Investigation of vibrational dynamics by femtosecond time-resolved CARS

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Abstract: We report the femtosecond time-resolved CARS in BBO crystal, ethanol, cresyl violet 670 and pyrromethene 650 using the various degrees of freedom such as the timing, polarization and wavelengths of the laser pulses.

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Femtosecond time-resolved coherent anti-Stokes Raman spectroscopy (CARS) has emerged as an attractive method for studying the vibrational dynamics of Raman modes in time-domain. Multiple Raman modes can be coherently excited simultaneously due to the spectrally broad femtosecond laser pulses. The restriction of the CARS resolutions are especially severe in the case of biological macromolecule, the separation and recognition of individual Raman modes become rather challenging. As three laser pulses are used for the generation of the CARS signal, many degrees of freedom can be varied [1]. By controlling the timing, polarization, and wavelengths of the laser pulses, the vibrational dynamics of different Raman modes are coherently excited and probed by CARS.

The experimental setup and methodology of femtosecond time-resolved CARS presented here has been described in detail elsewhere [2]. A commercial regenerative amplifier and two optical parametric amplifiers provide the three laser beams. The generation of CARS signal requires temporal and spatial overlap of the beams in the samples. The delay time between the pump and Stokes pulses defines T_{12}. The delay time between the probe and pump pulses defines T_{13}. This folded BOXCARS beam geometry ensures that the CARS signal propagates in a direction ($\mathbf{k}_{CARS}=\mathbf{k}_{pr}-\mathbf{k}_{st}+\mathbf{k}_{pu}$). The CARS can be in different applications by changing the delay time of laser pulses. Several Raman modes can be excited selectively by changing T_{12} due to the bandwidth and chirp of Stokes and pump pulse. The stretching vibration of C-C bonds and C-O bonds in ethanol are also selective excited by changing T_{12}. Fig. 1 shows the contour plots of spectrally dispersed transient CARS intensity of the ethanol solutions, when T_{12}=-40, 0 fs (a, b), a pump of wavelength $\lambda_{pu}=\lambda_{pr}=547$ nm and a Stokes wavelength $\lambda_{st}=580$ nm. In Fig. 1(a) and (b), the anti-Stokes signal has relative larger intensities centered on the detection wavenumbers of approximately 860 cm^{-1} and 1000 cm^{-1}. If T_{13} was set to zero, the signal can be got by changing T_{12}. The duration of pump and stokes beams can be got by fitting the signals [2].
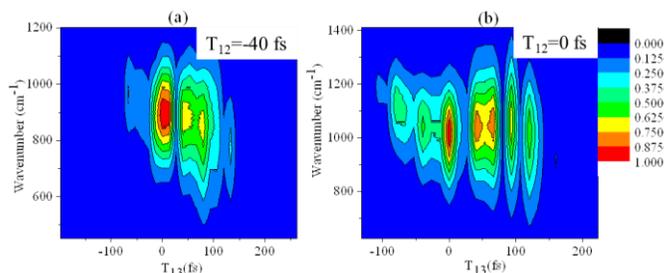

Fig. 1. Ethanol femtosecond CARS transient obtained for pump wavelengths $\lambda_{pr} = \lambda_{pu}=547$ nm and a Stokes wavelength $\lambda_{st} = 580$ nm

The ratio of intensity between vibrational modes can be changed by the polarization of pump pulses or crystal geometries. Zero degree is the best angle for second harmonic generation in BBO crystal. Fig. 2 (a) and (c) shows the time-integrated CARS intensity of BBO crystal with the different geometrical configurations (the angle between the crystal axis and the polarization) for a pump of wavelength $\lambda_{pu}=\lambda_{pr}=714$ nm and a Stokes wavelength $\lambda_{st}=800$ nm.

The fast Fourier transform (FFT) power spectra of the time-resolved CARS signal from fig. 2 (a) (c) is exhibited in fig. 2 (b) (d), respectively. The frequency difference between the modes is 200±2 cm^{-1} and 185±8 cm^{-1}. This corresponds to the Raman modes of B-O stretching vibrations of extra-ring B-O bonds (A', 1570cm^{-1}) and exrta-ring B-O' bonds (E', 1408cm^{-1}). Furthermore, signal noise ratio is smaller with the increase of angle. From Fig. 2 we can see that geometrical configuration will influence the ratio of intensity between vibrational modes. The reason is that polarizability tensor influences vibration modes. The polarization of pump pulses will also influence the intensity of the vibrational mode [2].
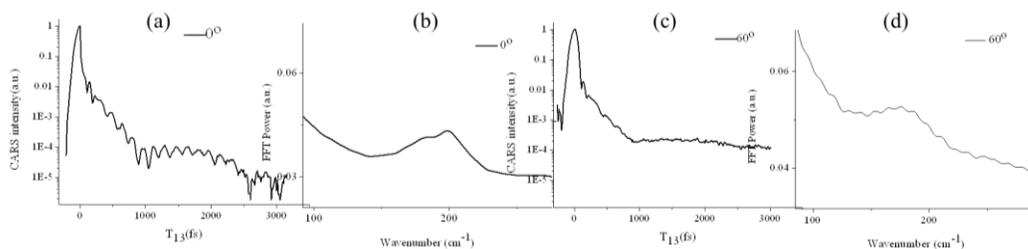
Fig. 2. The CARS of BBO crystal under different geometrical configurations (714 nm pump, 800 nm stokes)

The signal noise ratio of CARS can be increased by controlling the wavelength of laser pulse. For the measurements on dye the wavelengths of the pump and probe beams were therefore tuned to the absorption band of the dye. In order to generate the vibrational coherence, the difference frequencies of the pump and Stokes laser pulses must be tuned to match the Raman resonance. Recently He et al [3, 4] have achieved the selective excitation of the vibrational modes in cresyl violet 670 (CV670) and pyrromethene 650 (PM650) dye in diluted solutions (5×10^{-5} mol/L and 1×10^{-4} mol/L) by time-resolved CARS.

Fig. 3(a) shows dependence of femtosecond CARS signal on probe pulse delay for PM650-ethanol solution and CV670-ethanol solution. The red line shows result in CV670-ethanol solution obtained for $\lambda_{pu}=\lambda_{pr}=628$ nm and $\lambda_{st}=671$ nm. The black line shows result in PM650-ethanol solution obtained for $\lambda_{pu}=\lambda_{pr}=615$ nm and $\lambda_{st}=655$ nm.

The FFT power spectra from Fig. 3(a) are exhibited in Fig. 3(b), respectively. These power spectra confirm that the oscillations in the transient signal result from a coherent superposition of vibrational eigenstates with an energy spacing centered around 48 cm^{-1} and 81 cm^{-1}. The frequency difference 48 cm^{-1} may be link to the Raman modes between $v''=0$ and $v'=1$ bands in the ground electronic state in PM650 dye molecules. The vibrational dynamics in CV670 may be linked to the ring-breathing modes and ring-deformation modes of the six-folded ring.
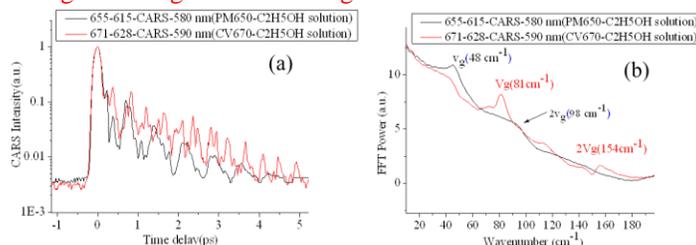

Fig. 3(a). Dependence of femtosecond CARS signals on T_{13} for CV670 and PM650 in ethanol solution;
Fig.3(b) The FFT power spectra of the CARS signal from Fig. 3(a).

The vibrational dynamics between the excited Raman transitions in organic molecules can be detected and investigated by simply changing wavelengths of pump or Stokes pulses. The three vibrational modes of ethanol are around 2973, 2927, and 2878 cm^{-1}. We observe a strong Raman vibrational mode with a wavenumber difference of about 46 cm^{-1} and 49 cm^{-1} in ethanol solution by varying wavelengths of the laser pulses.

In conclusion, the ultrafast vibrational dynamics in BBO crystal, ethanol, and dye were investigated by femtosecond time-resolved CARS. The vibrational modes can be changed by geometrical configuration and the polarization of pump pulses, varying the pulse sequence and wavelengths of the laser pulses.

Acknowledgements:

References
1.   A. Materny, T. Chen, M. Schmitt, T. Siebert, A. Vierheilig, V. Engel, and W. Kiefer, "Wave packet dynamics in different electronic states investigated by femtosecond time-resolved four-wave-mixing spectroscopy," Applied Physics B: Lasers and Optics **71**, 299-317 (2000)
2.   Y. Xia, Y. Zhao, Z. Wang, S. Zhang, Z. Dong, D. Chen, and Z. Zhang, "Investigation of vibrational characteristics in BBO crystals by femtosecond CARS," Optics & Laser Technology **44**, 2049-2052 (2012).
3.   D. Chen, P. He, R. Fan, Y. Xia, X. Yu, J. Wang, and Y. Jiang, "Femtosecond time-resolved ERE-CARS of CV670 dye in solutions," The Journal of Physical Chemistry C **116**, 5881-5886 (2012).
4.   P. He, R. Fan, D. Chen, X. Li, Y. Xia, X. Yu, J. Wang, and Y. Jiang, "Femtosecond time-resolved ERE-CARS of PM650," Opt Commun **285**, 3284-3288 (2012).