



Vibrational wave-packet dynamics in CV670 investigated by broadband femtosecond TR-CARS spectroscopy



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ABSTRACT

Broadband femtosecond time-resolved coherent anti-Stokes Raman scattering ((TR-CARS)) is utilized to investigate the wave-packet dynamics of Cresyl Violet (CV670) dye molecules in ethanol solvent at room temperature. An interesting behavior of wave-packet dynamics phenomena is observed and discussed for the first time, and several unknown Raman vibrational modes with frequency differences of 32 cm⁻¹, 38 cm⁻¹, 45 cm⁻¹, 50 cm⁻¹, 55 cm⁻¹, 65 cm⁻¹, 80 cm⁻¹, 95 cm⁻¹ and 101 cm⁻¹ are excited and obtained at the same time. This work makes possible high efficiency in the structure investigation as well as dynamics of intra-molecular processes by broadband femtosecond (TR-CARS) spectroscopy with fast Fourier transformation (FFT) analysis means.

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1. Introduction

In our previous publications, we have demonstrated that a selective excitation of specific vibrational coherences in a gas or liquid phase molecule is possible by using a resonance enhanced method in a coherent anti-Stokes Raman scattering (CARS) process, while a time delayed probe pulse ensures an efficient non-resonant background suppression [1–8]. On the one hand, the potential high selectivity of the proposed technique is based on the

fact that the CARS signal can be sensitive to both the electronic and vibrational signature of category under investigation. On the other hand, excitation with high intensity ultra-short (femtosecond) pulses can bring about high optical gain, and associated high brightness of the CARS signal, which offers prospects of high sensitivity and high selectivity of detection [9,10].

The current efforts of numerous groups on femtosecond CARS in organic systems have emphasized separation and recognition of individual vibrational modes. Due to the fact that the ultra-short femtosecond laser pulses are spectrally broad, in most cases several molecular states are coherently excited, resulting in wave-packet excitation and probing [11,12]. In fact, the separation of such individual frequencies and interpretation of these results are challenging. Furthermore, these measurements rely on the controlled shaping of ultra-short laser pulses to excite individual

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vibrational modes selectively, and thus require highly controlled conditions, such as laser-pulse configuration optimizing, laser polarization controlling, etc [13–16].

In this paper, we use a hybrid technique that combines 33 fs CARS spectroscopy with the advantages of time-resolved technique to directly observe the vibrational wave-packet dynamics of CV670 dye molecules in ethanol solvent (5×10^{-5} mol/L). By detecting the CARS signal of CV670 molecules, an interesting behavior of wave-packet dynamics phenomena is observed. By taking the fast Fourier transformation (FFT) of the 33 fs (TR-CARS) trace, the beat frequency spectrum with frequency differences of 32 cm^{-1} , 38 cm^{-1} , 45 cm^{-1} , 50 cm^{-1} , 55 cm^{-1} , 65 cm^{-1} , 79 cm^{-1} , 95 cm^{-1} and 101 cm^{-1} are obtained at the same time. The results show that 33 fs laser pulses allow a multitude of processes for preparation and investigation of molecular coherences with (TR-CARS) spectroscopy technique: no complicated controlled conditions are required for the 33 fs laser pulses. The possibility to excite and investigate several vibrational modes by broadband femtosecond (TR-CARS) spectroscopy with FFT analysis method, it opens up clear and quick pathways for the structure analysis as well as dynamics of intra-molecular processes.

2. Methodology and experimental

The basic idea of the broadband femtosecond (TR-CARS) experiment is shown in Fig. 1. As shown in Fig. 1a) three laser pulses interact with the low concentration of CV670 molecules. Two laser pulses called the pump (ω_{pu}) and probe (ω_{pr}) pulses have the same frequencies, $\omega_{pu} = \omega_{pr}$. The third laser (Stokes) is tuned to a lower frequency, ω_s , in such a manner that the difference in tuning between pump and Stokes laser frequencies is responsible for resonance with someone vibrational transition in the ground state of CV670 molecules. The pump-Stokes laser pulses create a coherent excitation of molecules (historically called the Raman coherence) in the sample at time t_0 . The third laser pulse (probe: ω_{pr}) interacts with this coherent state at time t_1 , creating a signal called the anti-Stokes pulse (ω_{CARS}) that can be used to map out the molecular resonances that identify particular chemical species or vibrational mode. For a homodyne detection scheme, the ensemble CARS signal (Fig. 1a), given by the third-order polarization $P^{(3)}$ [17,18],

$$S(\Delta t) = \int_{-\infty}^{\infty} dt |p^{(3)}(t, \Delta t)|^2 \quad (1)$$

where t is the time and Δt denotes the positive temporal separation between the single pump pulse and the Stokes-pump

pulse pair, reduces to the damped quantum beats of the prepared vibrational coherence:

$$S(\Delta t) \propto \sum_{v,v'} a_v a_{v'} \cos(\omega_v - \omega_{v'}) e^{-(\gamma_v + \gamma_{v'}) \Delta t} \quad (2)$$

with phenomenological dephasing rates $\gamma_{v,v'}$ that arise from the within sample averaging indicated by the angle brackets in Eq. (1).

Fig. 1b) shows the broad spectral bandwidth of the pump and Stokes frequency pairs that contribute to the excitation of the Raman coherence for the transitions near the $(\omega_{pu} - \omega_s) / 2\pi c = 1064 \text{ cm}^{-1}$ vibrational band of CV670.

The schematic of our experimental setup is shown in Fig. 2. The experimental setup is described briefly, as following: The laser pulses from a commercial femtosecond laser system Ti: sapphire regenerative amplifier (Coherent Inc.) at the central wavelength of 800 nm (6 mJ/pulse, 1 kHz and 33 fs) is split into two parts to pump two optical parametric amplifiers (TOPAS: Topas-Prime 1 and Topas-Prime 2 in Fig. 2). Two independent wavelengths in the range of 266–1150 nm can be generated by the TOPAS. The output of Topas-Prime 2 is split into two parts by a splitter to obtain the pump and probe pulses, while the output of Topas-Prime 1 serves as the Stokes pulse. For the 33 fs TR-CARS, a folded BOXCARS configuration is employed to separate the signal from the incoming pump-Stokes and probe beams. The generated beams of blue-shifted photons (CARS signal), whose propagation directions are determined by the phase-matching conditions [19],

$$\vec{k}_{CARS} = \vec{k}_{pr} + (\vec{k}_{pu} - \vec{k}_s) \quad (3)$$

The CARS signal is filtered by a spatial filter and collected by a silica fiber, dispersed in a spectrometer (ANDOR SR-750-B1-R) and detected by a fast photo-multiplier tube (PMT). The CARS signal-to-noise ratio (SNR) is further enhanced by using a boxcar integrator (SR250).

3. Results and discussion

The Fig. 3 shows the wavelength arrangement of the laser beams together with the CARS spectrum of CV670 in ethanol solvent (5×10^{-5} mol/L). The CARS signal at 594 nm is generated by a Stokes wavelength at 681 nm and a pump and probe wavelength at 635 nm. From the figure, it can be determined that the half-width of the anti-Stokes line of the CARS spectrum of CV670 in ethanol solvent amounts to 545 cm^{-1} , while the half-width of the pump-Stokes lines at 635 nm and 681 nm are about 441 cm^{-1} and 455 cm^{-1} , respectively.

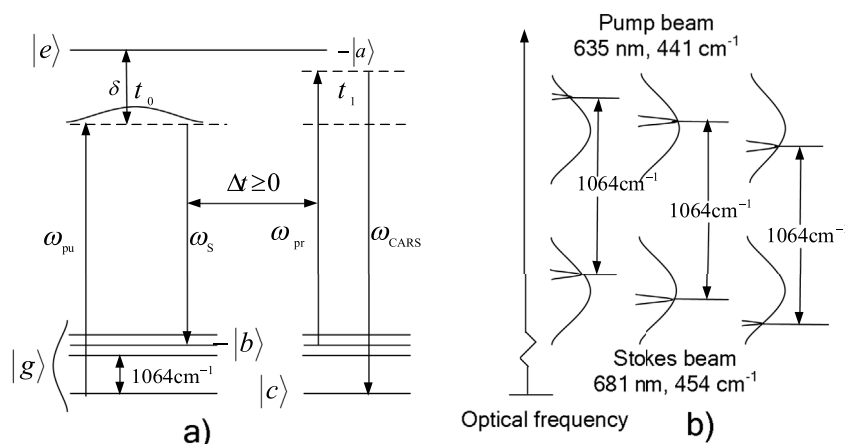


Fig. 1. Methodology of the bandwidth femtosecond (TR-CARS) experiment: a) The Energy diagram of the (TR-CARS) process, b) Schematic illustration of the pump-Stokes frequency pairs that contribute to the excitation of the Raman coherence near the 1064 cm^{-1} of CV670.

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