Femtosecond stimulated Raman scattering: development of a new facility for high temporal resolution Raman spectroscopy

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Introduction

Raman spectroscopy is routinely used as a tool for investigating the vibrational dynamics of molecules and their surroundings. Even though modern mode locked lasers can provide energetic pulses with femtosecond duration, Raman spectroscopists often turn to intermediate pulse durations (picoseconds) to maintain energy resolution within spectra, as the resolution of Raman shifted spectra depend upon the energy bandwidth of the original Raman scattering laser pulse. Femtosecond Stimulated Raman Spectroscopy (FSRS)[1] combines the energy-resolution of a narrow bandwidth picosecond pulse with time-resolution of a broadband femtosecond pulse.

In FSRS stimulated Raman scattering (SRS) is driven by femtosecond and picosecond pulses that are spatially and temporally overlapped and differ by the energy of Raman active vibrations of a sample. SRS acts as the probe following a femtosecond excitation pump pulse in FSRS. This approach allows one to follow vibrational dynamics on a femtosecond timescale via spectrally resolved Raman spectra. The spectra obtained are background free, as the Raman scattering is observed coherently as a gain or loss in the spectrum of the probe pulse. In addition, SRS increases Raman transition intensity compared to spontaneous Raman spectroscopy.

This development aims to provide a new capability in the Ultrafast Spectroscopy Laboratory and prepare for a new facility in the ULTRA laboratory.

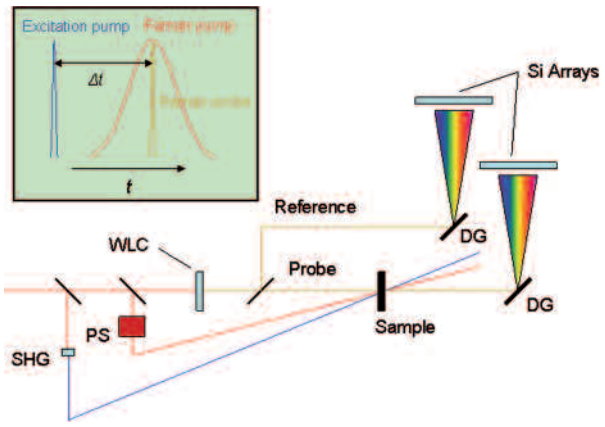

Figure 1. Schematic of spectrometer setup, with inset showing pump – probe pulse scheme. SHG – second harmonic generation; PS – pulse shaper (double pass grating filter); WLC – white light continuum generation; DG – diffraction gratings.

Experimental

The FSRS experimental principle and setup are shown in fig. 1. The laser system is a Spectra Physics Spitfire amplified titanium sapphire laser providing > 1 mJ, 150 fs, 800 nm pulses at 1 kHz.

A femtosecond pulse creates electronically excited or product states, which are then probed by stimulated Raman spectroscopy. The excitation pump used here was the second harmonic of the laser output, generating up to 100 μJ, 150 fs pulses at 400 nm. The Raman probe and Raman pump pulses are synchronised while excitation pump – Raman probe time delays, Δt in fig. 1, are achieved by sending the excitation pulse along a computer controlled optical delay line. The Raman probe light is a broadband WLC (white light continuum, 400 – 950 nm), ~ 100 nJ generated by focussing ~ 3 μJ of the 150 fs output of the laser into a 1 cm water cell[2]. The Raman pump pulse was generated by a double pass grating filter which spectrally filtered the broadband output of the femtosecond laser, see fig. 2. This provides Raman pump pulses with 1 ps duration (15 cm^{-1} energy resolution) and up to 20 μJ pulses.

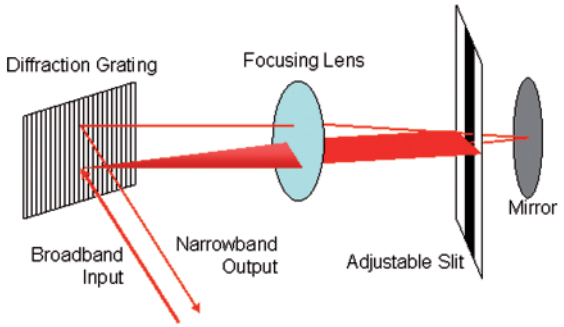

Figure 2. Double pass grating filter used to generate narrowband ps pulses.

The WLC is split into reference and probe beams. The probe arm is focussed into a sample and then dispersed by an imaging spectrograph, 2000 lines/mm, ~ 25 cm long, onto a 128 channel silicon photodiode array. The reference arm mimics the propagation of the probe arm, without sample, and is dispersed onto a second photodiode array. The reference spectrum is used to normalise the probe spectrum and remove shot noise (intensity and spectral modulations) of the WLC. Both beams pass through notch filters (30 nm bandwidth at 800 nm) to remove background from the Raman pump and probe beams.

Our data acquisition and processing methods are analogous to those used in our transient absorption experiments[2]. Basically, the excitation or Raman pump

laser is alternated on - off to obtain a difference spectrum of changes in the probe spectrum, with signal to noise levels of ~ 10^4. As mentioned above, in a FSRS experiment the excitation pump or the Raman pump can be chosen as the alternating pump. Typically, the Raman pump is alternated as the excitation pump aims to produce transient states which may have strong absorptions in the UV – NIR. Strong ground state and other signals are removed in the difference spectrum. The Raman pump may also cause these effects if there is a strong absorption of the Raman pump by ground state or intermediates produced by the excitation pulse, in which case it may be better to modulate the excitation pump. To be certain of removing all interference, both pumps must be alternated.

Results and Observations

The SRS technique without the excitation pulse was demonstrated using cyclohexane and DTTCI. These spectra, shown in fig. 3, can be compared to SRS spectra taken by McCamant *et al.* [3]. DTTCI's strong absorption peak around 750 – 800 nm resonantly enhances the SRS process. Strong fluorescence around 850 nm (DTTCI is a laser dye for this region) is easily removed from the spectra as they are collected on a coherent broadband pulse. The DTTCI spectrum was taken using shifted excitation Raman difference spectroscopy (SERDS) [4], to demonstrate the possibility with this technique to further remove background contributions from the spectrum.

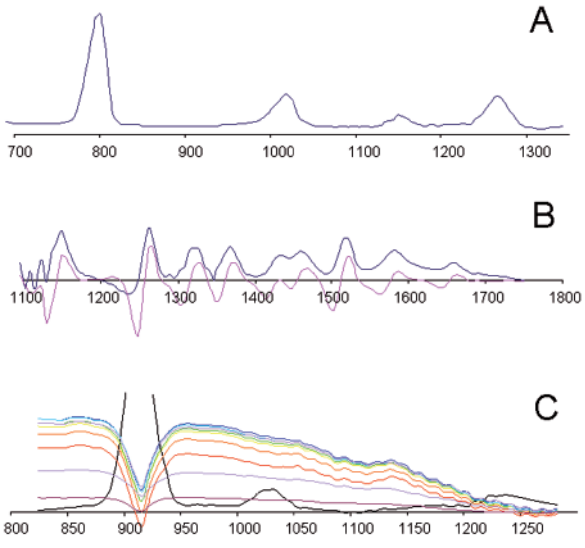

Figure 3. A – SRS spectrum of the ground state of cyclohexane; B – SERDS spectrum and deconvolution of DTTCI dye in ethanol; C – FSRS spectra of Exalite-428 dye in THF. Energy scales in cm^{-1}.

While measuring the stimulated Raman spectrum of the ground state of cyclohexane, we observed a *stimulated loss* spectrum in the region where we expected to see an anti-Stokes spectrum. The energy transfer in the molecule during the stimulated Raman process causes a gain in one beam intensity and a loss in the other. Previous FSRS experiments used the broadband probe to show the gain from the SRS process [1], although it can equally be used to probe the loss incurred in process, as fig. 4 shows. The obvious advantage in being able to use the two processes is that interfering backgrounds on the higher or lower energy side of the Raman pump may be avoided by probing the other side. It should be noted that if there are influencing resonance states in the SRS process, the interaction of the resonance state in the gain and loss mechanisms will be different.

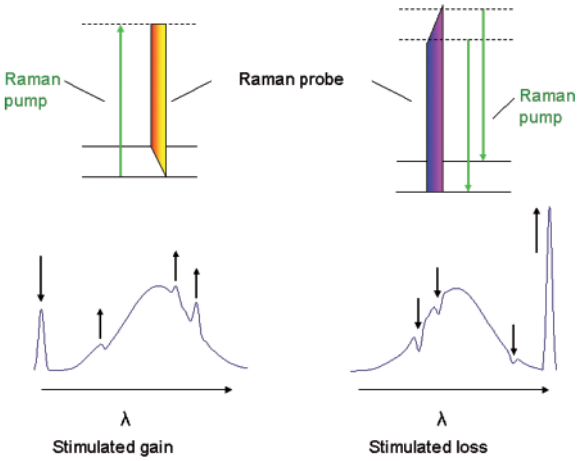

Figure 4. Stimulated Raman process, showing how the SRS gain and loss mechanisms are observed.

Subsequent experiments with a 400 nm excitation pulse were performed with the laser dye Exalite-428 in THF solution to demonstrate FSRS and observe dynamics of transient vibrational structure. Difference spectra were obtained by modulation of the Raman pump. Spectra over a range of pump – probe time delays, Δt, from 1 ps to 1 ns are shown in fig. 3C. The SRS spectrum of THF is shown in black. The broadband signals are dependent on the timing, Δt, of the 400 nm fs excitation pulse, so appeared to be FSRS signals. However, it is possible that the S_1 electronically excited state produced by the 400 nm fs excitation pulse is further excited by the 800 nm Raman pump pulse to a higher S_2 state or vibrational state of S_1, as Exalite-428 has broad absorption bands below 300 nm in its ground state UV-vis absorption spectrum. This secondary excited state could induce absorption or stimulated emission on the probe, providing another possible explanation for peaks within the spectra. Further evidence that we observe FSRS spectra is that the structure disappears when the Raman pump and Raman probe beams are temporally separated by several ps. Assuming that the secondary excited state survives more than a few ps, interfering absorption and stimulated emission signals should remain when separating the Raman pump and Raman probe in time. These are preliminary results and further experiments, such as transient absorption spectroscopy, are required to better distinguish the FSRS signals we observe. However, it is suggested from these spectra that rapid internal conversion within the molecule changes the structure of the spectrum, as the narrow feature at the position of a Raman band at 1140 cm^{-1} disappears on a timescale of ~ 300 ps to leave a slower decay of the broadband feature over ~ 1 ns.

Conclusions and Future Developments

FSRS is a promising tool for investigating ultrafast reorganisation dynamics, where other techniques may not be feasible. We have demonstrated the technique of SRS and FSRS, although it is possible that other processes interfered in the FSRS experiments due to the complex

system we were investigating. Indeed, the Exalite-428 data shows that the FSRS can have strong competition from secondary processes such as transient absorption and stimulated emission in the spectral region under investigation. Widely tunable wavelength ps and fs laser outputs would allow greater versatility (see ULTRA below), allowing one to avoid the problems seen in the Exalite-428 case, permitting experiments well away from interfering spectral structure. In addition, the use of stimulated loss and gain techniques can further verify the observations of FSRS.

A recent upgrade in the Ultrafast Spectroscopy Laboratory [5] now provides improved beam quality and higher energy, so future experiments will be considerably enhanced. A driving force behind this development was the technique's compatibility with the capabilities of the new ULTRA laboratory, currently in development in our laboratory. The ULTRA laser system is a 10 kHz dual amplified laser system providing synchronised ps and fs pulses. The tunability of the ps and fs outputs from UV – IR will enable application of FSRS over a wide range of systems, with access to various resonance enhancement conditions. ULTRA's increased repetition rate combined with new detector systems (developed through collaboration with the EID) should further increase the sensitivity and versatility of this technique in our laboratory.

References

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2. K. L. Ronayne and M. Towrie, *Upgrade to the Ultrafast Spectroscopy Laboratory,* CLF Annual Report 2006-2007.
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