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Impulsive Stimulated Raman Spectroscopy (ISRS) of nile blue

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This article is dedicated to Prof Pradeep K Gupta for his contributions to optics and photonics with biomedical applications

We present a method for recording coherent vibrational wavepacket dynamics using Impulsive Stimulated Raman Spectroscopy (ISRS). We use this technique to record Raman spectrum for a dye, nile blue, in methanol under resonant excitation. We show how this method can be used to suppress the background signals to get Raman active modes.

Keywords: Impulsive excitation, Vibrational wavepacket, Fourier transform, Raman spectrum, Resonance enhancement.

1 Introduction

The realization that wavelengths of scattered light are shifted from that of incident radiation due to exchange of energy between photon and molecule in an inelastic collision, led to the discovery of Raman effect [1,2]. Since then, Raman spectroscopy has revolutionized the field of molecular spectroscopy having wide-ranging applications in materials and biological sciences as well as analytical techniques [3]. The origin of Raman effect is usually explained in terms of scattering of photons involving quantized energy levels of molecules as depicted in Fig 1(a): a photon excites the molecule from its lowest vibrational level ($v = 0$) in ground electronic state to a virtual level (i) from which the molecule comes to a higher vibrational level (say, $v = 1$) in ground electronic state, leaving a scattered photon. Light scattered with a frequency lower (or higher) than that of the incident light is termed as Stokes (or anti-Stokes) radiation.

However, this photon-scattering picture is greatly oversimplified and does not capture the details of underlying dynamics of light-matter interaction. Truly speaking, in Raman scattering three sequential incident electric fields interact with the molecule resulting in a scattered field (and hence is a $\chi^{(3)}$ process), as shown in Fig 1(b): the first two field interactions (E_1 and E_2) create a coherent superposition of vibrational wavefunctions or a vibrational coherence which manifests the motion of nuclear wavepacket on the ground state potential energy surface (PES). This coherence oscillates with a timescale characteristic of the Raman active vibrational mode and decays within its dephasing time (typically a few picoseconds). A third field interaction (E_3) is followed by emission of a signal field (E_{signal}) which is frequency-shifted.

In a stimulated Raman scattering, the second field interaction may be induced by an external field to enhance this process [3-4] (note that for spontaneous Raman scattering this is induced by the vacuum field). As shown in Fig 1(c), it is possible to time-resolve the coherent wavepacket motion using a pair of time-delayed pulses provided the temporal width of the first pulse is shorter than time period of the vibrational mode to be probed. This technique is called Impulsive Stimulated Raman Spectroscopy (ISRS) where the

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Raman pump pulse initiates the vibrational coherence (by two field interactions) and a time-delayed probe pulse interrogates this coherence (by one field interaction); the signal is self-heterodyned with the probe pulse by virtue of momentum conservation of the fields known as phase-matching. Fourier transform of the time-domain interferogram gives the Raman spectrum [5].

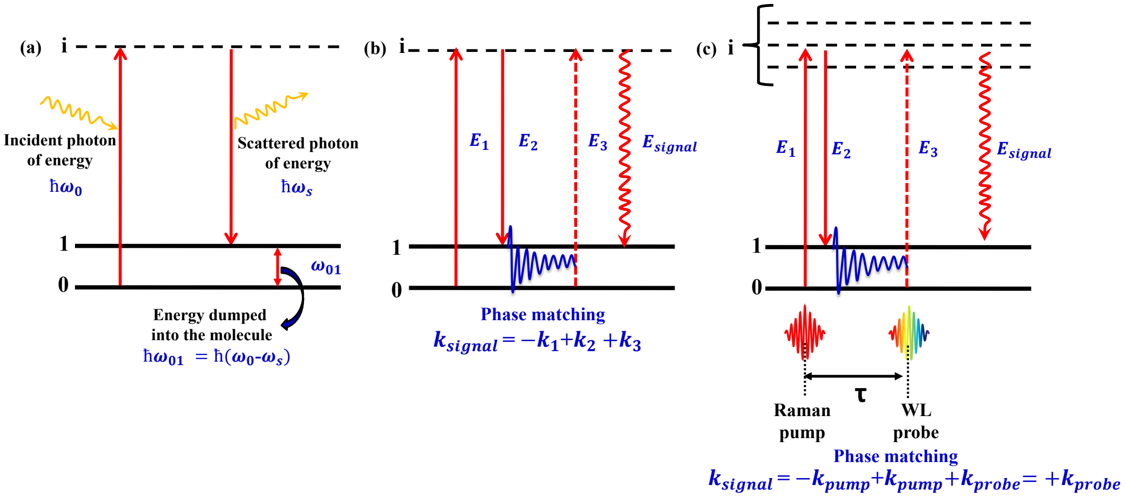

Fig 1. Energy level diagram of Raman scattering showing (a) photon scattering picture and (b) electric field interaction picture along with phase-matching criteria. (c) Pulse sequence in ISRS involving electric field interactions from pump and probe.

Note that in Figs 1(b-c), the solid/broken arrow corresponds to interaction of the field with bra/ket side of the density matrix [4-6] while wavy arrow corresponds to the signal; also, due to broad spectrum of an ultrashort pulse several virtual levels may simultaneously be accessed, as shown in Fig 1(c).

If the virtual level lies close to one of the molecular bright states, one can get a resonance enhancement of the scattered Raman signal. However, this resonance Raman signal is mixed with pump-probe signal (since both have the same resultant phase-matching) that needs to be removed. In this article, we present experimental method and data analysis procedure for isolating ISRS signal and recording Raman spectrum under resonant excitation of nile blue in methanol.

2 Experiment

A schematic of the set-up is shown in Fig 2. The whole set-up is based on a custom femtosecond transient absorption spectrometer (TAS, Newport) the details of which may be found elsewhere [7-8]. Raman pump, centered on ~690 nm was generated by pumping a Non-collinear Optical Parametric Amplifier (NOPA, Topas White, Light Conversion) with a titanium-sapphire regenerative amplifier (Libra, Coherent) producing ~45 fs pulses (FWHM width) centered on ~802 nm at 1 kHz repetition-rate. Broadband white light (WL) probe was generated by pumping a sapphire crystal with the same amplifier. Nile blue 690 perchlorate was purchased from Exciton and was used without any further purification. A methanol solution of nile blue was prepared keeping optical density at the absorption maxima at ~2.0 for a cuvette of 1 mm pathlength. After the Raman pump and WL probe beams were spatially overlapped inside the sample, the differential absorption (ΔOD) signal (heterodyned with probe), recorded by blocking alternate Raman pump pulse, was spectrally-dispersed and spectral slices at select wavelengths were analyzed, Fourier-transformed and plotted using MATLAB programming (version 2018b, Math Works)

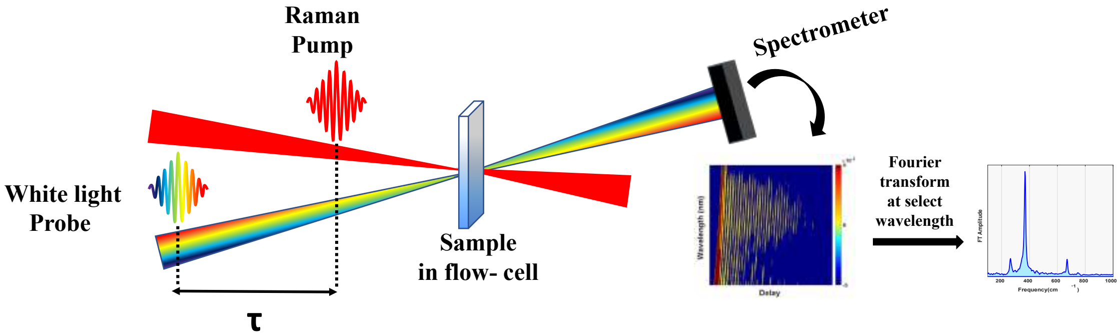

Fig 2. The experimental set-up for ISRS along with a scheme for obtaining Raman spectrum.

3 Results and Discussion

The steady-state absorption and fluorescence spectra for nile blue are shown in Fig (3b) along with the pump and probe pulse spectra. The spectral bandwidth was ~33 nm (FWHM of the Gaussian fit) corresponding to a maximum measurable Raman shift of ~700 cm^{-1} although in practice it can cover more (~1,000 cm^{-1}) considering the broad spectral wing. The pulse-width of the Raman pump was found to be ~31 fs using intensity autocorrelation.

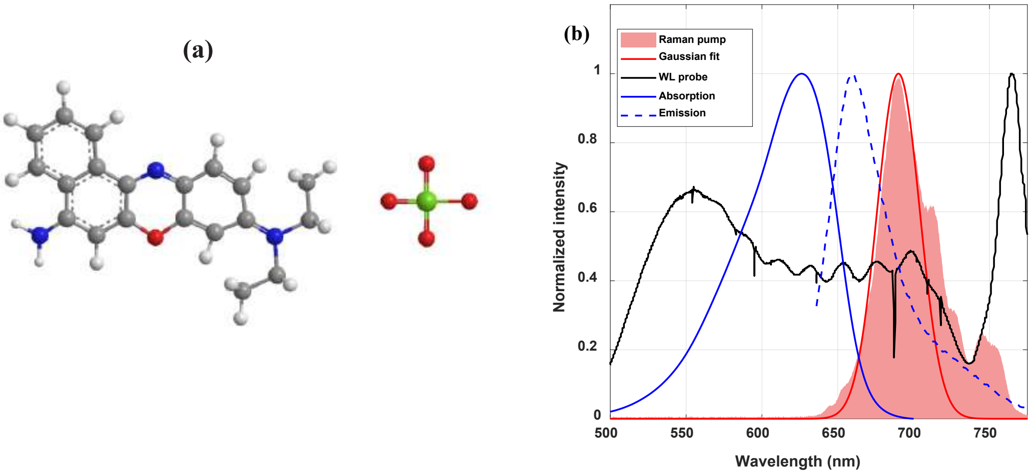

Fig 3 (a). Molecular structure of nile blue perchlorate (H: white, C: grey, N: blue, O: red, Cl: green). (b) Absorption spectrum (blue, solid line) and fluorescence emission spectrum (blue, dashed line) of nile blue, Raman pump spectrum (red, filled plot) along with Gaussian fit (red, solid line) and WL probe spectrum (black, solid line).

A spectral slice (at ~625 nm) of raw time-domain signal is plotted in Fig 4(a) along with a zoomed-in region around time zero shown in the inset. A sharp feature near time zero arises due to the coherent artifact [4]. Since the pump spectrum partially overlaps with the absorption spectrum and significantly overlaps with the fluorescence spectrum (Fig 3(b)), a strong pump-probe signal with negative ΔOD (indicative of a contribution from ground state bleach/stimulated emission signal) is observed [8] along with vibrational signatures. To remove this pump-probe feature, we considered the portion of raw data skipping the coherent artifact and fitted it with a polynomial (of degree 4); the residual is zero-padded and a Hanning window function is applied to get a processed data, as shown in Fig 4(b). This processed data is Fourier-transformed and plotted in Fig 4(c); the Raman spectrum shows a dominant 595 cm^{-1} mode corresponding to ring breathing motion of nile blue [9]. Note that in Fig 4(b) the time zero is re-defined (which does not affect the Fourier transform).

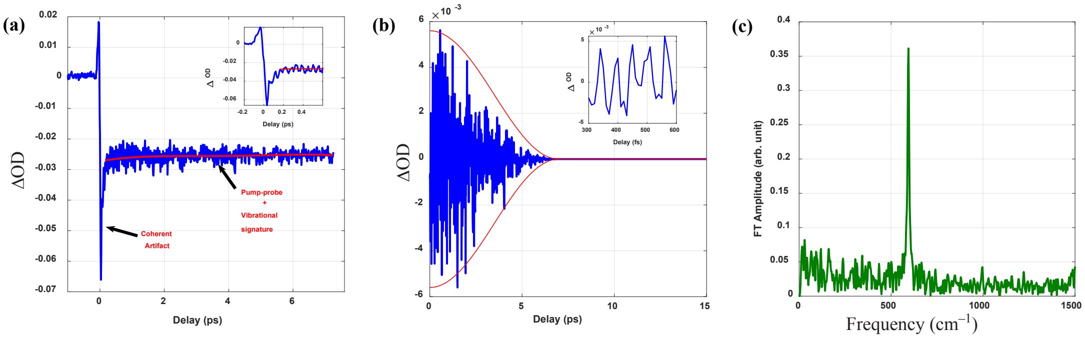

Fig 4. (a) Time-domain data (blue curve) at ~625 nm recorded for nile blue, polynomial fit to the data (red, solid line) and zoomed-in region around time zero inside the inset. (b) Processed data (blue curve), the Hanning window is also shown (red, solid line). (c) Fourier transform of processed data giving Raman spectrum showing 595 cm^{-1} mode.

When the same procedure is repeated for solvent (methanol), no vibrational mode other than the DC (zero frequency) component is observed after Fourier transform, as shown in Figs 5 (a-c); in fact, the zoomed-in time-domain data for methanol shows nothing but high-frequency noise (Fig 5(b)), whereas the same for nile blue shows a periodic oscillation of ~56 fs time-period (Fig 4(b)). This is because even the lowest frequency Raman active mode of methanol (1,033 cm^{-1} [10]) lies beyond the frequency range covered by the spectral bandwidth of the Raman pump pulse.

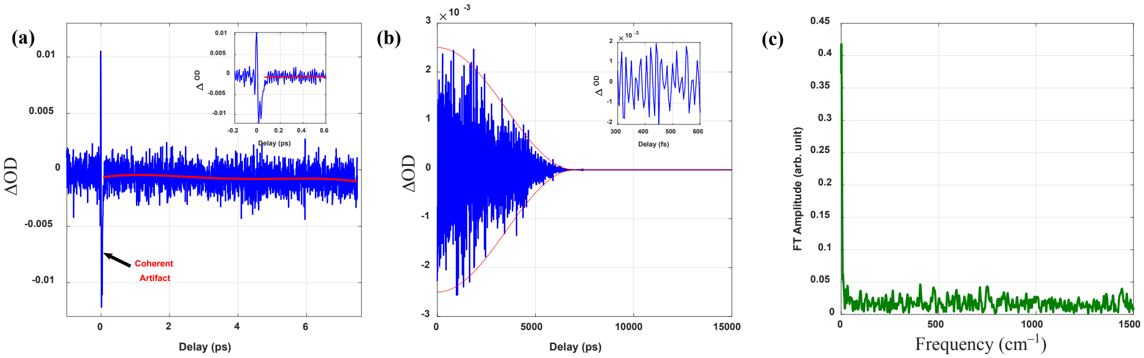

Fig 5. (a) Raw time-domain data (along with polynomial fit), (b) processed data (along with Hanning window) and (c) Fourier transform of processed data for methanol.

An extension of this technique, called Time-Resolved Impulsive Stimulated Raman Spectroscopy (TR-ISRS), that consists of an additional resonant actinic pulse (preceding the Raman pump pulse) can be employed to study structural dynamics in the excited electronic state [11] which is currently being explored in the authors' lab.

4 Conclusion

To conclude, we have shown how spectrally-dispersed ISRS enables us to directly monitor coherent nuclear wavepacket motion and thereby record Raman spectra. We showed how background signals can be easily suppressed and the signal-to-noise can be resonantly enhanced.

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The main focus of research in his group at IISER Mohali is to explore chemical and biological dynamics in condensed phase through a combination of theory and experiments.

Apart from routine picosecond fluorescence lifetime/anisotropy measurements, the group extensively use femtosecond pump-probe (transient absorption) spectroscopy. They have constructed a two-dimensional electronic spectroscopy (2DES) set-up (using an AOPDF pulse shaper) mainly to explore ultrafast energy/charge transfer dynamics within natural and artificial light harvesting systems as well as within fluorescent proteins. Quite recently, they have also started working on pump-dump-probe spectroscopy to capture dynamics involving transient ground states and built a time-resolved impulsive stimulated Raman spectroscopy (TR-ISRS) set-up to further explore structural dynamics in electronic excited state.

His group have also designed and built a versatile optical tweezer (OT) set-up having multimodal detection capabilities to explore non-linear optical effects in laser trapping under femtosecond pulsed excitation; for this they have also developed analytic theoretical models to numerically simulate force/potential. Quite recently, they have integrated laser beam shaping (using a 2D LC-SLM) to build a holographic optical tweezer (HOT) set-up for exploring long-range interaction between trapped particles in an array leading to emergence of collective phenomena.

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