Femtosecond Coherent Anti-Stokes Raman Spectroscopy (fs-CARS) with Nitrobenzene and Nitomethane

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Time-resolved coherent anti-Stokes Raman Scattering (CARS) is a nonlinear spectroscopic tool, which has gained importance with the development of ultrafast lasers due to its ability to probe ultrafast dynamical processes in molecules. Apart from the time resolution, the superiority of CARS over spontaneous Raman scattering derives from its high signal generation ability and coherent, laser like, signal emission. In this contribution, we describe the development of an experimental facility for the time-resolved coherent anti-Stokes Raman scattering spectroscopy and its application to study the vibrational dynamics of molecules containing nitro (NO_2) groups. fs-CARS experiments were carried out in neat liquids of nitrobenzene, nitromethane and their mixture. A detailed mapping of the dynamics initiated by the stimulated Raman process is achieved from the spectrum of the transient CARS signal. The CARS transient shows rich beating structure corresponding to frequencies as high as 10 THz. The Fourier transform of the transient allows accurate determination of the vibrational energy differences. This methodology is capable of providing the dephasing behaviour and spectral information of the molecular system at the same time. The results demonstrate that CARS spectroscopy with femtosecond time resolution and wavenumber-resolved detection is a powerful tool for the characterization of dynamics in the electronic ground state of molecules.

Key Words: Femtosecond; CARS; Vibrational Dynamics; Nitromethane; Nitrobenzene

Introduction

With the application of lasers, spontaneous Raman spectroscopy developed as a powerful analytical tool and is applied in a wide variety of areas. However, due to inherently weak signal levels and fluorescence background, its applicability is restricted when the sample concentration is too low or the sample is fluorescent. These difficulties associated with spontaneous Raman spectroscopy can be overcome by coherent Raman spectroscopy (Potma and Mukamel, 2013). Coherent Raman techniques are non-linear spectroscopic techniques and provide much higher signal levels compared to spontaneous Raman signals. While spontaneous Raman signal is emitted in all directions, the coherent Raman signal is a laser like emission in a well-defined direction, which makes the detection easier and background-free. Coherent Raman spectroscopic techniques are now widely being used as an alternative to conventional Raman spectroscopy due to its high signal levels and coherent nature of the signal.

Coherent anti-Stokes Raman scattering (CARS) (Potma and Mukamel, 2013; El-Diasty, 2011) is one of the coherent Raman techniques that has evolved as a versatile technique for material characterisation and imaging in various areas of science. Though

experimentally complex compared to conventional Raman, the high signal levels and natural rejection of fluorescence eliminates the most common factors plaguing the applicability of conventional Raman spectroscopy. Frequency domain CARS, using narrow band lasers, has proved to be an efficient vibrational spectroscopic tool in low-pressure gases, combustion processes, plasma and also in molecular spectroscopy and microscopy (Djaker *et al.*, 2007; Roy *et al.*, 2010).

The development of ultrafast lasers added another dimensionality to laser spectroscopy. Time-resolved spectroscopy using ultrashort laser pulses of pico/femtosecond duration made it possible to probe fast molecular dynamical processes in real time. The time scales provided by ultrafast lasers correspond to the vibrational period of molecular vibrations (100 fs ~ 150 cm^{-1}) and are ideal for time-resolved probing of vibrational dynamics in molecules. Most of the femtosecond time-resolved studies have been performed on investigation of dynamics of molecular systems in electronically excited states. Femtosecond time-resolved CARS (fs-CARS) is an experimental technique, which is capable of studying dynamics in the electronic ground state of molecular systems. It was first reported by probing ultrafast vibrational dynamics in several liquids (Leonhardt *et al.*, 1987). Using the broad spectral width of femtosecond pulses, several vibrational modes can be excited coherently (wave packets) and can monitor their relaxation processes in real time. As a result of the intense signal, sensitivity and inherent florescence discrimination, CARS is of considerable interest in time-resolved spectroscopy. Some of the applications of time-resolved CARS include studies of vibrational dephasing times in solution, collisional relaxation times, and study of the excited state properties (Schmitt *et al.*, 1998; Vierheilig *et al.*, 1999).The large spectral width of fs pulses limits the spectral resolution achieved by fs-CARS. Developments in pulse shaping technology (Weiner, 2011; Monmayrant *et al.*, 2010) provide a way to improve the spectral resolution in fs-CARS.

In this contribution, we describe the development of an experimental facility for time-resolved CARS

using femtosecond laser pulses and its application in probing time-resolved vibrational dynamics in nitrobenzene, nitromethane and their mixture. Many of the high-energy materials contain nitro groups and the aim of the CARS experiment was to explore the applicability of CARS in deciphering the electronic ground state vibrational dynamics of high energy materials. The paper is organised as follows: next section provides a brief account of the theory of CARS followed by the experimental description. The final section discusses the experimental results on nitromethane, nitrobenzene and their mixture.

Theory

The theory of time-resolved Four-Wave-Mixing (FWM) processes can be formulated based on third order perturbation theory, which is used to calculate the third order polarization, $P^{(3)}(t)$ responsible for the signal generation (Mukamel, 1995; Tannor, 2007). In the semiclassical picture presented here, the electromagnetic field is treated classically and the matter is described quantum mechanically using the wave function approach. The fundamental observable in CARS is the third order polarisation that is generated by the interaction of three laser pulses namely the pump $E_{pu}(\omega_{pu}, k_{pu})$, Stokes $E_s(\omega_s, k_s)$ and the probe $E_{pr}(\omega_{pr}, k_{pr})$ pulses. The time dependent polarisation $P(t)$ induced in a system with a state vector $\psi(t)$ is given by

$$P(t) = \langle \psi(t) | \mu | \psi(t) \rangle \tag{1}$$

where μ is the dipole operator. Inorder to calculate the third order polarisation,the perturbative expansion of the wave function is used.

$$|\psi(t)\rangle = \sum_{N=0}^{\infty} |\psi^{(N)}(t)\rangle \tag{2}$$

wave functions of different orders can be obtained iteratively as

$$|\psi^{(N)}(t)\rangle = -\frac{i}{\hbar} \int_{-\infty}^{t} e^{\frac{iH(t-t')}{\hbar}} H_{int}(t') |\psi^{(N-1)}(t')\rangle dt' \tag{3}$$

Through successive interactions with the three pulses of the CARS process, the wave function acquires spatial dependencies associated with each of the pulses (Faeder *et al.*, 2001). For higher order

wave functions, the order of the wave vectors denotes the time ordering of the interactions with the fields. For example, the third order wave function relevant for CARS is $|\psi^{(3)}_{k_{pu}-k_S+k_{pr}}(t)\rangle$ which is created by the absorption of a pump photon with wave vector k_{pu}, stimulated emission of a photon with wave vector k_s followed by the absorption of a photon with wave vector k_{pr}. This sequence of events in CARS can be pictorially represented using double-sided Feynman diagrams. The Feynman diagram relevant for CARS and the corresponding energy level diagram are shown in Fig. 1.

The third order polarisation responsible for the CARS signal generation can be written as

$$P^{(3)}(t) = \langle \psi^{(0)}(t) | \mu | \psi^{(3)}_{k_{pu}-k_S+k_{pr}}(t)\rangle + c.c \qquad (4)$$
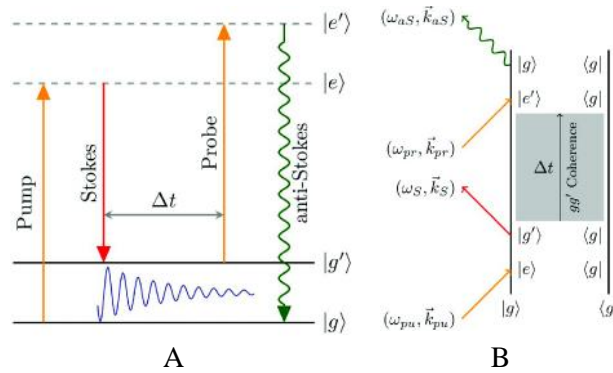

Fig. 1: Energy level diagram (A) and double sided Feynman diagram (B) corresponding to CARS process

The third order wave function $|\psi^{(3)}_{k_{pu}-k_S+k_{pr}}(t)\rangle$ can be written, assuming the energy level diagram given in Fig. 1 as

$$\psi^{(3)}(t) = \left(-\frac{i}{\hbar}\right)^3 \int_0^t \int_0^{t_{pr}} \int_0^{t_S} e^{-\frac{i}{\hbar}H_{e'}(t-t_{pr})}$$
$$\left[-\mu E_{pr}(t_{pr})\right] e^{-\frac{i}{\hbar}H_{g'}(t_{pr}-t_S)}$$
$$\left[-\mu E_S(t_S)\right] e^{-\frac{i}{\hbar}H_e(t_S-t_{pu})}\left[-\mu E_{pu}(t_{pu})\right] e^{-\frac{i}{\hbar}H_g t_{pu}} \qquad (5)$$
$$\psi_g(0) dt_{pu} dt_S dt_{pr}$$

This equation can be simply interpreted as the evolution of the ground state wave function $\psi_g(0)$ under the influence of the ground state Hamiltonian H_g till the interaction of the first pump pulse $E_{pu}(t_{pu})$ at time t_{pu}. The interaction of the pump pulse creates an excited wave function $\left[-\mu E_{pu}(t_{pu})\right] e^{-\frac{i}{\hbar}H_g t_{pu}}\psi_g(0)$ which is nothing but the ground state wave function scaled by $[-\mu E_{pu}(t_{pu})]$. This newly created excited wave packet then evolves under the excited state Hamiltonian H_e till the interaction with the Stokes pulse $E_s(t_s)$ at time t_s. This interaction causes a stimulated emission to an excited vibrational level g' and the new wave function generated by the stimulated emission then evolves under the $H_{g'}$ Hamiltonian, till the interaction with the probe pulse $E_{pr}(t_{pr})$ at time t_{pr}. The interaction with the probe pulse promotes the wave packet to the excited state, which then evolves under the excited state Hamiltonian $H_{e'}$ till the emission of the anti-Stokes field.

In order to calculate the intensity of the anti-Stokes emission, the third order polarisation given by equation (4) can be converted to the frequency domain (Fourier transform) and used as the source term in the Maxwell's equation.

$$\left(\nabla^2 + \frac{\omega^2}{c^2}\varepsilon(\omega)\right)E = -\frac{4\pi\omega^2}{c^2}P^3(\omega) \qquad (6)$$

The solution of this equation gives the signal intensity as

$$I_{CARS} \propto |\chi^{(3)}|^2 I_{pu}I_S I_{pr}l^2\left(\frac{\sin\frac{\Delta kl}{2}}{\frac{\Delta kl}{2}}\right)^2 \qquad (7)$$

Where, $\chi^{(3)}$ is the third order susceptibility, $I_i(i = pu, S, pr)$ are the intensities of the three input pulses and l is the interaction length. Δk is the phase mismatch which is given by

$$\Delta k = k_{pu} - k_S + k_{pr} - k_{aS} \qquad (8)$$

The phase mismatch is the wave vector mismatch between the three input fields and the

emitted signal. The sinc function dependence of the signal intensity on the phase mismatch suggests that the signal rapidly decreases to zero with increasing phase mismatch. Thus, for efficient CARS signal generation proper phase matching should be ensured. This is achieved by using a special beam geometry, which is described in the next section.

Experimental Setup for Time-Resolved CARS

Femtosecond laser pulses required for the experiment are generated by a commercial laser system (3 *mJ*, 1 *kHz*, Amplitude Technologies, Trident-M) delivering pulses of duration ~ 50 *fs* with central wavelength 800 nm. Two multipass optical parametric amplifiers (OPA; Light Conversion, TOPAS-C) are used in order to generate the different wavelengths required for the CARS experiment.Each of the OPA is pumped by 1 *mJ* of 800 nm output from the Trident-M system. One of the OPA output is continuously tunable from 450 nm to 10000 nm and the other from 250 nm to 2700 nm. The pulse characteristics are determined from autocorrelation and FROG traces (Pulse Check, APE). The pump and probe pulses were of the same wavelength and derived from one of the OPA output using a 50/50 beam splitter.

The pump and Stokes wavelengths were 590 nm and 635 nm respectively and correspond to a wavenumber difference of 1200 cm^{-1}. All the three laser pulse energies were fixed to be around 25-30 *nJ* using neutral density filters. The broad spectral width of the pulses enabled excitation of Raman modes within a region of +400 cm^{-1} from the centre of excitation. For an efficient CARS signal generation, perfect overlap of the input pulses has to be ensured both spatially and temporally. A schematic of the complete experimental setup for CARS is shown in Fig. 2. Spatial overlap of the pulses is necessary to achieve phase matching. The phase matching is ensured by using the Folded-BOXCAR arrangement of the input beams. In this arrangement, the three beams involved in the CARS process, pump, probe and Stokes are aligned parallel to each other and are made to pass through three corners of a rectangular box with the help of a mask as detailed in Fig. 3. The selection of wavelength was based on the nitro group vibration characteristics.

The three beams were then focused onto the sample using a lens of 10 cm focal length. The time delay between the pulses was adjusted using computer controlled linear translation stages (Newport ILS 150) mounted with retroreflecting mirrors. The pump and Stokes pulses for the CARS process were time coincident and the timing of the probe pulse was variable. The spatially separated CARS signal from the sample is collimated using another lens (f=10 cm) and sent to a spectrometer (ANDOR Shamrock) attached with a TE cooled CCD (ANDOR Newton). Neat liquids of nitromethane and nitrobenzene were
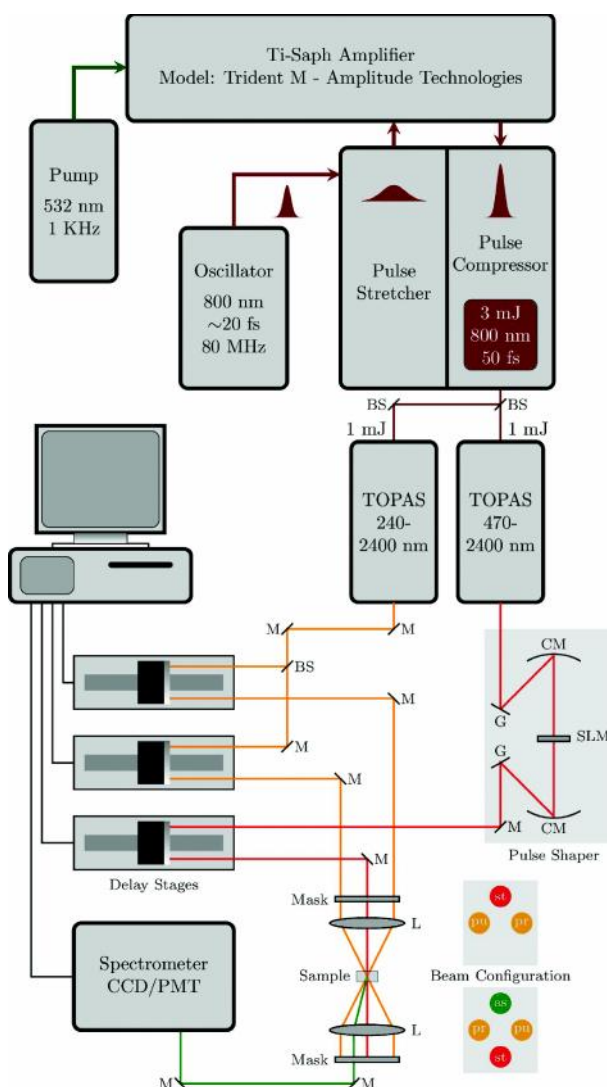

Fig. 2: Experimental setup for CARS using folded BOXCAR beam geometry: M-Mirror, BS- Beam Splitter, G-Grating, and L-Lens. The delay stages are linear translation stages fitted with a retroreflector
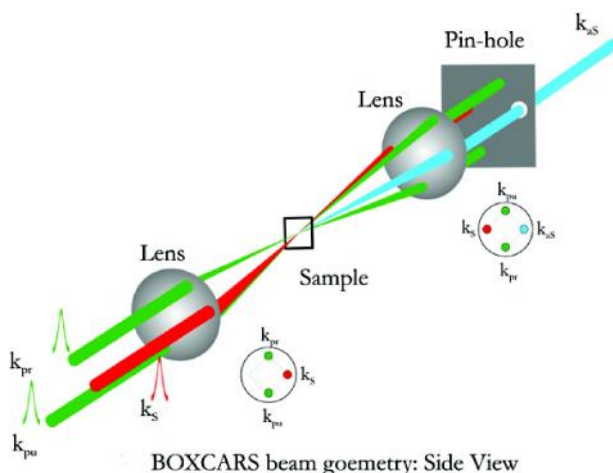
Fig. 3: Folded BOXCARS beam arrangement

Fig. 4: Time and frequency resolved CARS spectrum of nitrobenzene

used for the experiments.

Results and Discussion

In the following, results from the CARS spectrum obtained from neat liquids of nitromethane, nitrobenzene and their mixture are discussed. These molecules do not absorb in the visible spectral region, therefore the CARS process here does not involve any excited electronic state.

CARS on Nitrobenzene

The time and frequency-resolved CARS transient of nitrobenzene is shown in Fig. 4. The transient shows well defined beating structure arising due to the simultaneous excitation of different vibrational modes, which fall within spectral width of the excitation pulses. A beating structure is observed in the transient CARS signal. Such beating structures are well known and are due to quantum beating of the different coherently excited vibrational modes of the molecules.

To make these signal modulations more visible, Fig. 5A presents a frequency slice of the transient. An analysis of the beating frequency can be performed by fast Fourier transformation (FFT) and the frequency difference between the beating vibrational modes is shown in Fig. 5B. The peak location along the FFT wavenumber axis corresponds to the wavenumber differences of two coherently excited vibrational modes of nitrobenzene. It is now obvious
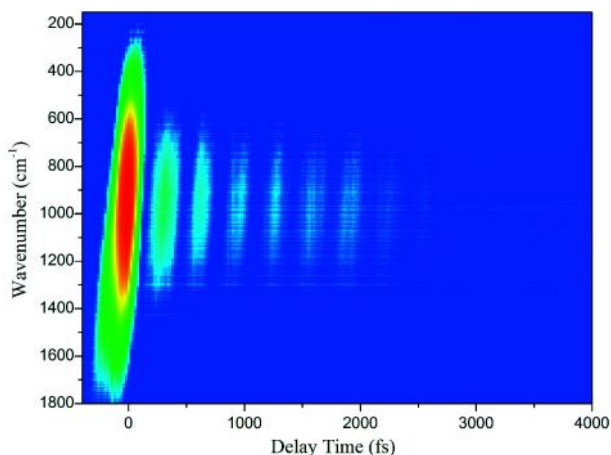
that the complex oscillatory pattern of the time domain signal is mainly attributable to four peaks.

An assignment of the beating wavenumbers is possible taking into account the Raman modes excited by the femtosecond pump and Stokes pulses. It is now appropriate to compare the obtained results with spontaneous Raman spectrum of nitrobenzene (Fig. 6).

The beat frequencies seen in the Fourier spectrum shows peaks at wavenumber positions 20 cm^{-1}, 103 cm^{-1}, 238 cm^{-1} and 337 cm^{-1}. These peaks correspond to the frequency difference between the 853 cm^{-1}, 1003 cm^{-1}, 1022 cm^{-1}, 1107 cm^{-1} and 1347 cm^{-1} vibrational modes of nitrobenzene. The highest beat frequency of 337 cm^{-1} between the nitrobenzene vibrational modes at 1003 cm^{-1} and 1347 cm^{-1} corresponds to a frequency of 10.1 THz. This is indicative of the high temporal resolution of the experiment, which enables probing of terahertz phenomena with appreciable accuracy.

CARS on Nitromethane and Mixture

Similar experiments were carried out in nitromethane and a mixture of nitromethane and nitrobenzene (1:1 v/v). The nitromethane CARS transient is dominated by a single Raman mode at 917 cm^{-1} and hence did not show any beating structure (Fig. 7B). In the nitromethane case, no FFT analysis was necessary as there was only one prominent Raman mode and
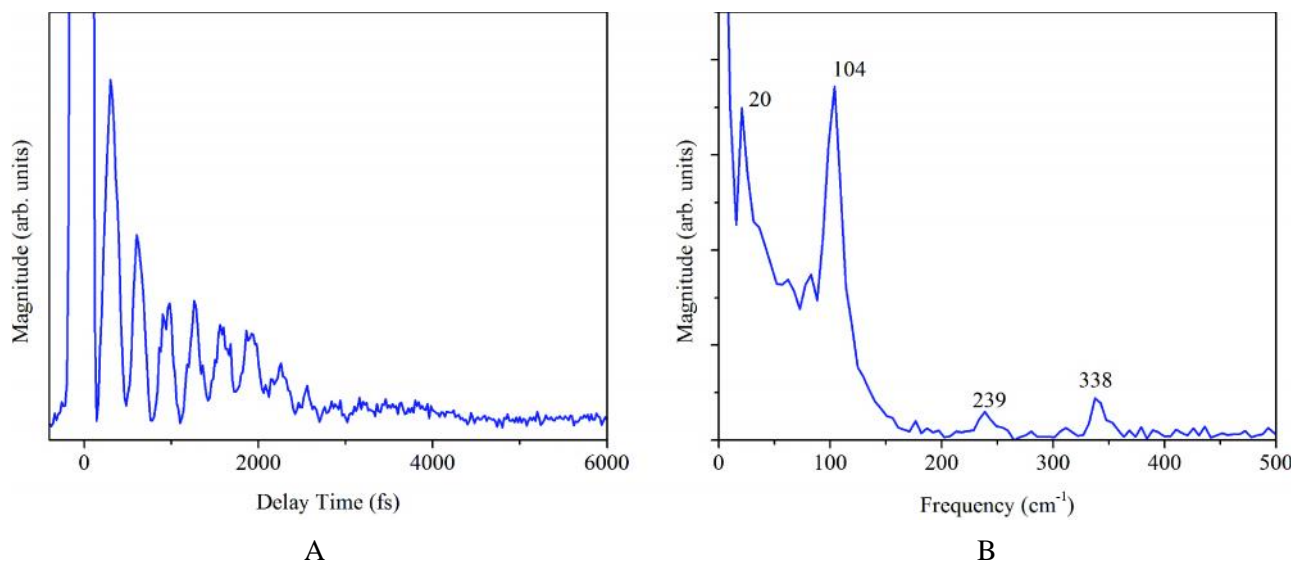
Fig. 5: A: Time-resolved CARS transient showing rapid modulations (spectral slice). B: FFT corresponding to the transient showing the beat frequencies
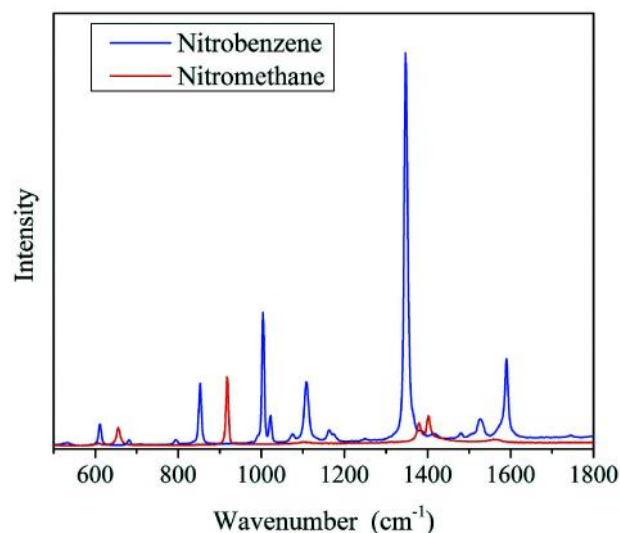

Fig. 6: Spontaneous Raman spectrum of nitrobenzene (blue) and nitromethane (red) displaying the vibrational modes excited by the femtosecond pump and Stokes pulses

the CARS signal decays exponentially. The decay time $\tau = T_2/2$ is ≈ 1139 fs (Shkurinov, 1994).

The CARS transient of the mixture showed modulations of the CARS signal (Fig. 7A) similar to the case of nitrobenzene. Fourier analysis of the CARS transient of the mixture showed an additional beat frequency component at 86 cm^{-1} (Fig. 8) which arises

from the beating between the vibrational modes of nitromethane (917 cm^{-1}) and nitrobenzene (1003 cm^{-1}). The presence of additional frequency components in the CARS transient can be used as a signature to identify components in a mixture. Further analysis is being carried out to extract the dephasing time of different participating vibrational modes and to analyse how the dephasing times are influenced in a mixture.

Conclusions

An experimental facility for time-resolved CARS using femtosecond laser pulses has been described with two examples of organic nitro compounds. Spectrally dispersed CARS signal leads to a two-dimensional (time and wavenumber) data set. An analysis of this two-dimensional time domain data on the basis of Fourier transform methods enables one to obtain detailed spectral information on the vibrational mode structure in addition to the vibrational dephasing times that are readily deducible from the decay behaviour of the transient signals. It has been demonstrated that CARS spectroscopy with femtosecond time resolution and wavenumber resolved detection is a powerful tool for the characterization of dynamics in the electronic ground state of molecules.
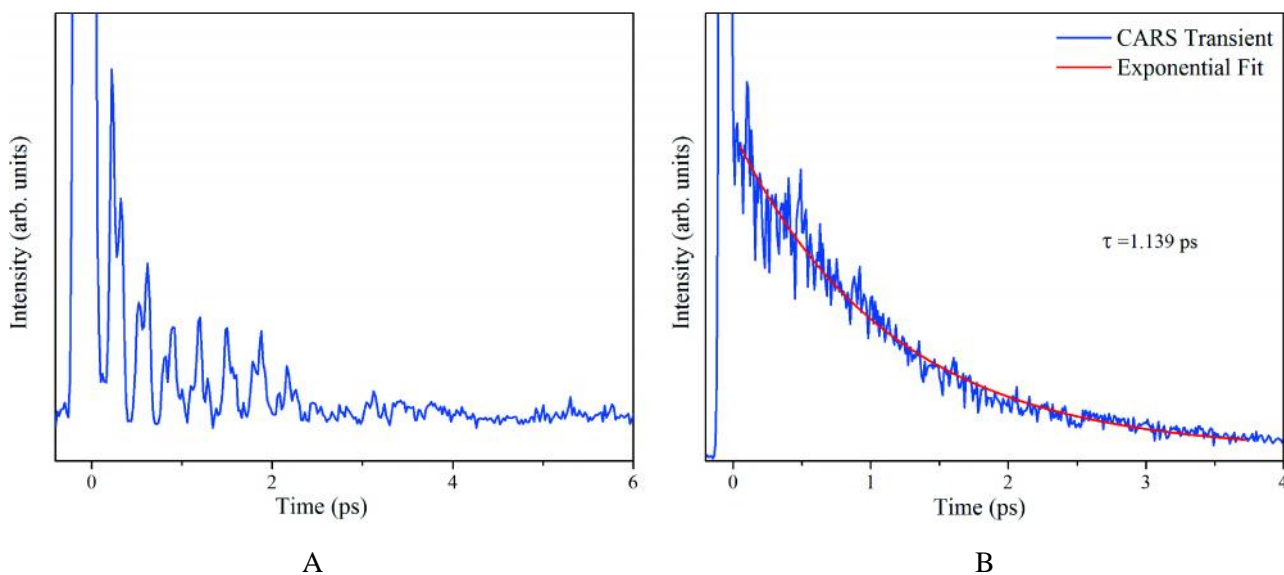
Fig. 7: A: CARS transient from 1:1 (by volume) mixture of nitromethane and nitrobenzene. B: CARS transient from pure nitromethane
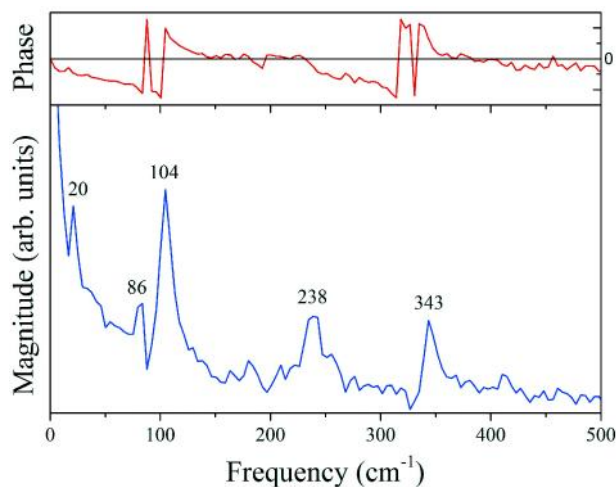

Fig. 8: FFT of the CARS transient of mixture

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