Femtosecond Non-Linear Laser Spectroscopy

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Introduction

The Loan Pool Verdi-Mira femtosecond laser system is being used in our laboratories to demonstrate the feasibility of novel diagnostic and materials characterisation techniques which, if successful, would have a significant impact on two of our major research programmes. Firstly, to support our work on the diagnostics and modelling of technologically important reactive gases and plasmas we are developing novel diagnostic techniques which exploit the precise, microscopic spatial extent of femtosecond laser pulses. Secondly, we are extending our use of non-linear Raman techniques to the fs pulse regime to both reveal the dynamical behaviour of the laser induced polarization and to revive, possibly, a somewhat dormant but potentially very important technique for materials characterization, namely hyper-Raman scattering.

Plasma Diagnostics

Our objective is to map precisely the temporal-spatial distributions of atomic species in plasmas in an electronically state-specific manner. In particular we are trying to obtain data on such states from the generally difficult to access plasma sheath regions near the plasma's boundaries. The experimental strategies being explored exploit the spatial transform of femtosecond laser pulses (100 fs ≡ 30 μm) to achieve high spatial resolution measurements of plasma species.

The laser system is unamplified and provides high repetition rate (> 70 MHz) tunable (fundamental is in near-ir region) pulses with average power of ≈ 1 W and ≈ 10 nm linewidth. Individual pulse energies are not adequate to operate a Kerr Gate and so a number of interesting plasma diagnostic techniques based, for example, on imaging of back scattered ballistic photons could not be explored during the loan period. Instead, emphasis was placed on exploring techniques in which small stationary regions of excitation are created inside the systems of interest using the colliding pulse geometries used in some autocorrelator designs. These small regions of excitation may be scanned systematically through plasmas to produce high spatial resolution 3-D maps of species or physical property distributions. The system's response could be measured, for example, via optogalvanic or fluorescence signals.

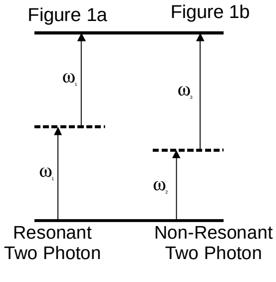

Figure 1. Resonant and Non-Resonant 2-photon excitation.

The principle of the technique was first evaluated using resonant two-photon excitation, Figure 1 (a) of dyes used in two-photon fluorescence microscopy using both single beam, single sided excitation (as used typically in this technique; simple focusing imparts some axial spatial resolution), and then the colliding (counter-propagating) pulse geometries of interest.

Resonant two photon excitation has the disadvantage, as seen readily in colliding pulse autocorrelators which image two-photon excited dye fluorescence, of showing a background track of excitation along the entire length of the path of the pulses. This track is, in effect, the two-photon excitation produced by the non-overlapping, but still two-photon resonant, pulses as they pass through the dye solution. The measurement becomes background-free if the two-photon excitation is made non-resonant, Figure 1 (b). The necessary beams can be created from the Loan Pool laser by using two angle tuned, narrow bandpass filters to spectrally separate two beams from the spectrally broad, 10 nm, 150 fs laser pulses from the oscillator; the first at a λ that is Δλ below that of the two-photon resonant peak, the second at a λ that is Δλ above the peak. The concept is illustrated below:

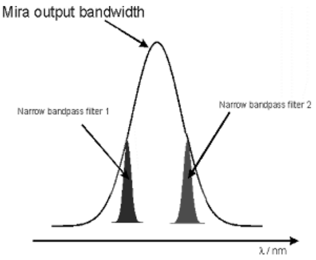

Figure 2. Laser Pulse Filtration.

As the two pulses are derived from the same Mira output pulse they are jitter free. The spectral narrowing lengthens the pulses in time but the consequent increased length of the overlap region of the counter-propagating pulses is still sufficiently small to be of diagnostic value. The peak powers are lowered which reduces the efficiency of non-linear excitation but the increased size of the overlap region compensates to some extent for this as more species of interest are present. A more flexible system to select λ of the individual pulses would give opportunities to exploit resonances with intermediate states.

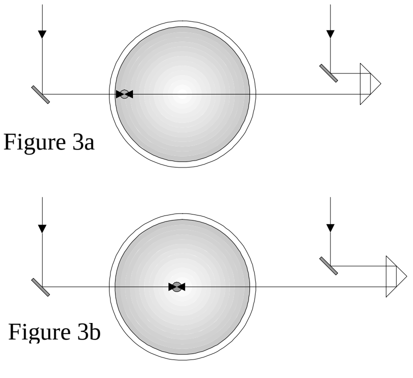
Figure 3a

Figure 3b

Figure 3. Experimental Configuration.

The configuration used in a colliding pulse diagnostic technique is represented in Figure 3. The collision region can be moved systematically along tracks through the system of interest using simple optical delay line techniques, e.g., the beam on the right hand side in Figure 3b has been delayed relative to the rhs beam in Figure 3a. Alternatively, and often more conveniently, the system itself may be moved through a fixed overlap region.

Plasma sheath regions are of considerable practical and theoretical interest and experimental techniques which can access these regions and retrieve data on species concentrations, etc., have high potential value. The optical track that is a diameter of a cylindrically symmetric plasma system (Figure 3; e.g., a lighting discharge) is of particular experimental convenience and theoretical interest. The two-photon technique represented in Figure 3 has the potential to provide spatial profiles along such tracks for a much greater proportion of the track's length than is possible with currently used techniques. For example, present single beam, line of sight, techniques are unable to access near wall regions sensibly because of the strong refractive effects of the walls at large angles of incidence. Evanescent wave techniques are able to access these near wall regions but not so conveniently and practically as being investigated here.

As an example of the specific systems we are investigating the Grotrian diagram of mercury below shows a strategy for the non-resonant two-photon excitation of the 7 $^1S_0$ excited state from the ground state with detection via the 408 nm emission to the 6 $^3P_1$ resonance state. The work extends earlier studies where we achieved spatial resolution by focusing of a pump beam into a low pressure Hg discharge and detecting the excited states using the optogalvanic effect$^{1)}$.

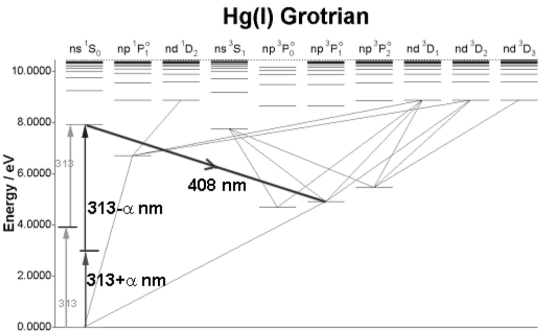

Figure 4. Grotrian Diagram for Mercury.

Non-linear Raman Techniques

Hyper-Raman Scattering: We are establishing a database of reference Raman spectra of materials of interest in light source science and technology (see www.shef.ac.uk/~htsl/raman/). The spectra are used to support studies of lamp chemistry $^{2)}$. The spectra are measured using Raman microscopy because it is compatible with the length scales present in the reference samples and samples requiring analysis. Many materials of interest give featureless Raman spectra with this technique because of their crystal structures; for example, the alkali halides are compounds where dipole modes are forbidden in Raman. These modes can often be observed using the complementary technique of infrared absorption but this technique does not have the versatility and convenience of Raman microscopy. We are evaluating a new technique that will make it possible to obtain both Raman and "infrared" spectra from the same instrument. The concept is to adapt a conventional Raman microscope to accept an alternative laser excitation source that would excite hyper-Raman scattering; the detection system required being identical to that used by the "standard" laser source (typically a dc Argon ion laser). The combined instrument would uniquely be able to measure both Raman and infrared spectra. The pulse stream from the Verdi-Mira system is ideally suited to be such an excitation source. The pulses have the necessary peak power for non-linear excitation of Raman scattering and the laser-material interaction in the fs regime minimises sample damage.

To realise the instrument we are modifying a commercial 514 nm Raman microscope to accept either 514 nm (dc or fs) or 1028 nm fs laser excitation (N.B. the long wave optic set for the Mira is required). The fs laser excitation is being delivered to the sample using low transmission loss hollow optical fibres developed by a Japanese group$^{3)}$. The vibrational modes seen in hyper-Raman using 1028 nm fs excitation will complement those seen in spontaneous Raman using 514 nm excitation and, in addition, make it possible to see "silent" modes.

When available the technique will be applied to a range of technologically important materials that are of interest to the group; these include metal halides, oxides of aluminium, silicon, titanium, etc., and doped silica glasses. It is expected that it significantly enhance the range of our analytical investigations. It could impact several other areas also.

Coherent anti-Stokes Raman Scattering (CARS): We have exploited the CARS technique for some time to provide spatially and temporally resolved spectra of species in reactive gases and plasmas$^{4)}$. Computer simulation of the spectra leads to information on species identity, temperature, pressure and relative concentration. The spatial resolution when using a folded-BOXCARS configuration is typically 50 μm x 50 μm x 1 mm and the temporal resolution is defined by the few ns pulses from the Nd:YAG pump and dye lasers.

We are attempting to perform fs CARS measurements of plasmas using the basic Verdi-Mira system. The CARS pump and Stokes beams are derived from the 2nd harmonic and fundamental, respectively, of the Mira. This configuration gives access to Raman resonances in the range from approximately 9,000 cm^{-1} to 13, 000 cm^{-1} (N.B. requires both mid and long range optics sets to achieve this range). This is a region known from previous work in our laboratories to be rich with Raman resonances from species that are not well characterised and which are probably dication species. Our previous CARS work to investigate this region was restrained by the constant need to change dyes in the dye laser to achieve the full range of interest.

The peak powers of the "pump" and "Stokes" beams from the Mira are comparable to those achieved in typical Nd:YAG CARS systems but the repetition rate and overall mark-space ratio are considerably greater. A major aim of the work with the loan system is to demonstrate whether or not the advantages of the fs system over the Nd:YAG translate into a more efficient CARS signal recovery (N.B. a 200 MHz lock-in detection system is used in the fs CARS experiments). Aside from the potential for gains in signal recovery there is the important added dimension of operating CARS in the fs time-frequency domain and we anticipate new layers of information on the collision processes in operating plasmas$^{5, 6)}$.

References

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