states. The pump wavelength of 350 nm was generated by mixing the fundamental output of the laser at 800 nm with the 622 nm signal output from the OPA.

J N Moore has studied rhenium complexes which act as light-controlled ion switches due to the presence of an azacrown ether within one of the ligands. Pump excitation at a wavelength of 350 nm was crucial to populate the key excited states, and the TRIR work provided valuable information on the structure, bonding and charge distribution within the excited states that drive ion release in this important class of molecules³⁾.

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Raman atomic force microscopy – a feasibility study

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Introduction

The provision of simultaneous molecular specificity and nanoscale spatial resolution is key to understanding structure and molecular function in materials, interface sciences, nano-devices, molecular wires, cell biology and medicinal chemistry. To date there are several methods capable of nanoscale spatial resolution including electron microscopy and scanning probe microscopies such as near-field aperture scanning optical microscopy (NSOM) and Atomic Force Microscopy (AFM). However, none of these techniques can provide detailed molecule specific, spectroscopic information with spatial resolution on the tens of nanometre scale. For example, apertures with diameter $\phi < 50$ nm are available, however, the poor transmission efficiencies in either excitation or collection modes limit the practicality of NSOM for Raman imaging. Recent work of several groups has demonstrated the feasibility of an entirely new approach to meet this critical requirement for a truly chemically specific imaging technique with nanoscale resolution¹⁾.

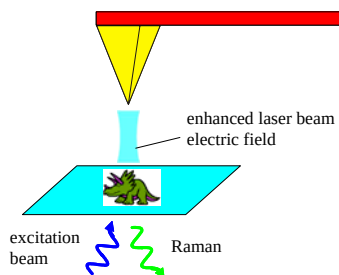


Figure 1. Schematic diagram of the setup: A laser beam illuminates the AFM tip for chemical specific analysis with sub-diffraction limit (nanoscale) spatial resolution.

In this apertureless Raman-AFM technique a metallised AFM tip mimics the effect of a single, noble metal nanoparticle used in the surface enhanced (resonance) Raman scattering technique, SE(R)RS that is much exploited for its high (single molecule) sensitivity. The enhanced electric field of the laser beam increases Raman scattering efficiency in this same region leading, for example, to reported enhancements of 4000 in Raman scattering¹⁾.

The methodology is still in its infancy but a number of exceptionally promising pilot experiments have already been performed demonstrating spatial resolution down to 35 nm with carefully chosen samples and conditions²⁾.

Experimental Study

As the first step in a long term programme leading ultimately to the establishment of a facility at RAL, we have demonstrated the Raman AFM enhancement effect with existing laser and detection instrumentation available at RAL. The experiment was performed on a silver coated substrate thinly coated with Rh6G, using 514.5 nm excitation beam (2 mW). This beam was focused to an estimated spot size of ~ 0.5 μ m diameter using a microscope objective lens. Spectra obtained with and without the tip are shown in Figure 2. The observed enhancement of the collected Raman signal with the tip was 2.7. The Raman

spectrum from the enhanced zone alone is obtained by subtracting the two spectra from each other. Taking into account the difference in the size of the enhanced zone of diameter ~ 200 nm, which is approximately equal to the dimensions of the AFM tip, and the size of the illuminated zone this corresponds to the local enhancement factor of ~ 20 under the AFM tip. This enhancement is commensurate with the radius ('sharpness') of the tip. A large enhancement is expected from smaller radius tips. Such tips will be required for achieving higher spatial resolution. The AFM tip, manufactured by Nanonics, consisted of a gold sphere of 200 nm diameter attached to a silicon AFM cantilever. The sample was mounted on a manual x,y-micropositioner used for coarse placement, whilst the tip was separately mounted on a computer controlled x,y,z-nanopositioner of accuracy 5 nm. The silver substrate was prepared using a method described in Reference 3 with thickness of a few nanometres to ensure partial optical transparency for the transmission of the probe and Raman signals. The spectra were collected at the backscattering geometry from below the sample using a Leica DM-IRB microscope and objective lens with numerical aperture of 1.2. The AFM tip was carefully positioned above the sample and gradually lowered to bring the enhanced electric field towards the sample surface. The spectra were collected using a liquid nitrogen cooled CCD camera and a single stage spectrometer.

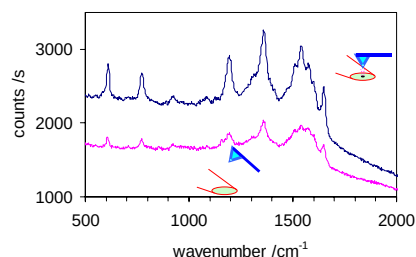


Figure 2. Raman spectrum (SERRS) of Rh6G with (top) and without (bottom) AFM tip. The acquisition time for each spectrum was 2 s.

Conclusion

The results demonstrate the viability of developing a prototype of the Raman AFM device based around existing laser and detection technology at RAL. The new concept holds promise to advance research across many areas including a study of macrostructure and molecular dynamics in photosynthetic membranes, membrane protein identification, design of new drugs, material sciences and direct DNA/protein sequencing.

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The development of a MAPS detector for fast position detection on the Optical Tweezers apparatus

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Introduction

Collaboration between the E&ID and CLF under the Centre for Instrumentation CFI is currently in progress to develop the next generation of detectors designed for fast, high-resolution, position detection measurement. The detectors are initially aimed for use with the optical tweezers apparatus in the Lasers for Science Facility. The detector will, for the first time, enable absolute femtonewton force and nanometer positional control of several particles held in multiple laser traps. The use of such a device to control a fast feedback system where fast laser beam steering can freeze out external forces such as Brownian motion at rates of >10 kHz is anticipated to revolutionise our force measurement capabilities. There are immediate applications for such a device, spanning areas such as medicine, cell biology, DNA studies, chemistry, and physics.

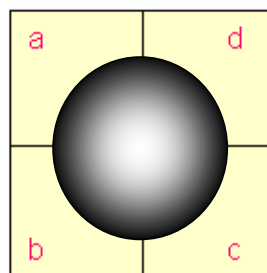
To date such fast feedback techniques have relied on quadrant photodiode (QPD) sensors¹ that measure the position of the image of an optically trapped object at typically up to rates of 10kHz. The positional information is used to control laser trap position that then apply gradient forces to counteract external forces. This simple method can measure, track and lock the position of an object to 3 nm accuracy.



Figure 1. The CCLRC designed “Star Tracker” active pixel sensor.

The detector will be a custom-designed monolithic active pixel sensor (MAPS) with a random access capability to simultaneously poll defined regions of interest (ROI). It should be noted that conventional CCD's and frame grabbers cannot be used for high resolution, fast force feedback control because their readout and image analysis rate is orders of magnitude too slow.

The starting point for this research program is to use a similar, although much slower, detector that can be used to specify the final design of the MAPS array. The array used is the CCLRC designed “Star Tracker” active pixel sensor², a 512x512 pixel array which has 10 bit intensity resolution. The “Star Tracker” is capable of 10 frames per second over the full field. In particular we are seeking information on the technical requirements regarding optimization of pixel size, bit resolution and light sensitivity. This will enable us to estimate the degree of nanometer scale positional accuracy that can be achieved with the new detector.



$$X = \frac{(a+b) - (c+d)}{(a+b+c+d)}$$

$$Y = \frac{(b+c) - (a+d)}{(a+b+c+d)}$$

Figure 2. Typical algorithms for position detection on quadrant based sensors where the relative signal intensity from the four sectors can be compared to provide X,Y displacement.

Experimental Study

The “Star Tracker” array was attached to a viewing port of a Leica DM-IRB microscope using a standard C-mount adapter. The microscope was then adjusted to enable standard bright-field imaging of a sample placed on the piezo-electric stage. However, as the acquisition times of the fast detector will be over 1000 times shorter than that of “Star Tracker”, a neutral density filter was placed before the illumination source to reduce the light intensity by a corresponding factor of 1000. This ensures that the light sensitivity levels will be comparable between these tests and when using the final detector. The target samples were polystyrene latex beads of 2.7 and 5.0 μm diameter that are commonly used in optical tweezing experiments. They were either dried onto cover slips to provide a fixed target or, dispersed in water and then optically trapped. Our aims were to assess the positional resolution of the existing detector and to track multiple objects in the field of view.

Results and Discussion

A series of image captures of polystyrene beads fixed to a cover slip surface were acquired. The positions of the beads were calculated using an algorithm that simulates the function of a QPD. The ROI containing the bead is subdivided into four smaller regions from which the intensities are compared to provide X and Y displacement (see Figure 2)

As the bead moves across a ROI (12 x 12 array of pixels) the relative intensity distribution changes as shown in Figure 3. The value of interest is the centre of the bead and this corresponds to the intercept of the longest slope with zero relative intensity (at a position of 20.2 in the example given). This technique can be calculated for each frame of the acquisition to generate a sequence of positional data. From this data, the beads attached to the cover slip were actually shown to be moving a few nanometers, which was attributed to a small drift of the piezo-electric stage. The resolution of movement detection was determined as 0.3 nm.

Using a similar technique the positions of two optically trapped particles were also determined over a period of 5 seconds. The particle tracking history is shown on Figure 4 and this illustrates that, even when optically trapped, particle movement due to Brownian collisions can be in the range of 100 nm. This

underlines the importance of being able to lock the particles into a force feedback control loop.

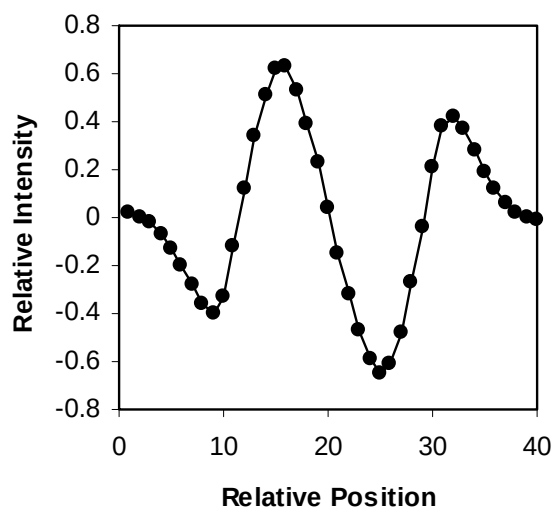


Figure 3. Plot of relative intensity of the X component of position movement using the equations described in Figure 2.

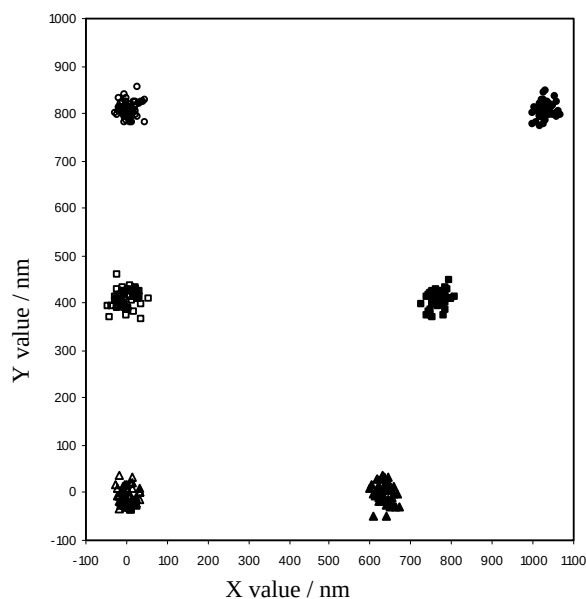


Figure 4. Plot showing the tracked coordinates of two optically trapped particles at separations of 6.2, 7.8 and 10.5 μm . The data is offset in Y for clarity and the X separation distance has been decreased by a factor of 10 to show greater detail in the particle movement.

Conclusion

We have proven that the light sensitivity and bit resolution of the prototype sensor readout will be capable of sub nanometer spatial resolution and 100 femtoNewton force resolution in the positional tracking and manipulation of multiple objects.

The sensor will be specified as a custom 512 x 512 pixel element and 25 μm pixel size CMOS active pixel sensor architecture. In the prototype this will read up to 6 ROI's, of 36 pixels each, that may be programmed to overlap with the optical trap and/or object positions. High quality force feedback will be attained by reading each of the ROI's continuously at a rate in excess of 10 kHz with >11 bit resolution on each pixel. The sensor will be switchable from

>20 kHz readout of ROIs to conventional full frame video readout to provide full images of the field of view that will aid targeting and capture of objects.

If necessary for the most accurate feedback measurement we would utilise over-sampling and pixel summation to give up to 16 bit effective resolution, which is ample for nanometer accuracy force feedback. Indeed, the proposed advanced pixel sensor design could be adapted to even greater speed, bit resolution and array size. In the future these will be only limited by processing speeds and fast laser control optics and not the sensor method.

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Design and construction of an optical parametric correlator (OPAC)

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Introduction

One of the main limiting factors restricting the contrast measurable using the conventional third order correlator is the signal to noise in the detector since the photon efficiency of the device is very low. It was realised that the substitution of an OPA instead of the THG crystal could provide the same contrast information but with a high photon gain replacing a high photon loss and a device based on this principle has been designed and developed.

The OPA correlator built for this project uses a very similar set-up to a conventional correlator except that the 3rd harmonic stage is replaced by an OPA. The probe pulse becomes pump and the fundamental the signal pulse. The gain of an OPA is exponentially dependent on the pump intensity and gains in excess of 1 million can easily be achieved.

The correlator is set so the pump pulse amplifies one short time segment of the signal pulse with a gain of 1 million (Figure 1). The OPA process creates a copy of this amplified segment in the idler direction, which can be measured. This technique has a number of advantages:

- 1) It reduces background noise since the measured signal is switched into a completely different direction.
- 2) Unlike the conventional correlator the signal is greatly amplified giving a bigger detectable signal, so the signal is no longer limited by detector noise.

However since the OPA is used at degeneracy in this case, the idler is at the same wavelength as the signal, so scattered signal light especially from the OPA itself could limit the overall performance. This scattered light is minimised by increasing the non-collinear angle, this being 20° (internal) in our case.

This work follows on from the report last year and describes improvements to increase the measured contrast ratio and automate the system. This project was undertaken as part of the European funded SHARP program.

Experimental Set-up

The experimental layout is shown in Figure 1. Approximately 2 mJ of the 20 mJ, 800 nm, 50 fs pulses in Astra TA1 were used. The input beam was telescoped down to 3 mm diameter and frequency doubled in a 2 mm thick BBO crystal. The

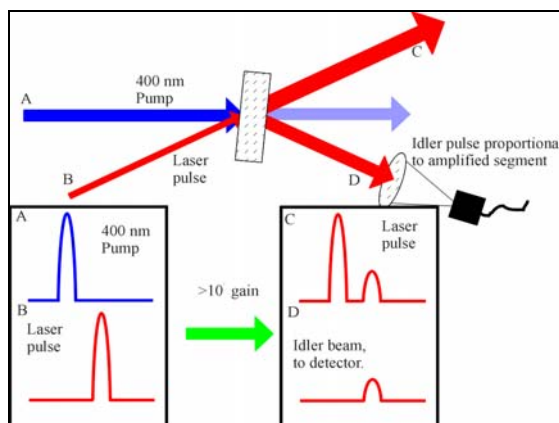


Figure 1. Operation of OPA Correlator (OPAC) Pump amplifies short segment of seed pulse and a copy is generated on the idler channel.

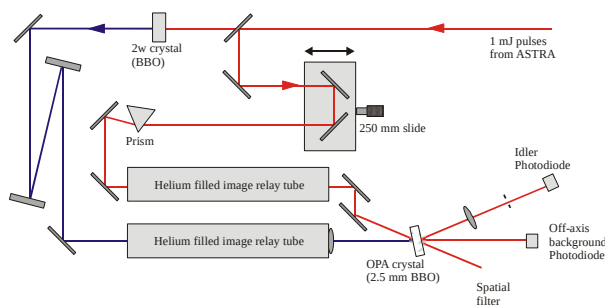


Figure 2. Set-up of OPA correlator.

400 nm light (conversion efficiency approx 10%) and residual 800 nm were then separated using a dichroic mirror. The 400 nm light was used to pump the OPA and the 800 nm as the OPA seed beam. To generate the necessary pump intensity for the OPA process whilst maintaining the beam quality, the pump beam was telescoped down by a further factor 3 and imaged through a helium filled relay tube. This gave a pump intensity of 20 GW / cm² in a 1.3 mm diameter beam at the OPA crystal. The seed arm was also reduced to 1.3 mm diameter using an identical image relay tube. This arm could be delayed or advanced with respect to the pump by a computer controlled Newport translation stage with 250mm of movement. The pump pulse length was measured as 200 fs. Due to the non-collinear geometry used in the OPA, the phase matching condition required the pump and idler to propagate in the OPA crystal at an angle of 10 degrees. This large angle helped reduce the scatter between seed and idler beams. To achieve high gain it was also necessary to disperse the seed pulse to ensure good group velocity (pulse front) matching with the pumps. This was done with a combination of a 60° SF10 prism and the reducing telescope. The prism dispersed the beam before the telescope and the telescope magnified the dispersion to the required value. The telescope was set to image the seed beam prior to dispersion where it was still circular, so that the seed beam at the OPA was spatially circular (and well matched to the pump), but spectrally dispersed. The dispersion was checked by observing the amplified fluorescence rings and rotating the crystal so the wavelength and direction of these rings matched the seed beam.

A large area (3.5 mm square) photodiode was used to measure the idler beam. The Photodiode only had a dynamic range of 1000, so it was necessary to be able to automatically attenuate the seed before the OPA. A computer controlled filter attenuator was built in-house to achieve this. It used bi-stable solenoid actuators to move up to seven sets of ND filters in and out of the seed before the OPA. The bi-stable nature of the actuators meant they were only powered when a filter had to be moved and thus did not add any additional heat sources to the device. Since the ND filters are only introduced into the seed arm are they effectively delay this arm relative to the pump beam. It was necessary to compensate for this delay by measuring the optical retardation due to each set of filters and correcting for it by adjusting the translation stage. The diode, filters and delay stage were linked to a PC. Software was written in LabVIEW to control the translation stage to scan the pump pulse relative to the signal and adjust the filters to keep the idler signal within the linear range of the photodiode. The computer recorded an averaged idler intensity at each point to build up a profile of the signal pulse and could take up to 3000 data points / hour.

Results

Measurements of the bandwidth showed an amplified bandwidth of 10 nm despite dispersing the beam to satisfy the group velocity matching condition. Changing the relative delay between the two pulses changed the central wavelength. It was assumed that this behaviour was due to a short (200 fs) pump pulse and residual chirp on the seed beam. The gain was measured as 10^5 .

Figure 3, shows a typical scan. The dips at either end were made by blocking either the pump or signal to leave just the scattered signal, or the pump-induced ASE respectively. They show a maximum measurable contrast below the 10^{-11} level. Most of the post pulses can be accounted for by multiple reflections in the attenuating filters. The pre-pulses are as yet unexplained. The trace agreed well with previous results taken with a third order correlator.

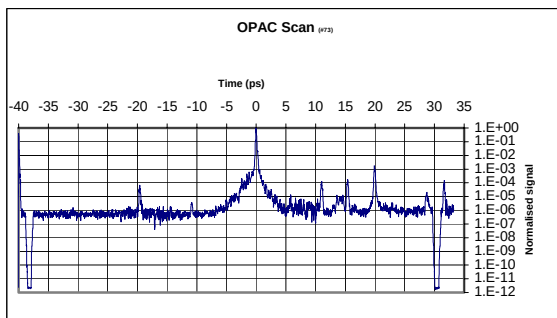


Figure 3. OPA correlator Trace. (5 samples/point, 10 fs steps. Dips show effect of blocking pump (lhs) or seed beams (rhs). Background measurable $< 10^{-11}$.

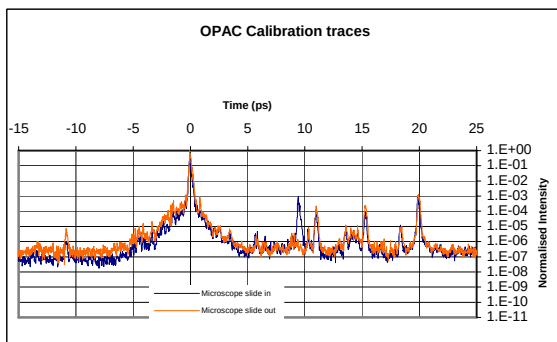


Figure 4. Temporal and intensity calibration scan.

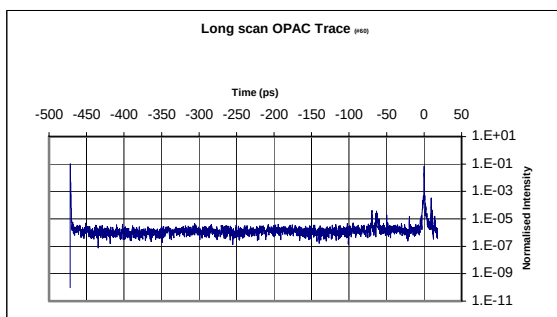


Figure 5. Long range pre-pulse scan.

The correlator was calibrated using an etalon to create multiple pulses in the seed arm, Figure 4. A single post pulse is evident at the time and intensity expected. The double reflection was undistinguishable from the ASE post pulse and could not be checked. A long scan showed that the device was capable of measuring over hundreds of picoseconds to the range where fast diodes can reliably be used, Figure 5.

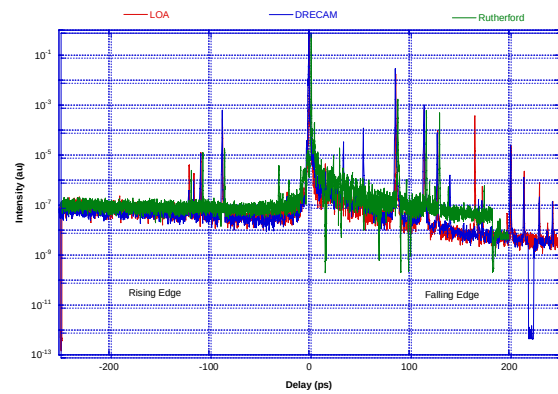


Figure 6. Comparison of OPAC with LOA, Drecam 3rd order correlators taken at LOA.

As a further test of the device it was taken to the Laboratoire d'Optique Appliquée, France (LOA) and run on their 100 TW system, Figure 6. Results were consistent with their 3rd order correlator. They showed the same asymmetry in the pulse shape with a sharper rising edge and picked out the same pre / post pulses. By comparing the traces taken the LOA correlator on the same laser it allowed OPAC artefacts and Astra post-pulses to be identified.

Conclusions

An OPA correlator was built and demonstrated the ability to measure a contrast ratio of 10^{11} , an order of magnitude greater than the original design. The improved design reduced the energy requirement from 10 mJ to 1 mJ / pulse and enabled the device to take a correlation in a single scan under computer control..

Tests on the Astra laser showed the compressed pulse had a contrast of just over 10^6 .

The design and results of the OPA correlator have been submitted for publication.¹⁾

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Design and construction of a SPIDER for Astra

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Introduction

As part of the Astra upgrade programme funded by the Basic Technology Initiative, a device called a “Dazzler”¹⁾ was purchased for Astra. The function of this device is to pre-compensate the spectral phase errors that arise from material dispersion and B-integral as the beam propagates down the laser chain, thus ensuring that the spectral components of the pulse are all in phase at the output of the laser. Provided this condition can be achieved, the resulting compressed pulse will be as short as it can be, and will have the lowest levels of uncompressed background. To make the best use of the Dazzler, the relative phases of the different spectral components of the pulse must be measured, so the amount of correction needed for each wavelength can be applied. The device known as a SPIDER²⁾ (Spectral Phase Interferometer for Direct Electric-field Reconstruction) is one of the best ways of making this measurement. This article describes the SPIDER technique and the design considerations for the instrument that has been built for Astra.

Principles of SPIDER

Full details of the SPIDER technique can be found in the article referenced above. The following is a brief description of how the device works.

The short pulse that is to be measured enters the device and is split into three components. Two of these are small fractions of the original pulse, separated by a short time delay which must, however, be long enough to ensure no overlap between them. One technique for achieving this is to reflect the input pulse from an uncoated etalon of suitable thickness: the reflected pulses are each 4% of the original, with a time separation equal to the etalon round-trip time. These two weak pulses can also be generated using a Michelson interferometer, with the advantage that the delay can be varied at will.

The remainder of the pulse contains most of the energy, and is stretched by a factor of several hundred in a prism- or grating-pair pulse stretcher. The chirp produced in this stretcher does not have to be exactly linear, but must be large enough that the phase can be considered constant over a time equal to the duration of the original pulse.

The pulse pair and the chirped pulse are brought back together on a polarizing beamsplitter and focused in a thin Type 2 frequency-doubling crystal, typically BBO. The paths of the two beams must be equal, and the polarization of one of them must be rotated by 90 degrees in order to achieve Type 2 phase matching.

The two pulses in the pair overlap in time with different frequencies in the chirped pulse, and consequently the upconverted pulses have a spectral shear between them. The upconverted light is sent to a spectrometer, where the two pulses interfere: at a point in the spectrum plane the light from each pulse is effectively monochromatic, so there is temporal overlap between them and interference can occur. The result is a spectrum that is modulated by a set of sinusoidal fringes.

The formation of the fringes can be understood as follows: for some frequencies, the time interval between the pulses corresponds to an even number of half-periods, and those frequencies will interfere constructively in the spectrum. For intermediate frequencies, the same time interval corresponds to an odd number of half-periods, so destructive interference will occur, resulting in dark fringes in the spectrum.

If all the frequencies in the original pulse are exactly in phase with one another, the fringes seen in the spectrum will be uniformly spaced. However, if there are out-of-phase frequencies as a result of dispersion or B-integral in the laser chain, the fringe spacing will vary across the spectrum. By recording and analyzing the fringe positions, the variation of phase with frequency in the original pulse can be measured.

Design considerations

The practical design of the SPIDER must include all the elements referred to above, i.e. the generation of the various pulses, timing adjustments, frequency upconversion and spectrum measurement. It was also decided to make the device small enough that it could be used inside the Astra TA2 pulse compressor chamber if necessary. After some trials with a simple CAD package, a layout was developed which fitted onto a 60 cm x 30 cm optical breadboard. The design was based on the paper by Shuman et al.³⁾, which describes a device that was made to analyze a similar length of pulse.

It was decided to use an existing 250 micron silica etalon to generate the pulse pair, and to use a double-pass grating pulse stretcher to produce the chirped pulse. For the spectrometer, a custom Czerny-Turner design was used, as none of the various small spectrometers on the market has the right combination of resolution and dispersion. With the right geometry, a spectrometer of this type can be made to have zero coma and a flat field⁴⁾.

A major concern was the bandwidth over which the spectrum could be measured. The nonlinearity of the upconversion process means that at the 10% intensity points in the wings of the 800 nm spectrum, the intensity at 400 nm will be 1% of its peak, which is close to the limit of detection using an 8-bit camera with 1 grey level of noise. It is highly desirable to be able to measure the spectrum, and hence the phase, further into the wings. To improve the signal-to-noise ratio, the spectrum must be broadened perpendicular to the dispersion direction, and the signal at each wavelength summed down the columns of pixels in the image. The SNR is improved by $\sqrt{N}$ where N is the number of pixels summed over, so that fringes further into the wings of the spectrum are detectable. The spectrum can be broadened by including a cylindrical lens in the optics that relay the 400 nm light to the spectrometer, so as to form a line image on the slit. The best performance will be obtained only if the slit, grating rulings and the columns of the CCD chip are all set accurately parallel, so the adjustments needed to achieve this condition (by rotating the slit and the grating) were included in the design.

The intensity in the chirped pulse will be less than that of the pair of pulses by an amount rather greater than the stretch factor, due to grating losses. This beam was therefore focused more tightly than the pulse pair, to reduce the mismatch in focal intensity between the beams. This also has the advantage of reducing the sensitivity of the SPIDER to alignment errors, as upconversion will occur whenever the small focal spot overlaps the larger one from the dual-pulse arm of the device.

Layout of the SPIDER

The final layout of the SPIDER is shown in Figure 1. The input beam is aligned through two irises, B and C, to ensure a consistent direction. The pulse pair reflected from the etalon is angled down towards the breadboard, and steered via M2, M3, the half wave plate, lens L1 and M7 to the beam combiner. The

main part of the pulse enters the stretcher via M1. The two gratings are mounted on an optical rail to allow easy changes in their separation, and the back mirror M4 returns the beam for a second pass of the stretcher to remove the spatial dispersion. The position of M4 is adjustable so that the optical paths in the two arms of the device can be equalized. The second pass beam is also angled down from M4, and arrives at the beamsplitter via M1 and M5 and the lens L2.

The two foci overlap in the upconversion crystal, and this common focus is imaged a few cm beyond the spectrometer slit by the spherical lens L3. The cylindrical lens L4 forms a line focus about 1 mm long on the slit, extending the spectrum over roughly 80 pixels and improving the SNR by nearly an order of magnitude. The blue filter absorbs the unconverted 800nm light.

Although the beams overlap in the crystal, they are not collinear. The long pulse beam is angled upwards from M5, and the pulse pair is angled downwards from the beam combiner, so their images are physically separated at the spectrometer slit. There are two reasons for this. First, the tuning of the crystal to the correct angle for type 2 phase matching may not be exact, or the polarizations of the two beams may not be exactly orthogonal. In either case, some frequency doubling may occur within one or both of the beams, producing a background on the SPIDER signal and reducing the contrast in the fringes. This background can be eliminated, or greatly reduced, if the two individual 400 nm beams are separated from the upconverted light, which appears in an intermediate direction. Second, the pattern of fringes formed from the pulse pair alone is used as a calibration for the instrument, when the crystal is tuned to give maximum conversion of that beam. The software is arranged to read that calibration data from a different part of the CCD image; the crystal merely needs to be rotated through 45 degrees to obtain the calibration fringes.

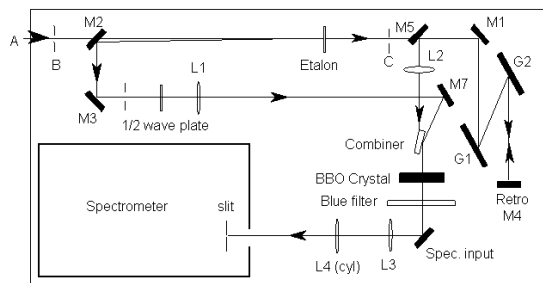


Figure 1. Layout of the SPIDER.

Setup and operation of the SPIDER

Once all the components had been mounted and placed on the breadboard, the alignment was relatively straightforward, using the compressed beam in TA1. The two beam paths were aligned, and the beams brought to a common focus at the BBO crystal. The spectrometer components were placed in positions found by calculation to give the necessary angles for the minimum-coma condition. The rotation of the slit was set with the grating in zero order, using a mercury lamp as a source, and a zoomed view of the camera display to make any tilt easy to see. The grating was then moved into first order, and itself rotated to minimize the observed tilt of a spectral line near 400nm. A cover was constructed for the spectrometer to shield it from ambient light. The remaining adjustment was the relative timing of the two beams, which was set by sliding M4 while viewing the frequency-doubled beams after the blue filter on a fluorescent card. The duration of the stretched pulse is about 10ps, so M4 was moved in steps of 0.5mm, and the vertical motion of M5 scanned to ensure there was overlap between the foci at some point. As the device is effectively an autocorrelator in this mode, a strong signal was seen once there was some overlap in time between the pulses. This light

disappeared when either arm was blocked, confirming it as a mixing signal, after which small adjustments of M4 and M5 were made to maximize the brightness. The spectrometer input mirror was adjusted to send the light through the slit, after which the upconverted spectrum of the input pulses, modulated by a fringe pattern, was seen on the camera monitor.

Analysis of the SPIDER fringes

The processing steps required to analyze the fringe data and extract the spectral phase can be summarized as follows. The intensity values are Fourier transformed into frequency space, where the basic fringe frequency appears as a large peak, and the modulations caused by phase errors appear as a smaller peak at lower frequency. The small peak is isolated by multiplying the transformed data set by a windowing function, which is unity around the peak but zero elsewhere. The windowed function is then back-transformed to yield the phase errors, which are displayed by the SPIDER software. Our copy of the code was obtained from Professor Walmsley's group at Oxford. The image below shows the output phase error as a function of wavelength between 750nm and 855nm; however, the data are unreliable outside the range 780nm to 825nm, because there is not enough light to detect the fringes consistently. Within the limits of good data the trace is fairly stable, while outside them it fluctuates wildly from shot to shot.

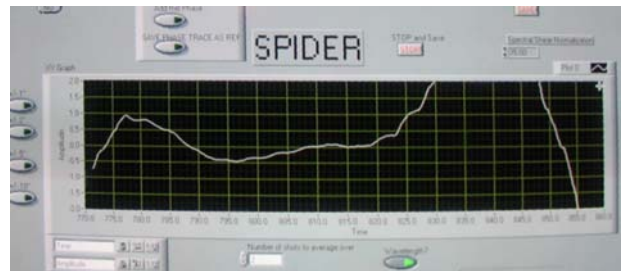


Figure 2. Example of a SPIDER phase-error trace.

Optimizing the compressor using the SPIDER

Aligning the TA2 pulse compressor has become much easier and more accurate following the completion of the SPIDER. The third-order dispersion arising from an incorrect incidence angle on the gratings is easily seen in the phase error trace, and can be eliminated to a far greater extent than was possible before, when an autocorrelator was the only pulse diagnostic. Typically, the departure from uniform phase after this optimization procedure is less than one radian at any point in the spectrum. Once the compressor has been optimized, a residual-error trace can be captured by the software, and the phase-versus-wavelength data transferred to the Dazzler control computer. The Dazzler then applies the required additional phase correction at the start of the laser chain, which typically reduces the maximum phase error to 0.5 radian or less. A measure of the success of this system is that the shortest pulses measured in Astra TA2 are now slightly less than 40fs, compared with a typical 70fs in pre-Dazzler days.

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Contrast enhancement using a Kerr gate

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Introduction

It is well known that the laser driven optical Kerr effect provides a fast optical gate and has been used, for example, to greatly enhance low energy Raman signals buried in a high level of background noise¹⁾. Since the response time of such a gate can be very short this offers the potential to gate out the background Amplified Spontaneous Emission (ASE) surrounding a short pulse and so greatly increase the pulse contrast.

Experimental details

The gating was tested in Astra TA1 using a Carbon disulphide (CS₂) as the Kerr media. The beam was split to give 90% of the energy for the gating pulse, leaving 10% to be gated, Figure 1. The polarizer was set to fully extinguish the gated pulse when the gating pulse was blocked. The polarization of the gating pulse was rotated through 45° by a half-wave plate. Both pulses enter the Kerr cell together, the more intense gating pulse causing the polarization of the weaker gated pulse to be rotated so it can pass through the polarizer.

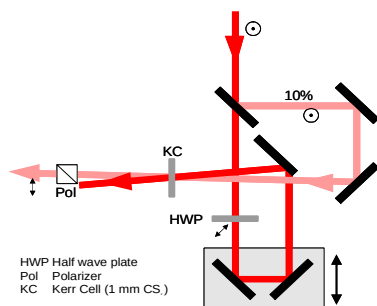


Figure 1. Layout for Kerr self-gating experiment.

Results

The gated signal vs the relative pulse delay was plotted to assess the response time of the Kerr gate, see Figure 2. The figure shows an asymmetric profile, with a fast rising edge and slower logarithmic decay. The gate duration was measured as 2.5 ps full width half max. To open the gate a minimum fluence of 300 $\mu\text{J} / \text{mm}^2$ was necessary.

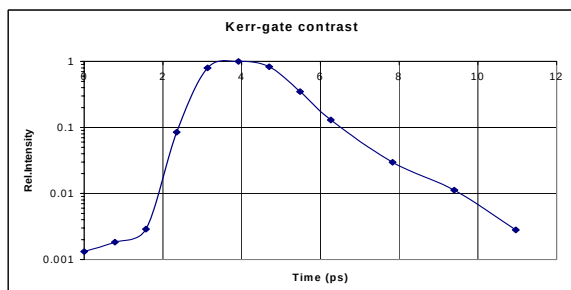


Figure 2. Relative intensity of gated pulse vs. inter pulse delay.

Observing the near field of the gated pulse it was found important to :-

- 1) propagate the beams close enough to collinear so that they fully overlap temporally in the media.
- 2) slightly advance the timing of the gating pulse so any non-linear effects in the more intense pulse are not transferred to the gated pulse.

Using the self-gating set-up the efficiency of this process is limited to around 5% of the total energy. 10% should be possible with further optimization. Higher throughput could be achieved using a separate gating pulse.

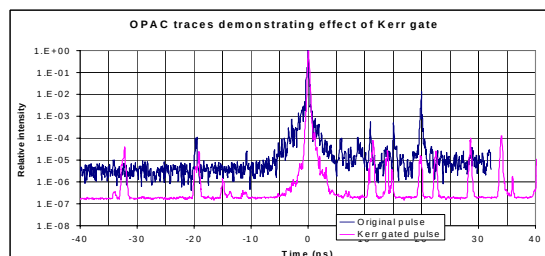


Figure 3. OPAC scan showing background and post-pulse suppression using Kerr gating technique.

The gated pulses were also measured with the OPAC, Figure 3. The results show a substantial improvement in the pulse shape within 5 ps of the main pulse. The rising edge is significantly steepened and the overall background level reduced. The apparent 10^{-7} level is above the true background level as the full dynamic range of the OPAC was limited by the low OPA pump intensity / gain. Comparing the amplitude of Astra characteristic post-pulses (i.e. at 20 ps) it can be seen that the gating process has suppressed the background by more than two orders of magnitude.

Practical implementation and future plans

Recently solid PbGaBi glass has been demonstrated as having similar Kerr properties²⁾. Since CS₂ is a volatile, toxic liquid it is intended to test this glass for its suitability of gating 800 nm, femtosecond pulses.

It is proposed install a Kerr gate (or other contrast enhancer) mid-chain on Astra. Unstretched oscillator pulses would be amplified to the μJ level before Kerr gating. They would then be stretched and amplified conventionally. To improve the low gating efficiency the gating pulse could be amplified separately.

Depending on the actual contrast enhancement of a single gate it may be necessary to repeat the process. This technique has the potential of placing two (or more) gates in succession with the same gating pulse used to open each of them. This would significantly enhance the contrast ($>10^2$ / gate) while only losing energy from the gating efficiency (efficiency up to 60% per gate).

Conclusion

Kerr gating has been demonstrated as possible contrast enhancing technique capable of suppressing the background by more than two orders of magnitude. Further optimization is expected to give a $>10^4$ times enhancement with 30% efficiency.

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Comparison of imaging plate, CCD, and film detectors

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Introduction

Imaging plates (IPs) have been found to be useful detectors in high x-ray flux regimes, such as synchrotron radiation and other strong x-ray sources. These detectors have high quantum efficiencies, a large dynamic range and a respectable signal-to-noise ratio compared to other widely used x-ray detectors, and operate over a wide wavelength range^{1,2)}.

This report compares the performance of two familiar detectors; CCD and film, with the less well known IP, in a weak X-ray signal regime. This signal is from spectroscopic measurements of aluminium *K*-shell emission, recorded with a standard single flat crystal spectrometer (SCS). The points of comparison considered are resolution, sensitivity, and practicality of use.

Experiment

The experiments were performed in Target Area West of the Vulcan laser facility. Four beams of the Vulcan laser were focused onto a 200 μm by 200 μm square, by 1 μm thick, aluminium dot target mounted on a 50 μm thick mylar ($\text{C}_{10}\text{H}_8\text{O}_4$) foil, see Figure 1. Each beam provided ~ 100 J at 1.053 μm in a 1 ns pulse. Random phase plates were used to ensure a uniform laser intensity profile in a 500 μm diameter focal spot, resulting in a average intensity on target of $1.8 \times 10^{14} \text{ W cm}^{-2}$. The laser foci overfilled the aluminium dot targets, which ensured a one-dimensional aluminium plasma expansion, as the aluminium plasma was confined on all sides by the expanding mylar.

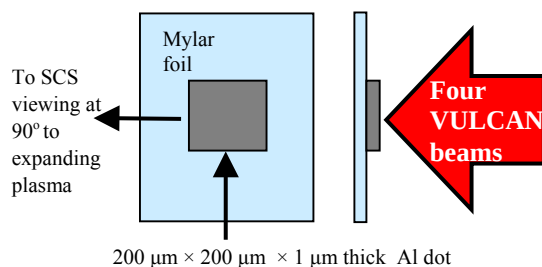


Figure 1. The experimental geometry, front and side view.

Spectroscopic measurements were made using a SCS viewing perpendicular to the expansion direction of the aluminium plasma, and using a 25 μm entrance slit to provide spatial resolution with a magnification of unity. The spectrometer used a potassium hydrogen phthalate (KAP) crystal, and recorded a wavelength range of 5.7 – 6.8 $\text{\AA}$ (2.2 – 2.6 keV). This wavelength range encompasses six aluminium *K*-shell emission lines, namely He- β , He- γ , He- δ , He- ϵ , Ly- β and Ly- γ . Here, Ly- denotes hydrogenic aluminium transitions ($1s\text{-}np$), and He- denotes helium-like aluminium transitions ($1s^2\text{-}1snp$). The spectra were recorded using three different detectors; a 16-bit x-ray Andor CCD camera fitted with an e2V CCD30-11 chip, Kodak Industrex CX x-ray film, and a Fuji Film BAS-MS imaging plate. The CCD was run at 5 $^{\circ}\text{C}$ with a signal integration time of 2 sec, the film was developed with Kodak D 19 developer, and the IP scanned with a Fuji Film BAS-1800II scanner. For each detector a known thickness of

aluminised mylar was used as a filter, and in the case of the CCD camera a 25 μm layer of beryllium was added. The response of these filter materials as a function of wavelength is well known, which allows the raw data to be corrected accordingly, and hence the performance of the three detectors to be directly compared. In this experiment, the spectral resolution of the SCS is dominated by the 200- μm width of the source, and is 0.013 $\text{\AA}$ for each detector.

Comparison of Resolution

Figures 2 and 3 show extracted cross-sections from the recorded spectra for each detector. The cross-sections are taken before any background subtraction, and averaged over a 100 μm wide strip. In Figure 2 data taken at 200 μm above the initial target surface are shown, and the positions of the six spectral lines are indicated. For all detectors the spectral lines are easily resolvable, however it can be seen that the IP and film detectors have more background noise than the CCD camera.

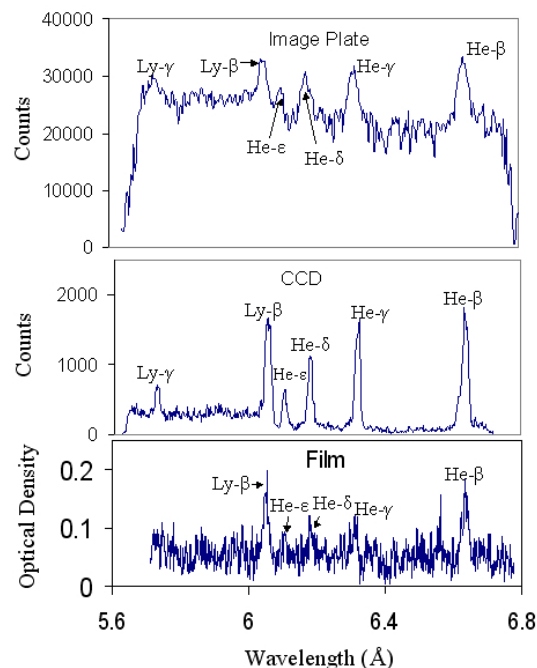


Figure 2. Cross-sections taken through the data at 200 μm above the target surface, averaged over a 100 μm wide strip.

The background subtracted signal-to-noise ratio was calculated to be 1.6 for the IP, 30 for the CCD camera and 2.5 for the film detectors, for the He- β line at 200 μm above the target surface.

Figure 3 shows similar data to that in Figure 2, taken 1000 μm above the target surface. The film detector recorded no signal at greater than 300 μm above the original target position. The spectral lines are still well defined for the image detected with the CCD camera. The IP data is of lower quality, with the He- ϵ , Ly- β and Ly- γ lines not clearly resolvable.

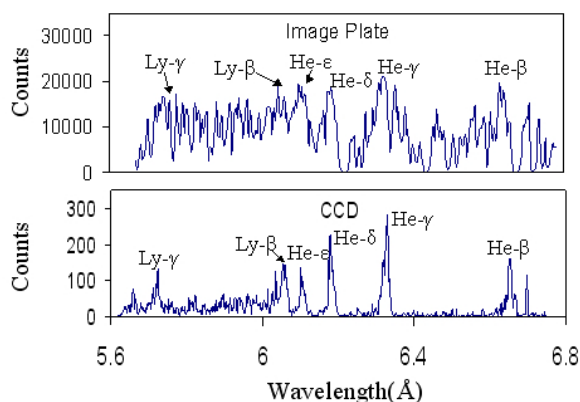


Figure 3. Cross-sections taken through the data at 1000 μm above the target surface, averaged over 100 μm wide strip.

In this experiment the spectral resolution is the same for each detector (0.013 $\text{\AA}$), since it is dominated by the 200 μm source size. The spatial resolution is dependent upon the effective element size of the detector, for the CCD this is just the pixel size of 27 μm . The IPs used here have a crystal size of 50 μm , and the scanner used has a step size of 50 μm . Higher resolution IP systems are available, where the crystal and step sizes are < 10 μm . The element of the film detector is ~ 1 μm , however the resolution is limited by the step size used when densitometering to extract the data. Film can be typically densitometered with a 5 μm step size, although this is time consuming, and 16 μm was used here. Convolving these effective element sizes with the 25 μm entrance slit size yields spatial resolutions of 56 μm for the IP, 36 μm for the CCD and 30 μm for the film detectors.

Comparison of Sensitivity

Sensitivity is defined here as the number of photons μm^{-2} needed to produce a count on the detector. The sensitivities of the CCD and film detectors are well known. By considering the raw data for these CCD camera, and removing filter responses, the number of photons μm^{-2} incident upon the detector surface is found. This value was then used to calculate the sensitivity of the IP at 200 μm above the initial target surface, see Figure 4(a).

It can be seen in Figures 2 and 3 that the image plate and film detectors are compromised by background noise, and so an important consideration is the number of photons μm^{-2} needed to produce a measurable signal on the detector. This was calculated by considering a series of cross-sections through the data (averaged over 100 μm), moving progressively further away from the target surface. At some height above the initial target position a given spectral line is no longer resolvable above background noise, and the number of photons μm^{-2} incident on the detector at this point is taken to be the threshold level for a measurable signal. Figure 4(b) shows how this threshold level varies with wavelength for each detector, where the CCD has been used as the absolute detector.

Comparison of Practicality of Use

IPs are flexible, large area detectors, which can be cut to the required size and mounted like film. The data is extracted by scanning, which does not require a darkroom. Scanning times are a few minutes, and each IP is re-usable after being erased.

CCDs offer an instant data access and a quick turn-around time, however the area of the chip limits the size of the image. The dimensions of a CCD camera mean that it is unsuitable for some geometries, and CCDs can be susceptible to radiation damage.

Film can be cut to the required size, and the image is permanent once developed. However, it is sensitive to development

technique, and its response is non-linear particularly for weak and intense signals. Data extraction via densitometry is very time consuming.

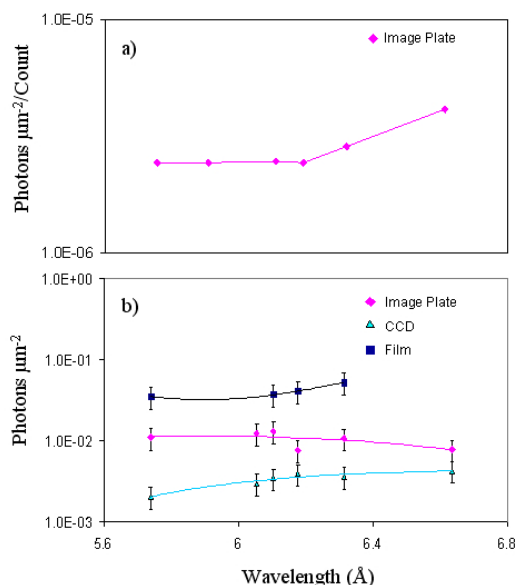


Figure 4. a) Then number of photons μm^{-2} needed to produce a count on the IP. b) The minimum number of photons μm^{-2} needed to produce a measurable signal for each detector in this wavelength range.

Conclusion

The suitability of three detectors for use in a weak x-ray signal regime was investigated for the wavelength range 5.7 – 6.8 $\text{\AA}$. The detectors in question are: a 16 bit x-ray Andor CCD camera fitted with an e2V CCD30-11 chip, Kodak Industrex CX x-ray film and a Fuji Film BAS-MS imaging plate.

The resolution of the CCD camera is limited by the 27 μm pixel size, CCDs with pixels as small of 10 μm are available. IPs with spatial resolution of 5 μm are available, and film can be densitometered with a step size of 5 μm , although this is not always practical due to time considerations. When the resolution of the detector is not important (for example when using an SCS, with the spectral resolution dominated by the source size) the CCD camera is by far the most suitable detector, offering much greater signal-to-noise ratio and sensitivity.

When high spatial and spectral resolution is necessary (for example when using bent crystal spectrometers³⁾ film is currently the most suitable detector in this wavelength range. Nevertheless, it has been shown that IPs provide improved sensitivity to film, and with a high-resolution scanner could match film for resolution. It should also be possible, with care, to reduce the background noise on IPs. Given the ease of use of IPs compared to film, they may provide an excellent alternative.

Acknowledgements

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High-resolution X-ray spectroscopy using toroidally bent crystals

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Introduction

Collisional processes and the thermal state and density of the plasma influence emission spectra from laser-produced plasmas. Processes such as Doppler and pressure broadening, opacity and electric fields in the plasma may modify the shape of individual emission lines. Examination of emission line profiles may therefore reveal detailed information on plasma conditions. In the case of mid-atomic number elements, K-shell emission spectra occur in the X-ray region and a spectrometer that can resolve wavelengths to mÅ levels is required. A device based on a toroidally bent crystal allows such measurements to be made with the desirable characteristics of high luminosity, coupled to high spectral and spatial resolutions¹⁾. The signal strength produced by these spectrometers also allows time resolution using a streak camera.

A toroidally bent crystal forms a surface that has both horizontal and vertical radii of curvature; the lattice planes are assumed to be parallel to the crystal surface and as free from defects and imperfections as possible. Crystals can now be grown and then bent with a sufficient degree of accuracy that the dynamical theory of x-ray diffraction gives excellent agreement with the experimentally measured crystal parameters^{2,3)}. The crystal bending radii in the horizontal, R_h , and vertical, R_v , directions determine focal distances in each plane. These foci are given by equations 1 and 2 respectively.

$$f_h = R_h \sin \theta_B / 2 \quad (1)$$

$$f_v = R_v / 2 \sin \theta_B \quad (2)$$

where R_h and R_v are horizontal and vertical crystal bending radii and θ_B is the central Bragg angle. If $f_h = f_v$ then monochromatic imaging of the source is achieved with a high two dimensional spatial resolution and a spectral range of a few mÅ⁴⁾. When f_h and f_v differ, the crystal can be used as a spatially resolving spectrometer. As an example of a high-resolution spectrometer geometry, consider Figure 1.

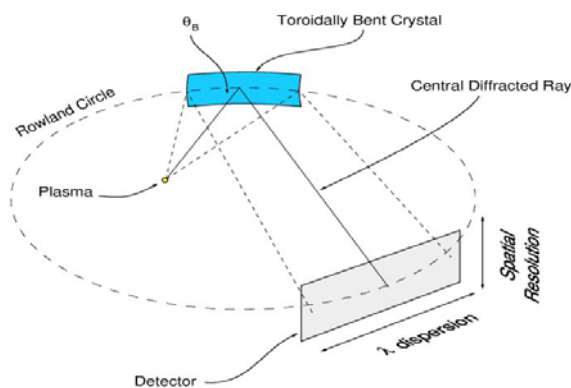


Figure 1. Magnifying, high-resolution spectrometer geometry.

The geometry is based on the Rowland circle with radius of $R_c = R_h/2$ and with spectral dispersion taking place along the horizontal direction of the crystal surface. The detector is placed on the Rowland circle and the source positioned at the vertical focal point of the crystal. Spatial resolution is in the vertical direction. The spatial magnification factor, M , is given by the ratio of the crystal-detector distance (d_{cd}) to plasma-crystal

distance (d_{sc}). The spectrometer geometry shown in Figure 1 has $M > 1$, this results in the vertical extent of the source being magnified at the image plane. The image plane lies on the Rowland circle with $d_{cd} = R_h \sin \theta_B$. The source is located within the Rowland circle, and the source-crystal distance is given by Equation 3.

$$d_{sc} = R_v R_h \sin \theta_B / (2 R_h \sin^2 \theta_B - R_v) \quad (3)$$

Note that for fixed bending crystal bending radii, d_{sc} and M vary with wavelength. Over small wavelength ranges these variations are small. It is important to note that the bending radii and Bragg angle of the crystal determine the spectrometer geometry as well as the spectrometer performance.

Analysis

A ray tracing method is used to determine the properties of a toroidal crystal spectrometer such as the spectral range, spectral and spatial resolution, in addition to source size broadening effects and instrument luminosity. In its current version, a point monochromatic X-ray source emits uniformly into a solid angle of 4π and is then diffracted from the crystal. Since the crystal is curved in both horizontal and vertical directions it is essential to determine the angle of incidence for each wavelength accurately. This is most conveniently performed using a vector approach. For a given wavelength the vector from the source to crystal surface is found, then the scalar product with the normal to the crystal surface gives the angle of incidence to the crystal surface. Bragg's law is used to determine the diffracted vector. This vector is propagated from the crystal surface to its point of intersection with the detection plane. This approach allows an accurate calculation to be made of the diffracted wavelength distribution across the crystal surface, leading to the dispersion characteristics at the detector.

Spectral characteristics and resolution

A spectrometer suitable for high-resolution X-ray spectroscopy of a highly ionised aluminium plasma⁵⁾ could use a quartz crystal with the (10.0) lattice planes parallel to the crystal surface and a 2d spacing of 8.5098 Å. Representative crystal dimensions are 30×20 mm with bending radii of 1404.5 mm and 312.8 mm in the horizontal and vertical directions respectively. If the central Bragg angle is set for the Heβ ($1s^2 \ ^1S - 1s3p \ ^1P$) line of helium like aluminium at 6.635 Å then this results in a spatial magnification, in the vertical plane, of 4.46.

To examine the spectrometer properties, we performed the ray trace calculations at wavelengths of 6.615 Å, 6.635 Å, and 6.655 Å using Gaussian spectral profiles with a full width at half maximum (FWHM) of 2mÅ. The intensity distribution of diffracted wavelengths on the crystal surface is shown in Figure 2. This demonstrates that the wavelength dispersion occurs mainly in the horizontal crystal direction. The curvature of the diffracted lines results mainly from the change in Bragg angle due to the crystal curvature in the vertical direction. This curvature is small yet important.

The corresponding intensity distribution in the *image* or *detector* plane is shown in Figure 3. This illustrates both the spectral resolution along the horizontal plane and spatial

resolution in the vertical plane. The wavelength dispersion is slightly nonlinear, and at non-central wavelengths the images are slightly defocused. Defocusing occurs where the flat detector, for example a charged coupled device (CCD) chip, moves off the Rowland circle (see Figure 1). For closely lying spectral lines the effect of defocusing is small but distinct. This is shown in Figure 3a where the spectral lines at 6.615 Å and 6.655 Å have slightly lower peak intensities than the central line at 6.635 Å.

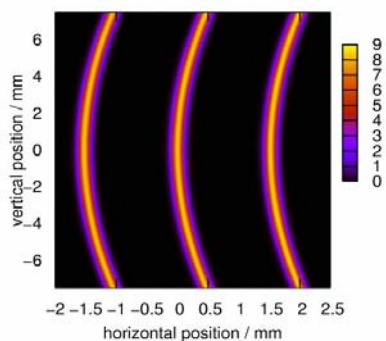


Figure 2. Intensity distribution of diffracted wavelengths on the crystal surface assuming a point x-ray source. The wavelengths from left to right are 6.655 Å, 6.635 Å and 6.615 Å.

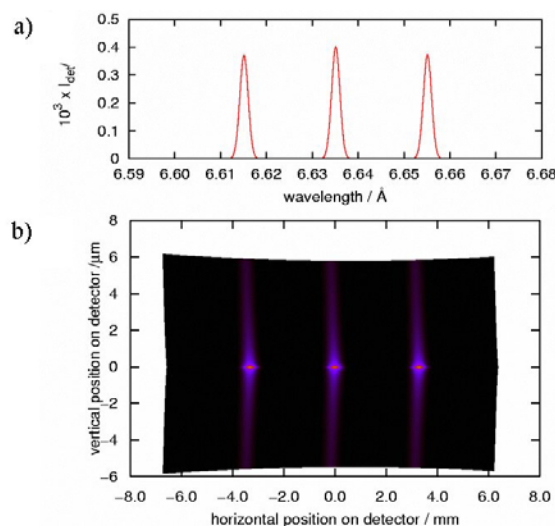


Figure 3. Intensity distribution of diffracted x-rays in the detector plane; a) wavelength against intensity in the horizontal plane and b) the corresponding 2-dimensional intensity distribution of the x-rays.

Figure 3 illustrates the high dispersion of the instrument; the 40 mÅ spectral range extends over 7 mm of detector. Typical detector sizes result in only a small portion of the total diffracted x-rays from the crystal being recorded. This limits the spectral coverage to 100 mÅ on a 21 mm long detector. On a typical CCD camera with pixel size of 12-μm × 12-μm, each pixel covers a spectral range of 0.057 mÅ. This is less than the wavelength interval (0.73 mÅ) corresponding to the FWHM of the quartz (10.0) rocking curve ($\Delta\theta_{RC}=28.2$ arcseconds equivalent to 1.37×10^{-4} rad at 6.635 Å)³. The observed spectrum is therefore not deteriorated by the detector pixel size.

Another factor limiting the spectral resolution of the spectrometer follows from broadening of the spectral lines introduced by an extended source. Generally, if these effects are to be negligible, this broadening must be substantially smaller than both the width of the spectral line and the crystal-rocking curve. The focusing geometry of a toroidal spectrometer eliminates the effects of a large source size. For example the broadening of a spectral line at the detector due to an extended source of 500 μm is only ~0.2 μm, i.e. much smaller than a typical detector element size.

Luminosity

A key advantage of a toroidal spectrometer is the high luminosity provided by the large collection solid angle and focusing of X rays. Here luminosity, B , is defined as the ratio of the maximum intensity of X rays on the detector I_{det} to the source intensity I_0 measured at a fixed distance from the source. I_{det} and I_0 are calculated in photons m⁻². If B is known and the detector has an absolute calibration, then this can be used to estimate total number of photons emitted from the X-ray source at a particular wavelength.

The luminosity is calculated using the ray trace approach for the geometry shown in Figure 1. The calculation assumes a central wavelength of 6.635 Å (the Al Heβ transition) emitted from a point source with the FWHM Gaussian spectral profile of 2 mÅ. The crystal response is included by representing the crystal-rocking curve as a Gaussian⁵. The line profile recorded at the detector is given by adding in quadrature the rocking curve width and the incident radiation line width, here 2 mÅ. This subtends an angle of 3.75×10^{-4} rad about the central Bragg angle to give measured linewidth at the detector plane of 3.98×10^{-4} rad.

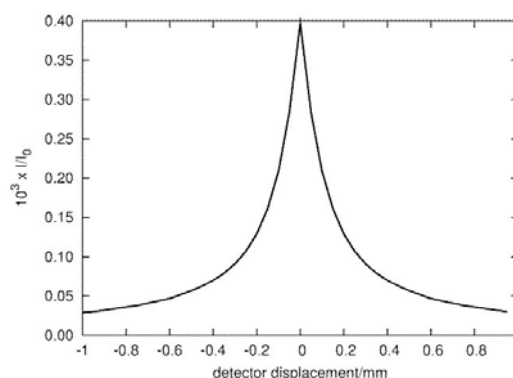


Figure 4. Luminosity, I_{det}/I_0 as a function of detector displacement from the Rowland circle for $M = 4.46$

Figure 4 shows the variation of luminosity for a detector displaced from the Rowland circle for a point X-ray source, illustrating the effect of detector misalignment. The peak corresponds to the detector being placed on the Rowland circle, where the vertical focus is formed. This underlines the importance of placing the detector to within 200 μm of the Rowland circle to maintain high luminosity. Accurate detector alignment is also required to avoid the effects of defocusing and to maintain high spatial resolution.

Conclusions

The geometry and spectral characteristics of a spectrometer based on a toroidally bent crystal are presented. A ray tracing approach is used to determine the geometry, dispersion, magnification, and luminosity. Modeling clearly shows a toroidal spectrometer is not influenced by extended source size, and the spectral resolution better than mÅ is readily achieved. Luminosity calculations demonstrate the high collection efficiency characteristics. These features make toroidal crystal spectrometers ideal instruments to obtain high-resolution spectra even from low radiance plasmas, and suitable for coupling to time resolving instruments e.g. X-ray streak cameras.

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A photoinjector laser system for the 4GLS ERL prototype

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Introduction

4GLS (the 4th Generation Light Source) aims to be the world's most flexible accelerator-based light source, providing ultra-high brightness pulsed radiation from the IR to the XUV (Figure 1). The technology is based on an ERL (Energy Recovery Linac) and FELs (Free Electron Lasers) alongside undulators and bending magnets. The ERL allows tailored pulse characteristics, experimental flexibility and very high quality electron beams.

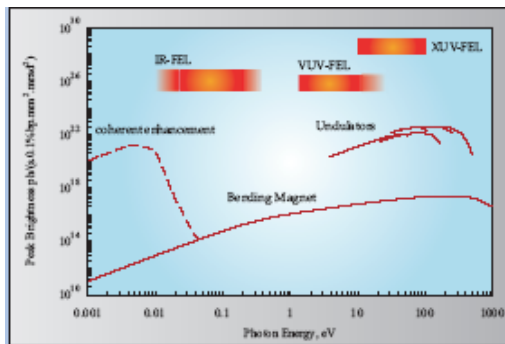


Figure 1. Spectral range and brightness of 4GLS.

In a conventional synchrotron light source the electron beam travels around a storage ring and every time the beam is bent synchrotron radiation is emitted. At the end of each orbit the radiated energy is replaced from an RF field. In the case of an ERL the electrons only go around the machine a few times, so optimum beam parameters can be maintained. At the end of the cycle the electrons arrive at the accelerating cavity 180° out of phase. Their energy is recovered into the RF field and is then re-used to accelerate a fresh electron bunch. Since 2003 a 4-year program has been under way at the Daresbury Laboratory, developing a prototype ERL (ERLP – Figure 2) to resolve some of the design issues for 4GLS.

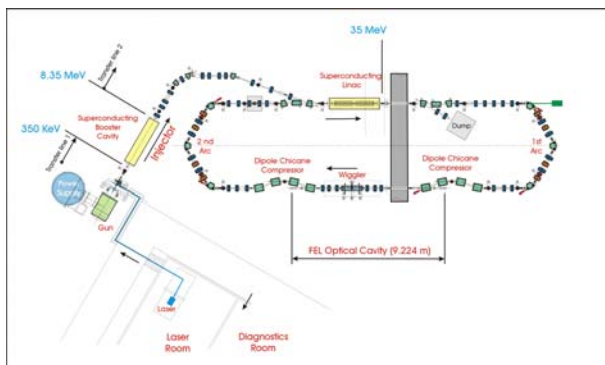


Figure 2. The proposed scheme for 4GLS ERL Prototype.

The electrons for the ERLP will be provided by a laser-driven photoinjector which, together with the superconducting accelerator technology, will generate high stability, low emittance electron bunches. This requires very tight control of the laser's pulse amplitude and timing stability.

Photoinjectors have several desirable properties. They can deliver high average currents with flexible time structure and

very high beam brightness. These are well-suited to the needs of high brightness colliders, FELs and laser-plasma accelerators.

System description

The photoinjector consists of a master RF (Radio Frequency) source, which provides the timing reference for a mode-locked laser oscillator and the input for the accelerator RF system. The laser oscillator output is amplified, converted to the right wavelength (dependent upon the bandgap of the photo-cathode material) and chopped into trains of pulses which provide the required charge per bunch from the cathode. Since the electron source is a photocathode illuminated by a laser, the designer has very good control over the spatial and temporal characteristics of the emitted electrons.

Table 1 shows the ERLP electron gun parameters and the corresponding requirements for the laser.

Cathode material	Cs:GaAs
Electron bunch charge	80 pC
Bunch length	20 ps
Bunch repetition rate	81.25 MHz
Pulse train length	1 bunch and 20-100 μ s
Pulse train repetition rate	Single shot and 1-20 Hz
Cathode efficiency	1 %
Laser wavelength	532 nm
Laser pulse energy at cathode	20 nJ
Average power at cathode	<4 mW
Pulse length	<20 ps
Beam diameter at cathode	2-6 mm (FWHM)

Table1. ERL prototype electron gun and laser parameters.

Stability

The stability of the photoinjector is mainly dependent upon the stability of the drive laser. The temporal stability of current laser systems is excellent (see below). The major remaining issue is the pulse energy stability, both pulse train to pulse train and within each pulse train. A typical laser system consists of a mode-locked oscillator and a cw or qcw power amplifier. Without careful feedback stabilization this can achieve <10% amplitude stability. To reach high energy and stable long (μ s) pulse trains is a difficult task. However for the ERLP test phase, with low current operation, a commercial laser oscillator and a stable cw amplifier can deliver the desired performance.

A second issue, which can be critical to the operation of the machine, is the pointing stability of the laser, as it will determine the stability of the emission from the cathode. In some circumstances a 100 μ m transverse shift of the beam on the cathode can degrade the system performance.

The oscillator-amplifier

As mentioned before the relatively low pulse energy requirement for ERLP allowed us to choose a commercial solution for the laser. The HighQ Laser IC-10000 ps Nd:YVO₄ oscillator and amplifier is based on SESAM (Semiconductor Saturable Absorber Mirror) technology and, after frequency conversion, delivers 67 nJ/micropulse at 532 nm (Table 2), which is well above the required pulse energy on the cathode. The system consists of a diode pumped mode-locked oscillator and an amplifier, which doubles the power in the IR (1064nm). These are followed by a temperature stabilized second harmonic generator crystal, based on non-critical phase-matching, which achieves 50% conversion efficiency. The unique feature of the

system is the user-replaceable diode module, which can be replaced in case of failure or degradation by the user. The typical lifetime of the diodes is 10,000 hours.

Laser material	Nd:Vanadate
Average output power	>10 W
Wavelength	1064 nm
Pulse repetition rate	81.25 MHz
Pulse length (FWHM)	7 ps
Beam quality	TEM ₀₀ M ² ≤ 1.2
2ω (532 nm) average power	5.5 W

Table 2. High Q Laser system specifications.

Time structure

The repetition rate of the oscillator was chosen to be 81.25 MHz, the 16th sub-harmonic of the 1.3 GHz accelerator RF. For the prototype phase the laser has to deliver several different pulse structures, from single shot to a 100 μs long train of pulses, at 1 Hz to 20 Hz repetition rate. This requires a combination of a fast electro-optic gate (Pockels cell), and mechanical choppers, the latter to prevent the Pockels cell crystal from thermal load and to increase the contrast between the short pulse train and the background. For single pulse operation the gates will be placed in the IR beam for high contrast. For pulse train operation they will be moved to the visible beam to give constant thermal load on the second harmonic crystal so that high stability can be achieved.

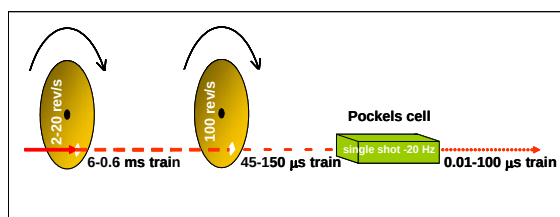


Figure 3. Schematic of the pulse train gating hardware.

Timing synchronization

One advantage of photoinjection is that the electron and laser sources can be used in combination, with good synchronization between them. The ERLP electron gun will be a DC design, however the accelerator system will run at 1.3 GHz, so synchronization issues have to be considered even in the prototype phase of the project. The electrons from the gun have to arrive at the accelerator at exactly the right phase of the RF cycle, in order to get the right energy spread for subsequent bunch compression. The timing accuracy should be $\leq \pm 1$ ps. An issue which will be important later in the project is synchronization to the FELs, which will need much higher stability, in the region of 100's μs or even 10's of fs.

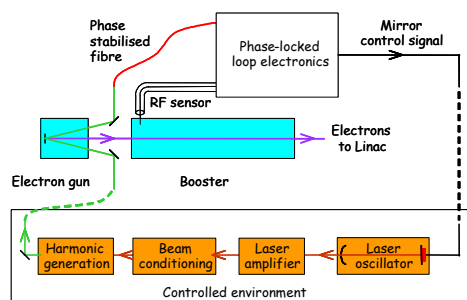


Figure 4. Schematic of the synchronization loop.

There are several environmental factors which can affect the synchronization. These include mechanical vibrations, temperature variations, electrical noise and refractive index changes. However laser-to-RF synchronization to < 1 ps can now be achieved routinely. Commercial synchronizers move one of

the laser oscillator cavity mirrors using fast mechanical and piezo actuators. A phase-locked loop ensures locking of the laser pulse frequency to the RF reference. The synchronization unit that we have purchased from HighQ Laser is specified to lock the photoinjector laser to clean RF with a jitter of < 400 fs. One possible architecture for using this synchronizer on ERLP is shown in Figure 4.

Beam transport

The beam path from the second harmonic crystal to the photocathode is just over 13 m long. For ERLP the beam size on the photocathode should be easily changeable between 2 mm and 6 mm diameter from outside the accelerator area. There is a ~2 m thick shield wall between the laser room and the accelerator area, where optics cannot be placed, and there is no access to any optics in the last meter before the cathode. The beam transport system shown in Figure 5 is designed to image the plane of the second harmonic crystal onto the cathode in order to get the best beam profile. The optics have been chosen so that this will be valid for the 3 mm diameter beam, and will be a close approximation at other beam sizes. The size of the beam will be changed by moving the final lens inside the laser room.

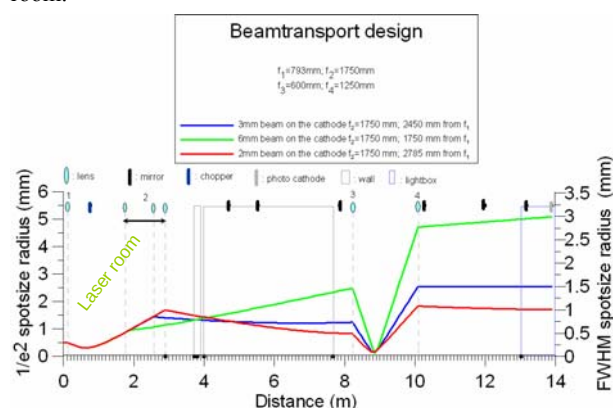


Figure 5. Beam sizes through the beam transport system.

Although for initial tests a Gaussian beam is suitable, ideally the laser pulse should be rectangular in time and space when arriving at the photocathode. Gaussian to flat-top beam shapers are available on the market, with $\pm 5\%$ amplitude variations across the beam. A similar beam profile can be achieved by using a small f-number lens and “pulling” the rays from the wings of the Gaussian beam across its center by spherical aberration. A test measurement for this can be seen in Figure 7. This method creates a wide range of angles in the beam, which means that efficient transport over a long path is difficult. The interference patterns created by coherent rays may also cause beam modulation and the effect of this on the emittance from the photocathode is not clear.

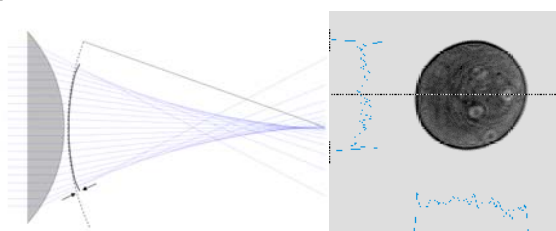


Figure 6. Beam shaping via spherical aberration.

Conclusion

A photoinjector laser for ERLP is being developed using the latest technology in diode pumping and synchronization. It will be delivered to Daresbury in the Autumn of 2004.

Vulcan Operational Statistics

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Vulcan has completed an active experimental year, with 11 full experiments and two one week experiments taking place in target areas TAE, TAW and TAP between April 2003 and March 2004. This was the first complete operational year for the Petawatt target area (TAP), which has proved very productive. From mid-December until the beginning of March, the Vulcan laser was shut down to enable improvements to the infrastructure to be made.

Table 1 below shows the operational schedule for the year, and illustrates the shot rate statistics for each experiment. Numbers in parentheses indicate the total number of full energy laser shots delivered to target, followed by the number of these that failed.

The total number of full disc amplifier shots that have been fired to target this year is 703 with 71 of these failing to meet user requirements. The overall shot success rate to target for the year is 90%, compared to 80% for the previous year. Figure 1 shows the improvement in reliability over the past two years, now standing at 94%. Analysis of the reasons for failure

of the individual shots enables a breakdown of these causes into specific categories. This is discussed below.

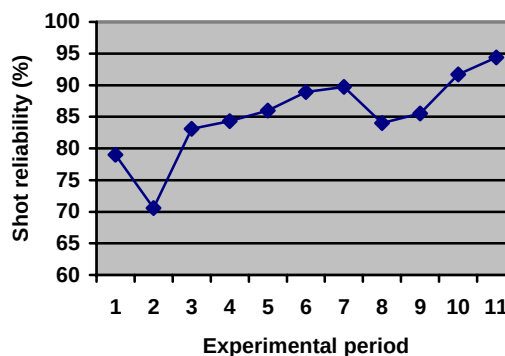


Figure 1. All areas shot reliability for each experimental period for 2002-3 (periods 1-5) and 2003-4 (6-11).

PERIOD	TAE	TAW	TAP
31 Mar – 27 Apr			Contract – AWE Petawatt laser interactions (45, 5)
12 May – 22 Jun	GR/R25699 – J Wark Diffraction from metals under shock (81, 9)		GR/N33188 – K Ledingham Petawatt solid target laser interactions (45, 4)
30 Jun – 10 Aug	GR/R12626 – N Woolsey Development of x-ray lasers (66, 13)	GR/N36554 – G Pert Development of x-ray lasers (28, 2)	
25 Aug – 31 Aug		MOD Access – C Edwards Commercial contract (76 Faraday shots)	
18 Aug – 12 Oct		R36039 – N Woolsey Ultra-high intensity atomic physics (76, 15)	GR/R16778 – P Norreys Studies of advanced fast ignitor (26,1)
13 Oct – 19 Oct			EU Access – O Willi (8,0)
27 Oct – 7 Dec	R05062 – K Krushelnick Hohlraum (85, 10)		LLNL Access – M Key Petawatt laser interactions (48, 1)
1 Mar – 11 Apr	R31768 – I Ross OPCPA development (131, 6)		R23909 – K Krushelnick Electron acceleration (64, 5)

Table 1. Experimental schedule for the period April 2003 – March 2004.

This was the first full year of operations for the Petawatt target area, with 6 full and 1 one-week experiments. The total number of full disc amplifier shots that have been fired to TAP is 236 with 16 of these failing to meet user requirements. The overall shot success rate to TAP for the period is 93.2%. Figure 2 shows the reliability of the individual experimental campaigns as the year progressed. Over the last six months (four experiments), there have been only 7 failures in 146 full energy shots (95.2% reliability).

Figure 3 shows the identified failure modes and their individual failure rates. The most serious causes of failed shots are the oscillators (29 failed shots, or 40%), alignment (16 shots, 23%) and the 9mm amplifiers (14 shots, 20%). The latter figure is significant. The 9mm amplifiers have been the primary cause of failure for the past two years, accounting for 48 failed shots (or 28%) last year and 34 failed shots (36%) during 2001-2002. The problem was targeted during the infrastructure shutdown period when the 9mm power supplies were replaced. Up until the shutdown, the 9mm amplifier contribution to the failure rate was running at 23%. There has not been a single failure attributable to this cause since the shutdown.

There is a requirement which was originally instigated for the EPSRC FAA that the laser system be available, during the four week periods of experimental data collection, from 09:00 to 17:00 hours, Monday to Thursday, and from 09:00 to 16:00

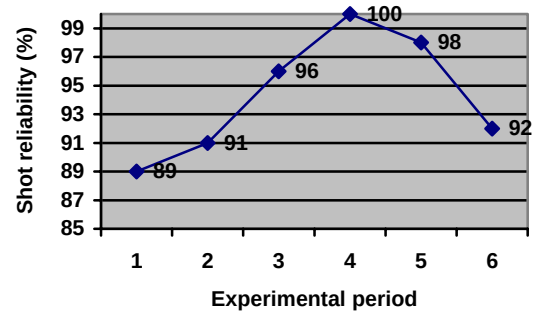


Figure 2. TAP shot reliability for each experimental period.

hours on Fridays (a total of 156 hours). The laser has not always met the startup target of 9:00 am but it has been common practice to operate the laser well beyond the standard contracted finish time on several days during the week and to operate during some weekends.

On average, Vulcan has been available for each experiment for 74.8% of the time during contracted hours and 103.9% overall. However, each experiment has also experienced an average of 3.5 hours of laser downtime.

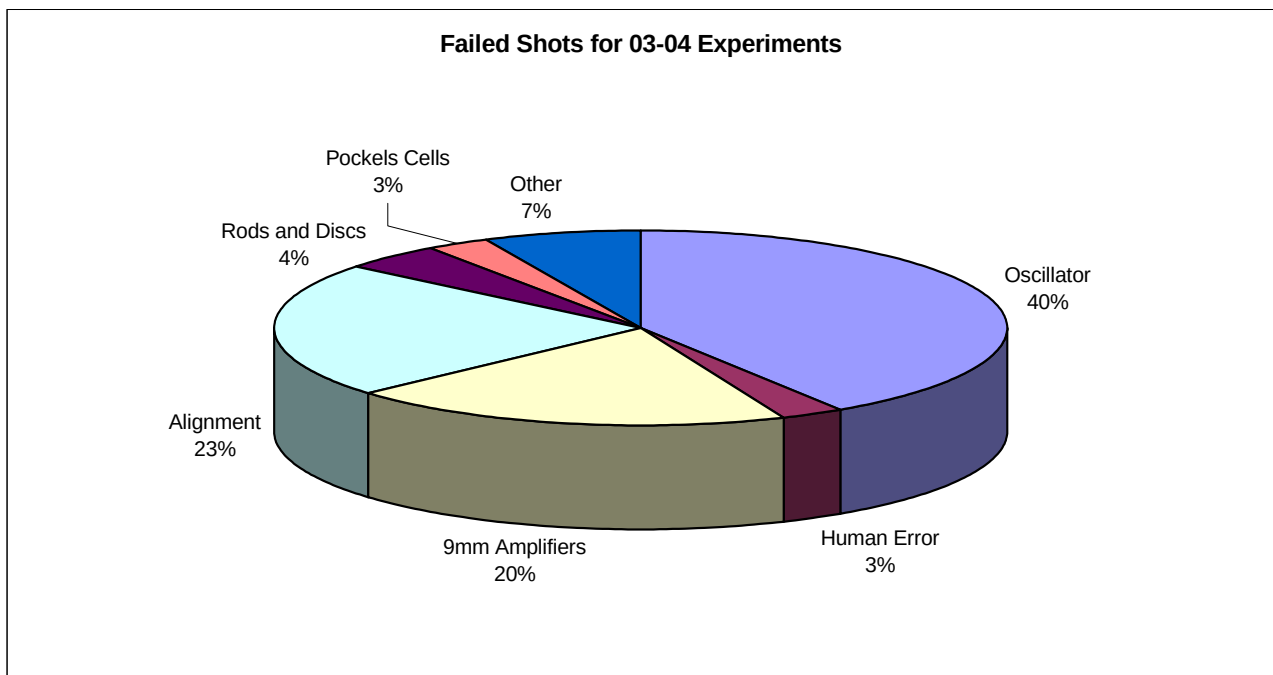


Figure 3. Analysis of Vulcan failure modes.

Astra Operational Statistics

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A total of 9 experiments were carried out with the Astra laser during the reporting period April 2003 to April 2004. Of these experiments 8 were supported by the UK research councils and these used 40 experiment weeks including 5 of the newly introduced set-up weeks designed to enable experimenters to prepare equipment before they receive laser beam-time. The remaining experiment was associated with the EU funded SHARP programme and took place over 6 experiment weeks.

The Astra laser was available to researchers for an average of 79% of the contracted hours. However, taking into account out-of-hours working the laser was available 125% of the contracted hours. Laser reliability over all operating hours was 86% taking into account all recorded downtime.

We had the opportunity to carry out 21 weeks of facility development this year, the details of which are described in detail elsewhere in this report. They included: implementation of acousto-optic phase control using a DAZZLER, construction of a SPIDER pulse diagnostic, implementation of grating cleaning by RF plasma discharge inside the compressor, improvements to the near-field distribution from the 3rd amplifier using image relaying and spatial filtering. The experiments carried out within the SHARP programme included construction of an optical parametric device for measuring pulse contrast and an investigation of Kerr gating for contrast enhancement.

Table 1. Astra Experiment Schedule 2003/2004.

Date	Target Area 1 (TA1)	Target Area 2 (TA2)
31 Mar - 6 Jun 03	Facility Development	
12-May-03	SHARP experiments	
19-May-03		
26-May-03		
02-Jun-03		
09-Jun-03		
16-Jun-03	Newell/Williams Laser interactions with ions UCL/QUB	Krushelnic Basic technology experiments
23-Jun-03		
30-Jun-03		
07-Jul-03		
14-Jul-03		
21 Jul - 1 Aug 03	Facility Development	
04-Aug-03		Set up
11-Aug-03		Riley Scattering experiments QUB
18-Aug-03		
25-Aug-03		
01-Sep-03		
08-Sep-03		
29-Sep-03		Set up
06-Oct-03	Newell/Williams Laser interactions with ions UCL/QUB	Krushelnick Relativistic investigations IC / Strathclyde
13-Oct-03		
20-Oct-03		
27-Oct-03		
03-Nov-03		
10 Nov - 21 Nov 03	Facility Development	
24-Nov-03	SHARP experiments	Ledingham Nuclear Interactions Strathclyde
01-Dec-03		
08-Dec-03		
15-Dec-03	CHRISTMAS	
22-Dec-03		
29-Dec-03		
5 Jan - 20 Feb 04	Facility Development	
23-Feb-04	Set up	Set up
01-Mar-04	Newell/Williams Laser interactions with ions UCL/QUB	Krushelnic Alpha-X Programme IC / Strathclyde
08-Mar-04		
15-Mar-04		
22-Mar-04		
29-Mar-04		

LSF Operational Statistics

S M Tavender, E L Belcher, M Towrie, A W Parker

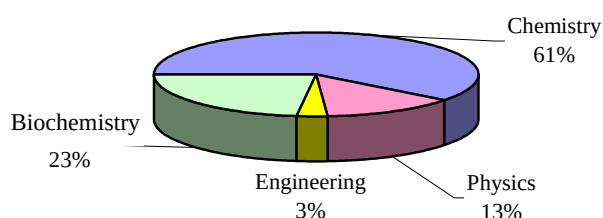
Central Laser Facility, CCLRC Rutherford Appleton Laboratory, Chilton, Didcot, Oxon, OX11 0QX, UK

Main contact email address s.m.tavender@rl.ac.uk

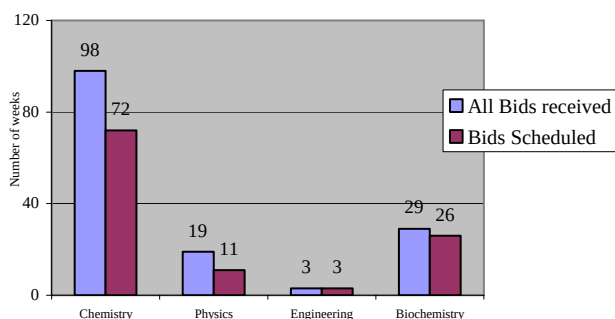
RAL-Based Experiments

In the reporting period (April 2003 to March 2004), 30 different User groups performed a total of 61 experiments in the LSF laboratories at RAL. A total of 100 weeks of formal scheduled time meant 3900 operational hours were scheduled to the UK User community and 13 weeks or 507 hours to European Users throughout the year and a total of 4708 hours were delivered with only 169 hours downtime. Once again, a wide spread of disciplines was covered and a breakdown is shown in Figure 1 with the RAL-Based schedule in Table 1. There were a total of 31 publications, 13 conference proceedings and 4 PhDs published during the reporting year.

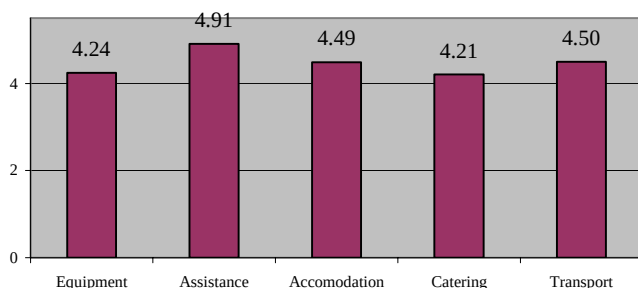
Fig 1 RAL bids by subject group



No. weeks RAL based experiments by subject



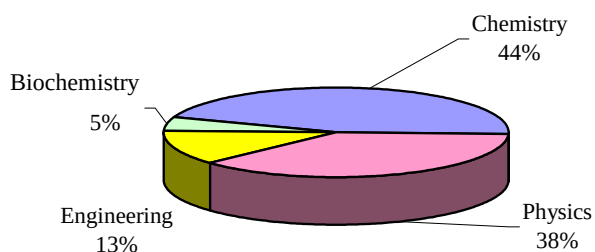
RAL based Average User satisfaction marks



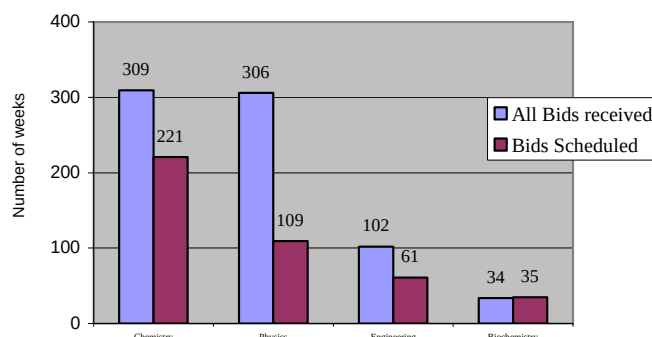
Loan Pool

The Loan Pool delivered 426 weeks of laser time in the reporting period. Downtime was 33 weeks and was mainly due to minor breakdowns throughout the year. In the laser loans there were 4 groups new to the Loan Pool. The chemistry community was once again the biggest user with 43% of allocated time but there was a big increase in allocations to the physics community due to the new ultrafast laser. The breakdown is shown in Figure 2, and the Loan Pool schedule is shown in Table 2. There were a total of 14 publications, 7 conference proceedings, 1 PhD and 3 reports published during the reporting year.

Fig 2 Loan Pool bids by subject group



Loan Pool experiments by subject



Loan Pool average user satisfaction marks

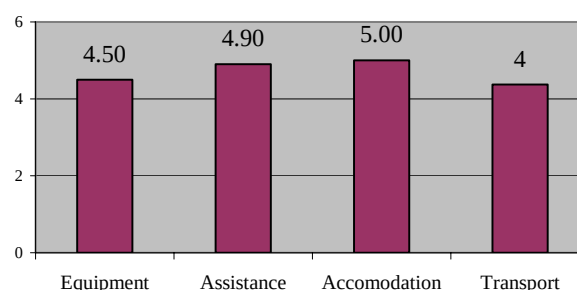


Table 1. LASERS for SCIENCE FACILITY RAL-BASED SCHEDULE: 2003-4

Date	Laser Microscope Laboratory	Nanosecond Science Laboratory	Ultrafast Spectroscopy Laboratory	X-Ray and UV Laboratory
Mar 31	INSTRUMENT DEVELOPMENT	NIR GENERATION	MAINTENANCE	COMMERCIAL
Apr 7	MAINTENANCE	MAINTENANCE	M TOWRIE (RAL) Increasing PIRATE Tunability US10P1/03	COMMERCIAL

Date	Laser Microscope Laboratory	Nanosecond Science Laboratory	Ultrafast Spectroscopy Laboratory	X-Ray and UV Laboratory
Apr 14	K BRINDLE (Cambridge) <i>Proteins in vivo</i> CM8B1/03		MAINTENANCE	COMMERCIAL
Apr 21			M GEORGE (Nottingham) <i>DNA Base Photoionisation</i> US8C1/03	MAINTENANCE
Apr 28	MAINTENANCE	A VLCEK <i>Charge Transfer of Organometallics</i> NL9C1/03		M GEORGE (Nottingham) <i>DNA Base Photoionisation</i> XU4C1/03
May 5	LSF USER MEETING and WORKSHOP			
May 12	R MELDRUM (B'ham) CM2B1/03		M TOWRIE (RAL) <i>Increasing PIRATE Tunability</i> US10P1/03	A FITZGERALD (Dundee) <i>Electron Beam Nano-fabrication of Metal Bilayers</i> XU1E1/03
May 19			MAINTENANCE	
May 26	N QUIRKE (IC) <i>Imbibition and Pumping of Hydrocarbons in Carbon Nanotubes</i>	M CHESTERS (Nottingham) <i>Ultraviolet Resonance Raman Studies of Adsorbates on Metal Surfaces</i>	A VLCEK (QMWC) <i>Early Photochemical Dynamics of Charge Transfer Exited Organometallics</i> US1C1/03	
June 2				SKELDON (UMIST)
June 9	CM3C1/03		M GEORGE (Nottingham) <i>Picosecond IR Measurements in Supercritical Fluids</i> US6C1/03	R MELDRUM (B'ham) <i>High Resolution Induction of UV Photoproducts in Cellular DNA by 3 Photon Near Infra-Red Absorption</i> XU2C1/03
June 16	R BISBY (Salford) CM4B1/03	NL4C1/03		
June 23		MAINTENANCE	D PHILLIPS (IC) <i>Time Resolved Spectroscopy Intramolecular Electron Transfer</i> US11C1/03	
June 30	P O'NEILL (MRC) <i>DNA Characterisation</i> CM6B1/03			
July 7	C BAIN (Oxford) <i>Coalescence between oil emulsion droplets</i>		A GOODSHIP (RVC, Hatfield) <i>Raman Photon</i>	SKELDON (UMIST)
Date	Laser Microscope Laboratory	Nanosecond Science Laboratory	Ultrafast Spectroscopy Laboratory	
July 14	C BAIN CM1C1/03	P ROACH (Southampton) <i>Raman Studies of Fe-S Cluster Containing Enzymes</i> NL7C1/03	A GOODSHIP <i>Migration in Bone Phantoms</i> US5C1/03	
July 21	J J McGARVEY (QUB) <i>DNA Interactions</i> CM7C1/03		J J McGARVEY (QUB) <i>Probing DNA Interactions at colloidal surfaces and with Metal Complexes</i> US3C1/02	
July 28	R BISBY (Salford) <i>Hyperluminescence of Biomolecules on Multiphoton Excitation</i> CM4B1/03	J MOORE (York) <i>Nanosecond temperature jump studies of azo dyes</i> NL3C1/03		
Aug 4				
Aug 11		P MATOUSEK (RAL) <i>Atomic Force Microscopy with Chemical Specificity - A Feasibility Study (Instrument Development)</i> NL6P1/03	K REID (Nottingham) <i>Time-Resolved Photoelectron Angular Distributions Using a New Imaging Photoelectron Spectrometer</i> US4C1/03	
Aug 18				
Aug 25				
Sept 1	MAINTENANCE	J CALLOW (Birmingham) <i>Adhesion Chemistry of Marine Spores by Raman Microscopy</i> NL2B1/03	D PHILLIPS (IC) <i>Time Resolved Spectroscopy Intramolecular Electron Transfer</i> US11C1/03	
Sept 8				
Sept 15	R MELDRUM (B'ham) <i>Induction of UV Photoproducts in Cellular DNA by 3 Photon Absorption</i> CM2B1/03	R BISBY (Salford) <i>Hyperluminescence of Biomolecules on Multiphoton Excitation</i> NL8B1/03	S BARSBERG (Denmark) <i>The electronic states of Lignin</i> USEV35C1/03	
Sept 22				
Sept 29	R BISBY (Salford) CM4B1/03 <i>Hyperluminescence of Biomolecules on Multiphoton Excitation</i>	MAINTENANCE	MAINTENANCE	
Oct 6	M RUTLAND (Stockholm) <i>Surface Forces Measurement using Laser Tweezers Techniques</i> CMEV31C2/03	F ISMAIL (LJMU) NL16C2/03 <i>Unravelling the Mechanism of Artemisinin and other Antimalarial Drugs: A Time-Resolved Spectroscopy Investigation</i>	EXPERIMENTAL SET-UP	
Oct 13			R HICKEN (Exeter) US16P2/03 <i>Transient Reflection Study of Metals</i>	
Oct 20	MAINTENANCE		EXPERIMENTAL SET-UP	

Date	Laser Microscope Laboratory	Nanosecond Science Laboratory	Ultrafast Spectroscopy Laboratory
Oct 27	K BRINDLE (Cambridge) CM9B2/03 <i>Novel Fluorescence Technique</i>		A-S JÄÄSKELÄINEN (Finland) <i>KG Study of Lignin Samples</i> USEV33C2/03
Nov 3	M RUTLAND (Stockholm) <i>Surface Forces Measurement using Laser Tweezers Techniques</i> CMEV31C2/03		
Nov 10			
Nov 17		J SANDERSON NL11B2/03 (Durham) <i>Liposomal Membrane Interactions Studied by Raman Tweezers</i>	
Nov 24	J McGARVEY (Belfast)CM12C2/03 <i>Ps energy and electron transfer</i>		A VLCEK (London) US17P2/03 <i>Early Photochemical Dynamics</i>
Dec 1			P MATOUSEK (RAL) <i>Development</i> US15P2/03
Dec 8	R BISBY (Salford) CM13B2/03 <i>Hyperluminescence of Biomolecules on Multiphoton Excitation</i>	P ROACH (Southampton) NL12B2/03 <i>Resonance Raman Studies of Fe-S Cluster Containing Enzymes</i>	J WEINSTEIN (Nottingham) US19C2/03 <i>Photo-excited State of Metal Thiolates</i>
Dec 15			
Dec 22 Dec 29	CHRISTMAS & NEW YEAR		
Jan 5		R BISBY (Salford) NL15B2/03 <i>Hyperluminescence of Biomolecules on Multiphoton Excitation</i>	D PHILLIPS (IC) US14C2/03 <i>ICT in Extended Systems</i>
Jan 12	O'NEILL (MRC) CM11B2/03 <i>Characterisation of DNA Damage Induced by IR Multi-photon</i>		Exp setup to IR
Jan 19			A VLCEK (London) US17P2/03 <i>Early Photochemical Dynamics</i>
Jan 26	MAINTENANCE	P JAYCOCK (Loughborough) NL10B2/03 <i>Determining the biomechanical properties of the cornea</i>	M GEORGE (Nottingham) <i>Probing DNA Damage</i> US20C2/03
Feb 2	R BISBY (Salford) CM13B2/03 <i>Hyperluminescence of Biomolecules on Multiphoton Excitation</i>		
Feb 9			
Feb 16	D OELKRUG (Germany) <i>Time-resolved fluorescence spectroscopy on single oligophenylenevinylene nanoparticles</i> CMEV30C2/03	MAINTENANCE	A VLCEK (London) US17P2/03 <i>Early Photochemical Dynamics</i>
Feb 23		M McCOUSTRA (Nottingham) <i>Ultraviolet Resonance Raman Studies of Adsorbates on Metal Surfaces</i> NL14C2/03	D PHILLIPS (IC) US14C2/03 <i>Ultra-fast Studies of Intramolecular Charge Transfer in Extended Systems</i>
Mar 1			
Mar 8	A VLCEK (London) US17P2/03 <i>Early Photochemical Dynamics</i>		
Mar 15	MAINTENANCE		J MOORE (York) US18C2/03 <i>Studies of light-controlled ion switches</i>
Mar 22			

Table 2. LASERS for SCIENCE FACILITY LOAN POOL SCHEDULE: 2003-4

Date	NSL1 POWERLITE/ SIRAH + DFG	NSL2 SURELITE III- 10/ SIRAH	NSL3 SURELITE III- 10/ SIRAH	NSL4 CONTINUUM 8010/ND6000	NSL5 FLUORIDE EXCIMER	NSL6 Nd:YAG/ DYE/SHG	CWL2 VERDI/MIRA + SHG & THG	CW3 FREQUENCY DOUBLED ARGON ION
Mar 31	SIMS	STACE	ATTENBOROUGH	MASON			LINFIELD	WITHNALL
Apr 7	(Birmingham)	(Sussex)	(Hull)	(Open University)	HANCOCK		(Cambridge)	(Greenwich)
14	Astrochemistry:	Gas Phase			(Oxford)	SIMONS		
21	Collisional energy	Ligand Field	Laboratory	Simulation of	Chemical	(Oxford) MASON		
28	Transfer studied	Spectroscopy	simulation	Space	processes	(Open	LP34P3/02	
May 5	by IR-VUV double		of sonic	Weathering on	Studied by	University)		LP35P3/02
12	resonance at	LP27C3/02	booms	Mercury	Time resolved			
19	very low				FTIR		DEVONSHIRE	
26	temperatures				spectroscopy		(Sheffield)	CHESTERS

Date	NSL1 POWERLITE/ SIRAH + DFG	NSL2 SURELITE III- 10/ SIRAH	NSL3 SURELITE III- 10/ SIRAH	NSL4 CONTINUUM 8010/ND6000	NSL5 FLUORIDE EXCIMER	NSL6 Nd:YAG/ DYE/SHG	CWL2 VERDI/MIRA + SHG & THG	CW3 FREQUENCY DOUBLED ARGON ION
June 2	LP32C3/02		LP29E3/02	LP26P3/02	LP16C1/03	LP7C1/03 LP21P2/02		(RAL/N'ham)
9		STACE			HANCOCK	SIMONS MASON	DEVONSHIRE	
16		(Sussex)			(Oxford)	(Oxford) (Open	(Sheffield)	LP10C1/03
23	SIMS		ATTENBOROUGH	BISBY		Anti-Viral University)		
30	(Birmingham)		(Hull)	(Salford)		Agents and		
Jul 7			(YAG)	Time resolved		Immuno-		LINFIELD
14	Astrochemistry:			Resonance		suppressive Laser		(Cambridge)
21	Collisional			Raman		Drugs: Simulation		
28	energy	Gas Phase		Spectroscopy of		Gas phase of		
Aug 4	transfer	Ligand		the free radicals		Conform- Space		Differential
11	studied by	Spectroscopy	Laboratory	by pulse	Chemical	ational Weathering		spectroscopy
18	IR-VUV	Field	simulation	radiolysis	processes	Studies	Femtosecond	of
25	double		of sonic	- a feasibility	Studied by	Of the	Non-linear	Biomolecules
Sep 1	resonance at		booms	study	Time resolved	frentizole	Raman	
8	very				FTIR	analogues	Scattering:	
15	low			COLE	spectroscopy	phenylurea	Novel	
22	temperatures			CMSD		and	Techniques and	
29				HANE		Diphenyl -	applications	
Oct 6				CMSD		urea		
13						LP7C1/03		
20								
27								
Nov 3						SIMONS		
10						(Oxford)		
17	LP11C1/03							
24					LP16C1/03			
Dec 1						LP21P2/02		
8			LP02E1/03					
15					HANCOCK			
22			ATTENBOROUGH	LP15B1/03	(Oxford)			
29			(HULL)					
Jan 5 '04	FIELDING					PILLING		LP12P1/03
12	(UCL)			VOLK		(Leeds)		
19	Dynamics of	LP8C1/03	Laboratory	(Liverpool)	Reaction			
26	Electronic and		Simulation		Dynamics	Conform-		
Feb 2	Nuclear Wave	JAYCOCK	Of		Studied	ational		
9	Packets: A	(Loughborough)	Acoustic		By sensitive	Juggling		
16	Spectroscopic	Determining the	Shock	Fast	absorption		LP01C1/03	
23	Analysis of	Biomechanical	Waves	Processes	techniques			McCOUSTRA
Mar 1	Wave Packet	Properties of		Of Alpha-Helix				(Nottingham)
8	Composition	The Cornea		Folding			TAYLOR	
15							(Oxford)	LP20C2/03
22	LP27C2/03	LP18B2/03	LP22E2/03	LP24C2/03	LP26C2/03	LP25P/03 LP38C2/03	LP29P2/03	

Vulcan Laser Programme

JOURNAL PUBLICATIONS, BOOKS AND PUBLISHED PROCEEDINGS

Y Abou-Ali, A Demir, G J Tallents, M Edwards, R E King, G J Pert

Comparison of simulated and experimental time resolved emission for a Ne-like nickel X-ray laser

J Phys B **36** (20) 4097-4106 (2003)

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Conference on Lasers and Electro-Optics, Baltimore, USA (June 2003)

D Neely, K Krushelnick, S Mangles, R Clarke, J Collier, A E Dangor, C N Danson, R D Edwards, S Fritzler, A Gopal, P Hatton, R Heathcote, C Hernandez-Gomez, K W D Ledingham, P McKenna, Z Najmudin, B Walton, M Wei
Particle acceleration using the Vulcan petawatt laser

LULI Seminaire 2003, Porquerolles, France (June 2003)

M Borghesi
Proton probing of laser plasma interaction experiments

4th Low Energy Ion Beam Facilities Meeting, Belfast, UK (July 2003)

P McKenna
A review of high-intensity laser-driven ion acceleration and induced nuclear phenomena

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H Habara
Ion dynamics from beam-fusion neutron spectroscopy in ultra-intense laser plasmas

K Krushelnick
Particle acceleration using PW lasers

K Lancaster
Bright neutron sources from laser accelerated ion beams

P McKenna
Nuclear Activation Measurements on Vulcan Petawatt

C Murphy
Photon acceleration as a plasma diagnostic

D Neely
PW lasers at the Rutherford Appleton Laboratory

Soft X-Ray Lasers and Applications V, San Diego, USA (Aug 2003)

O Guilbaud, M Edwards, A Klisnick, D Ros, G Jamelot, D Joyeux, D Phalippou, H Tang, P Neumeyer, D Ursescu, G J Tallents, T Kuehl, K Cassou, K Bouhouch, M Kado, M Nishikino, K Sukegawa, M Kishimoto, M Ishino, K Nagashina, H Daido, W Seelig, S Borneis, E W Gaul, W Geithner, C Hafner, P P Wiewior
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Approaching the transform limit for X-Ray laser pulses

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M Borghesi
Rilevazione di campi elettromagnetici in esperimenti di interazione laser plasma con tecniche di proton imaging

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F Amiranoff, S D Baton, H Popescu, J J Santos, M Koenig, E Martinoli, C Rousseaux, M Rabec le Gloahec, L Gremillet, T Hall, D Batani, E Perelli, F Scianitti, T E Cowan, D Neely, R J Clarke, J-C Adam, A Heron, C Andersen, J King, J M Hill
Fast electron generation and transport in laser-irradiated targets at relativistic intensities

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Laser-generated Z-pinch

E L Clark, T T Eagleton, M A Dunne, R D Edwards,
R G Evans, W J Garbett, T J Goldsack, S James
*Experimental investigation of the transport of electron and
proton beams generated by the VULCAN petawatt laser*

G W Collins, P L Celliers, D Hicks, D Bradley, J Eggert,
J Kane, S J Moon, M Koenig, A Benuzzi, G Huser, E Henry,
D Batani, J Pasley, O Willi, P Loubeyre, R Jeanloz, K M Lee,
L R Benedetti, D Neely, M Notley, C Danson
*Using lasers to recreate core states of extrasolar and solar
giant planets*

R Freeman, F Amiranoff, C Andersen, D Batani, S D Baton,
T Cowan, N Fisch, L Gremillet, T Hall, S Hatchett, J Hill,
M H Key, J King, J Koch, M Koenig, B Lasinski, B Langdon,
A MacKinnon, E Martinolli, P Norreys, P Parks,
E Perelli-Cippo, M Rabec le Gloahec, M Rosenbluth,
C Rousseaux, J J Santon, R B Stephens, F Scianitti, R Snavely
*What we know versus what we speculate concerning the
generation and transport of laser-generated fast electrons in
dense materials*

M H Key, F Amiranoff, C Andersen, D Batani, S D Baton,
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K Tanaka, R Town, T Tsutsumi, R Stephens
*Studies of electron isochoric heating and its applicability to fast
ignition*

J A King, M Key, R A Snavely, R R Freeman, P Norreys,
K Lancaster, R Stephens, C Stoeckl, M Zepf
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R Kodama
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K Krushelnick, S P D Mangles, R J Clarke, J Collier,
C N Danson, E L Clark, A E Dangor, S Fritzler, A Gopal,
R Heathcote, C Hernandez-Gomez, K Ledingham, P McKenna,
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Particle acceleration using the Vulcan petawatt laser

D Neely, R Clarke, J Collier, C N Danson, C B Edwards,
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M H R Hutchinson, A Kidd, W Lester, P Norreys, D A Pepler,
I N Ross, T B Winstone, P N M Wright, R W W Wyatt,
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Radiological characterisation of petawatt laser interactions

P A Norreys, H Habara, K A Lancaster, C Murphy, S Karsch,
R Clarke, R Heathcote, S Hawkes, C Hernandez-Gomez,
D Neely, M H R Hutchinson, J King, B Zhang, K Akli,
R Freeman, S Hatchett, M H Key, R Stephems, Y Toyama,
R Kodama, D Brown, M Zepf, C Stoeckl
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Laboratory*

J Pasley, P Nilson, M Haines, O Willi, M Notley, W Nazarov
XUV imaging of indirectly driven foam-foil packages

N C Woolsey, A D Ash, D M Chambers, C Courtois,
R A D Grundy, R O Dendy, R Heathcote, M M Notley,
M Tolley
*Collisionless laboratory experiments with applications to shock
physics*

Workshop on Ultrashort Pulse Laser-Plasma Interactions, Prague, Czech Republic (Sept 2003)

M Borghesi
*Diagnostic use of proton beams in laser plasma interaction
experiments*

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E Breschi, M Borghesi, M Galimberti, D Giulietti, L A Gizzi,
L Romagnani, O Willi, H Campbell, A Schiavi
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proton beams from dosimetric measurements*

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R D Edwards, M A Sinclair, T J Goldsack, E L Clark,
K Krushelnick, F N Beg, M Tatarakis, M Zepf, A E Dangor,
Z Najmudin, V Malka, R J Clarke, D Neely, M Norrefeldt,
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Laser driven gamma/X-ray sources

I C E Turcu
Soft X-ray laser-plasma X-ray sources and applications

M Zepf, K Krushelnick, P Norreys
*Gamma ray beam production and probing in laser matter
interaction*

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A J MacKinnon, P K Patel, D Hicks, D Price, R P Town,
S Hatchett, B Lasinski, B Langdon, M H Key, M Borghesi,
L Romagnani, G Pretzler, T Toncian, O Willi, J King,
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M Borghesi, S Bulanov, L Romagnani, G Pretzler, O Willi,
A Schiavi, F Pegoraro, M Galimberti, L A Gizzi,
A J MacKinnon, P K Patel
*Investigation of high-intensity laser-plasma interactions by
means of proton probing*

A Schiavi, M Borghesi, M Galimberti, L A Gizzi,
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Modelling and analysis of proton imaging experiments

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T Esirkepov, M Borghesi, S V Bulanov, G Mourou, T Tajima,
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Relativistic laser piston

International Kick-Off Workshop on Extreme Field Science and Relativistic Engineering, Kizu, Japan (Jan 2004)

M Borghesi
*Detection of quasi-static EM fields in high-intensity
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M Galimberti, M Borghesi, E Breschi, A Giulietti, D Giulietti, L A Gizzi, A Schiavi, O Willi
Produzione e caratterizzazione di fasci di protoni generati dall'interazione laser-plasma

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Sviluppi nell'interpretazione di esperimenti con fasci di protoni generati da laser

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P McKenna
Laser-plasma based nuclear science

THESES

J M Hill
Fast electron transport in overdense laser-induced plasmas
Ph D, Ohio State University

A-M McEvoy
K-alpha emission from ultra-short pulse laser plasmas
Ph D, Queen's University Belfast

A M M Schiavi
Study of laser-produced plasmas by X-ray and proton radiography
Ph D, ICSTM London

B Walton
Optical diagnostics of laser plasma particle acceleration experiments
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Astra Laser Programme

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K Bowes, J Cole, S Husheer, L Ooi, P Raithby, H Sparkes, I Clark, M Goulay, A Parker, M Towrie, S Teat
Single crystal X-ray crystallography of photoinduced terpyridine

RSC Coordination Chemistry Discussion Group Meeting, Manchester, UK (Jul 2003)

M K Kuimova, E S Davies, P Matousek, A W Parker, M Towrie, M W George
Designing infrared probes of DNA

2nd International Conference on Vibrational Spectroscopy, Nottingham, UK (Aug 2003)

M K Kuimova, D C Grills, P Matousek, A W Parker, M Towrie, M W George
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Direct ionisation of 2-aminopurine in fluid solution and glass matrices

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K Attenborough
Nature and use of acoustic shock waves from focused laser beams for studies of surface acoustics

Q Qin, K Attenborough
Use of acoustic shock waves from focused laser beams for studies of surface acoustics

K Attenborough, P Boulanger, Q Qin
Acoustical effects of surface roughness

Imperial College Nanomaterials Symposium, London, UK (Sept 2003)

M Longhurst
Trapping of n-decane aerosol droplets from an oil mist

Fast Reactions in Solution Discussion Group Meeting, Wittenberg, Germany (Sept 2003)

J J McGarvey
Time-resolved vibrational spectroscopy of some DNA-binding and spin-crossover metal complexes

NRPB Laser Safety Forum, Loughborough, UK, (Oct 2003)

P D Jaycock, L Lobo, J Jones, J Tyrer, J Marshall
Laser safety management

Photonics West 2004, San Jose, USA (Jan 2004)

E Goodship
Raman photon migration in bone phantoms

M D Morris
Kerr-gated picosecond Raman spectroscopy and Raman photon migration of equine bone tissue with 431 nm excitation

Nanotech 2004, Boston, USA (Mar 2004)

N Quirke
Interaction of fluids with nanomaterials: simulation, theory and experiment

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D Oelkrug
Time-resolved fluorescence spectroscopy on single oligophenylenevinylene nanoparticles

THESES

K F Bowes
Preliminary studies in photocrystallography: structural determination of photo-induced species using X-ray crystallography
Certificate of postgraduate studies, University of Cambridge

C S Colley
PhD, University of Nottingham

J Dyer
PhD, University of Nottingham

R Emery

Antiviral agents and immunosuppressive drugs: gas-phase conformational studies of the frentizole analogues, phenylurea and diphenylurea

Part of 2-part thesis, University of Oxford

S L G Husheer

Crystallography of photo-induced transient species

Part of 2-part thesis, University of Cambridge

O S Jina

PhD, University of Nottingham

M Longhurst

MRes, Imperial College London

R A L Smith

Molecular electron wavepackets

PhD, King's College London

Laser Science and Developments

JOURNAL PUBLICATIONS, BOOKS AND PUBLISHED PROCEEDINGS

C B Edwards, J C Aldis, R Allott, P A Brummitt, J Collier, R J Clark, C N Danson, R Day, M Dominey, B C Eltham, A J Frackiewicz, J A Govans, B J Gray, S Hancock, P E Hatton, S Hawkes, C R Heathcote, C Hernandez-Gomez, P Holligan, C Hooker, M H Hutchinson, A R Jackson, A Kidd, T Knott, W J Lester, J M Loose, A J MacPhee, J Monk, Z A Miljus, D Neely, D R Neville, P Norreys, M Notley, J O'Dell, D A Pepler, M R Pitts, C J Reason, D Robinson, K J Rodgers, D A Rodkiss, D Rose, S J Rose, I N Ross, A J Ryder, M R Selley, T Strange, G P Warner, R Wellstood, G N Wiggins, T B Winstone, P N Wright, R W Wyatt, B E Wyborn, C Ziener
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Operation of a newly commissioned interaction facility

D Neely, R J Clarke, J Collier, C N Danson, C B Edwards, R Edwards, A J Frackiewicz, S Hancock, P E Hatton, S Hawkes, R Heathcote, C Hernandez-Gomez, P Holligan, C Hooker, M H R Hutchinson, A K Kidd, W J Lester, P A Norreys, D A Pepler, M R Pitts, C J Reason, I N Ross, R Wellstood, B E Wyborn, T B Winstone, P N M Wright, R Wyatt, C Ziener

Radiological safety issues on a petawatt interaction facility

Diffraction Optics 2003, Oxford, UK (Sept 2003)

D Pepler, B Parry, C Danson, D Neely

Design of a diffractive optic element for use with a petawatt class laser

3rd International Conference on Inertial Fusion Sciences and Applications, Monterey, USA (Sept 2003)

J Collier, I Ross, O Chekhlov, L Cardoso, C Hernandez-Gomez, P Matousek, D Neely, M Notley
Progress towards petawatt level OPCPA

C N Danson, P A Brummitt, J L Collier, R J Clarke, M Dominey, C B Edwards, R Edwards, A J Frackiewicz, J A C Govans, S Hancock, P E Hatton, S Hawkes, R Heathcote, C Hernandez-Gomez, P Holligan, C Hooker, M H R Hutchinson, A Jackson, A K Kidd, W J Lester, J Monk, D Neely, D R Neville, P A Norreys, M Notley, D A Pepler, M R Pitts, C J Reason, D Robinson, K J Rodgers, D Rose, I N Ross, A J Ryder, M R Selley, D Shepherd, T Strange, M Tolley, R Wellstood, G N Wiggins, T B Winstone, P N M Wright, R W W Wyatt, B E Wyborn, C H Ziener
The Vulcan Petawatt interaction facility

5th Symposium on Advanced Laser Research, Kansai, Japan (November 2003)

D Neely, R Clarke, J Collier, C N Danson, E Divall, P Foster, A Frackiewicz, S Hancock, P Hatton, S Hawkes, R Heathcote, C Hernandez-Gomez, P Holligan, C Hooker, M H R Hutchinson, A Kidd, A Langley, W Lester, P Norreys, D A Pepler, I N Ross, T B Winstone, P N M Wright, R W W Wyatt, B Wyborn
The petawatt laser interaction facility at Vulcan

4th Asian Pacific Laser Symposium, Yongpyong, Korea (March 2004)

C N Danson
Vulcan Petawatt – design, operation and interactions at $5 \times 10^{20} \text{ W cm}^{-2}$

C N Danson
Fusion energy research in the UK

Panel Membership and CLF Structure

PANEL MEMBERSHIP

VULCAN AND ASTRA SCHEDULING ADVISORY PANEL (for Period II 2003/04)

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Queen's University of Belfast

Professor J Wark
Physics Department
Oxford University

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Plasma Physics Group
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Dr D Neely
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Facility Access Panels where introduced during the year

LSF/Astra TA1 Facility Access Panel 2003/04

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Inst. de Chimie Moléculaire et Biologique (ICMB)
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Vulcan/Astra TA2 Facility Access Panel 2003/04

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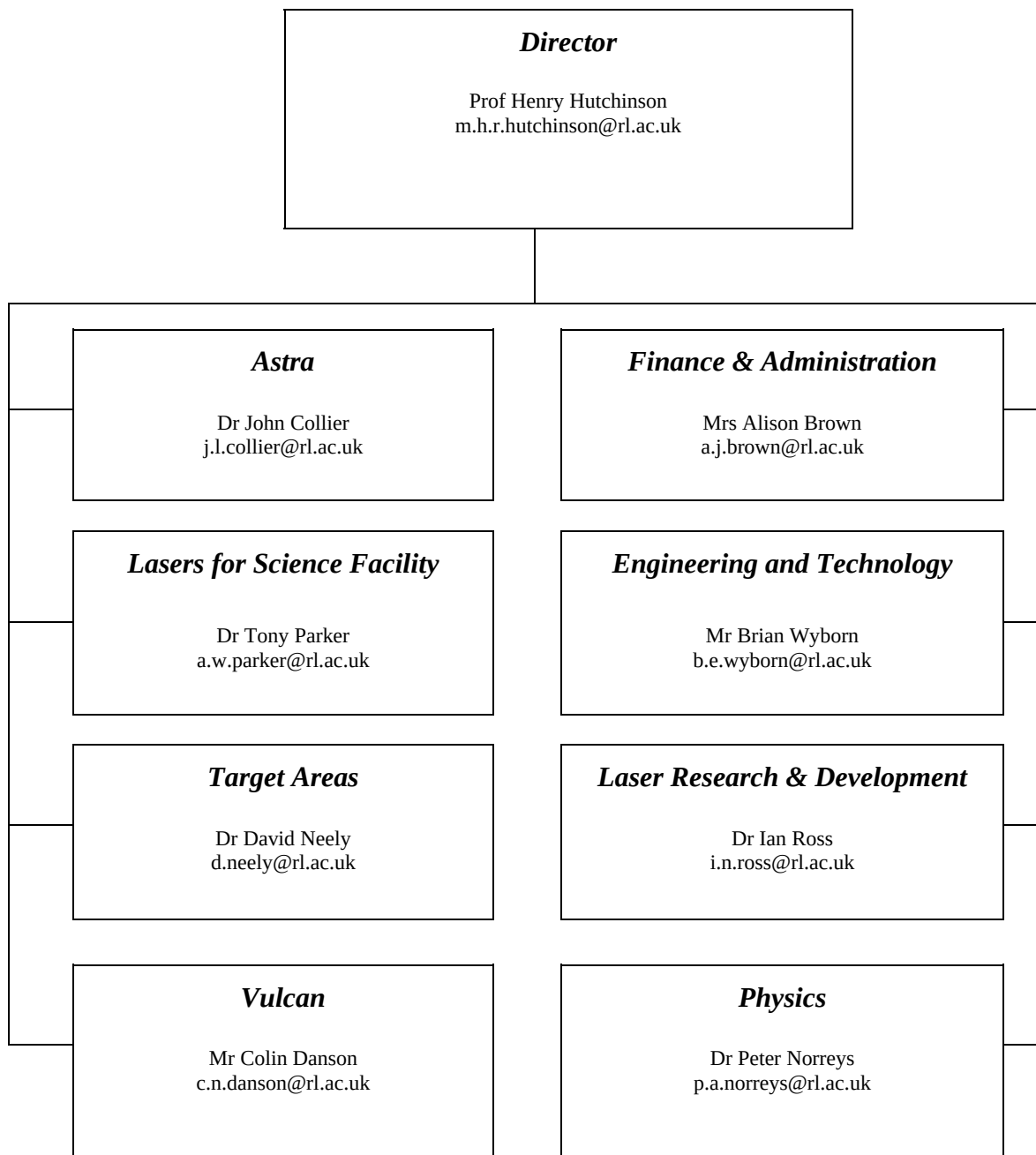
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