Coherent coupling between vibrational modes of C–H bonds at different positions studied by femtosecond time-resolved coherent anti-Stokes Raman scattering*

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(Received 14 September 2011; revised manuscript received 11 October 2011)

We performed femtosecond time-resolved coherent anti-Stokes Raman scattering (fs-CARS) measurements on liquid toluene and PVK film. For both samples, we selectively excited the CH stretching vibrational modes and observed the expected quantum beat signals. The frequency of the well-defined beats is in good agreement with the energy difference between the two simultaneously excited modes, which demonstrates that a coherent coupling between the vibrational modes of the C–H chemical bonds exists at the different positions of the molecules. The dephasing times of the excited modes are obtained simultaneously.

Keywords: femtosecond time-resolved coherent anti-Stokes Raman scattering, coherent coupling, quantum beat

PACS: 42.65.Dr, 42.50.Md, 78.47.J–, 78.47.je **DOI:** 10.1088/1674-1056/21/3/034210

1. Introduction

The femtosecond time-resolved coherent anti-Stokes Raman scattering (fs-CARS) technique has been successfully applied to gain information about the dynamics properties of molecules in the ultrafast time regime.[1−8] It has proved to be a valuable tool to study the dynamics of molecular systems both in the electronic ground state and the excited state. Time-resolved CARS is a third-order nonlinear process. Firstly, two synchronous laser pulses, with frequencies $\omega_{\rm p}$ and $\omega_{\rm s}$ and wave vectors $k_{\rm p}$ and $k_{\rm s}$, referred to as pump and Stokes pulses, respectively, interact with the sample, and the frequency difference between the two pulses is chosen to match frequency ω_0 of the Raman active vibrational mode of the molecule. The vibrational mode is coherently excited. Subsequently, the vibrational coherence is probed by the time-delayed third probe pulse with frequency $\omega_{\rm pr}$ and wave vector $\boldsymbol{k}_{\rm pr}$, giving rise to the CARS signal with frequency $\omega_{\rm c} = \omega_{\rm p} - \omega_{\rm s} + \omega_{\rm pr}$ and wave vector $\boldsymbol{k}_{\rm c} = \boldsymbol{k}_{\rm p} - \boldsymbol{k}_{\rm s} + \boldsymbol{k}_{\rm pr}$. The signal is recorded as a function of the delay time between the probe pulse and the pump/Stokes pulse pair.

The large spectral bandwidth of the femtosecond laser pulse may cause a simultaneous coherent excitation of two or more neighboring vibrational modes.[9] Therefore, quantum beat phenomena on the terahertz frequency scale are often observed in fs-CARS experiments.[2−4,10] In most cases, the quantum beats originate from the interference between the different vibrational modes of the same chemical bond. However, it is not very clear whether there is a coherent coupling between the vibrational modes of the same kinds of chemical bonds at different positions in the molecules. In the fs-CARS process, since each excited vibrational mode irradiates an electromagnetic field, the sum of these fields consists of a coherent sum of the induced polarizations of all the components. This opens the possibility to observe the quantum beats between the vibrational modes of the same kinds of chemical bonds at different positions.

Toluene ($C_6H_5CH_3$) is one of the simplest organic compounds and is important because of its wide use as a solvent and an industrial feedstock. Neat toluene is usually used as a preliminary sample due

*Project supported by the National Natural Science Foundation of China (Grant Nos. 20573028 and 20973050).

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to its relatively simple Raman spectrum, as well as its use for Raman spectroscopic calibration. Poly (N-vinylcarbazole) (PVK), a typical organic semiconducting polymer, has been widely used in various optoelectronic devices.[11,12] For toluene and PVK, the C–H bond is an essential part of their molecular structures and is crucial for their properties. In both molecules, there are two neighboring CH stretching modes originating from the vibrations of the C–H bonds at different positions, which makes them suitable for the study of coherent coupling between the vibrational modes of the same kinds of chemical bonds at different positions.

In this study, we use the ultrabroadband white-light continuum (WLC) for the Stokes pulse. Due to the temporal chirp characteristics of the WLC, no complicated laser system is required for tuning the wavelength of the Stokes pulse. We have achieved the selective excitation and probe of the CH stretching vibrational modes near 3000 cm^{-1}. In the fs-CARS signals of both liquid toluene and PVK film samples, we observed clear quantum beats, which demonstrates that a coherent coupling exists between the vibrational modes of the C–H chemical bonds at different positions of the molecules. The dephasing times of the excited modes are then obtained. This work has provided meaningful information about dynamic molecular processes and opened up new possibilities for investigating many interesting aspects of molecular dynamics.

2. Experiment

A schematic diagram of our experimental setup is shown in Fig. 1(a). A Ti:sapphire laser system (Spectra-Physics) is used to create the femtosecond pulse. The duration, repetition rate, center wavelength and single pulse energy of the pulse are 110 fs, 1 kHz, 800 nm and 500 μJ, respectively. By employing two beam splitters (BS), the laser pulse is divided into three parts. Two of them are used as the pump and the probe pulses, and the third one is focused onto a 4 mm thick Al_2O_3 crystal to produce the WLC used for the Stokes pulse. The Stokes pulse defines an arbitrary time zero point. Two delay lines are used, one to produce the temporal overlap of the pump and the Stokes pulses, and the other to provide the variable time delay for the probe pulse. The WLC has an ultrabroadband spectral profile, ranging from 300 to 1100 nm. Based on the chirp characteristics of the WLC, the frequency difference between the pump and the Stokes pulses can be tuned by changing the delay time between the pump and the WLC pulses. Therefore, we can selectively excite the CH stretching vibrational modes without a complicated laser system. The energy level diagram shown in Fig. 1(b) describes the CARS process for the case where two vibrational modes are excited simultaneously. The beam geometry is in the folded BOXCARS configuration (Fig. 1(c)), which satisfies the phase matching condition. The detection setup consists of a spectrometer (Optice 250 IS/SM, Bruker) and an intensified charge coupled device (ICCD) detector (IStar 740, Andor).

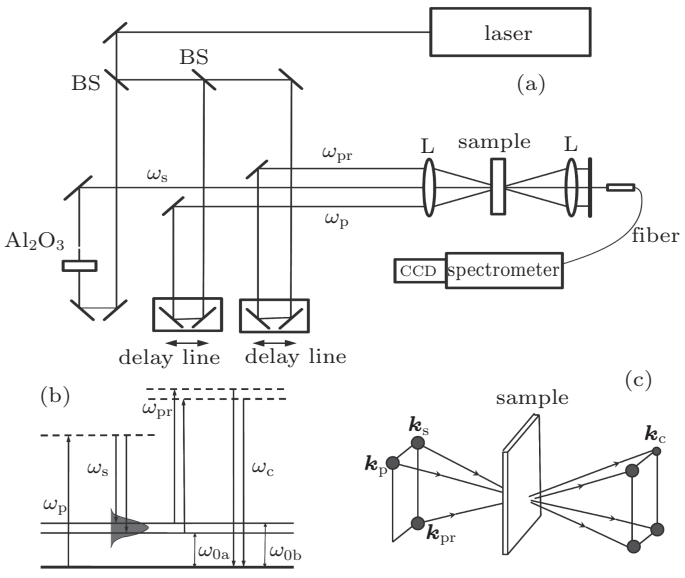


Fig. 1. (a) The experimental setup of the fs-CARS, (b) an energy level diagram, and (c) a folded BOXCARS configuration.

The liquid toluene used in the experiment is purchased and used without dilution or further purification, and its purity is 99.9%. The sample is contained in a 1 mm thick quartz cell. The PVK film with a thickness of $\sim$ 1 μm is fabricated on the glass substrate by the spin coating method, and after drying the film in air at room temperature for several hours, the solvent is volatilized.

3. Results and discussion

The time-integrated CARS signal intensity is recorded as a function of the delay time τ between the probe pulse and the pump/Stokes pulse pair[13]

$$I_{\rm c}(\tau) \propto \int_{-\infty}^{+\infty} |P_{\rm c}^{(3)}(\tau, t)|^2 {\rm d}t. \quad (1)$$

The CARS signal generated from the nonlinear polarization $P_{\rm c}^{(3)}$ can be separated into two parts, a nonresonant part due to the response of the electronic system and a resonant part due to the contribution of the excited coherent vibrations.[13] Correspondingly, the transient fs-CARS signal consists of an initial fast decay that originates from the electronic contribution and follows the instrumental response, and a subsequent slow decay that results from the response of the excited vibrational modes and provides valuable information on the dynamic properties of the modes. If only one mode is excited, the fs-CARS signal will show a single unmodulated exponential decay. If two or more modes are excited simultaneously, the quantum beats arising from the interference of the excited different modes can be observed. By changing the time delay of the probe pulse, we can eliminate the contribution from the strong nonresonant signal and monitor the vibrational coherence dynamics in real time.

Toluene is a mono-substituted benzene derivative, where a single hydrogen atom in the benzene molecule has been replaced by a methyl (CH_3) group. There are two CH stretching vibrational modes at the frequencies of 3058 and 2920 cm^{-1}. They are assigned to aromatic and methyl CH stretching vibrations, respectively.[14] The detection wavenumber of the CARS signal is set at 2990 cm^{-1}, which corresponds to the average arithmetic wavenumber of the two CH stretching modes. According to the energy conservation, only the near-infrared part of the WLC is used as the Stokes pulse. In the fs-CARS signal, the nonresonant part does not provide any information on the vibrational modes. It has to be separated from the resonant signal. Therefore, we analyze the signal with a delay time longer than 200 fs (shown in Fig. 2). The signal shows well-defined quantum beats with a fixed period, which indicates that two vibrational modes are excited simultaneously.

For the case of two excited modes, the delay time dependence of the CARS signal is fitted with the following function:[4]

$$I_{\rm c}(\tau) \propto |A\exp(-\tau/T_{2,{\rm a}}) + B\exp(-\tau/T_{2,{\rm b}} + {\rm i}\,\Delta\omega\tau + {\rm i}\,\Delta\phi)|^2 + C, \quad (2)$$

where $T_{2,{\rm a}}$ and $T_{2,{\rm b}}$ represent the dephasing times of the two modes, respectively, $\Delta\omega$ and $\Delta\phi$ are the frequency difference and the phase shift at $\tau = 0$ between the modes, respectively, A and B are the constants defined by the transition strengths and the experimental conditions, and C is the constant used to describe the background in the signal.

According to the fitting, $\Delta\omega$ is 138 cm^{-1}, which exactly coincides with the frequency difference of the aromatic and methyl CH stretching vibrational modes. We confirm that the two modes are coherently excited at the same time, and that the beat signal is ascribed to the interference between them. The obtained dephasing times are $T_{2,{\rm a}} = 1830$ fs and $T_{2,{\rm b}} = 1000$ fs. According to the intensities and linewidths of the Raman peaks, as well as the ratio of A to B, we are able to assign the longer dephasing time to the methyl CH stretching mode and the shorter one to the aromatic CH stretching mode.

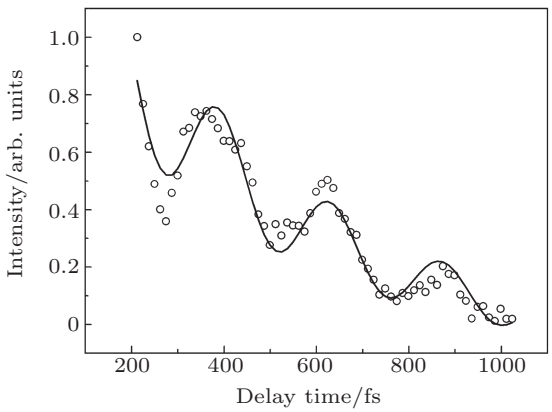


Fig. 2. The fs-CARS signal of liquid toluene for a probe pulse delay time longer than 200 fs. The open circles show the experimental data and the solid line gives the fitting curve.

The molecular structure of PVK is shown in Fig. 3. It is constituted of a linear chain of repeated $(CH_2–CH)_n$ groups, with the pendant carbazole side groups linked directly to the main chain. There are two CH stretching modes located at 3055 cm^{-1} and 2938 cm^{-1}. They are assigned to the aromatic CH

stretching vibration of the carbazole pendant groups and the CH_2 antisymmetric stretching vibration of the main chain, respectively.[15,16] Similar to the case of the toluene sample, the detection wavenumber of the CARS signal is set at 3000 cm^{-1}, and we analyze the transient signal of the PVK film with a delay time longer than 200 fs (shown in Fig. 4). The signal also shows clear quantum beats with a fixed period. The experimental data are fitted using formula (2), and the value of $\Delta\omega$ obtained is 110 cm^{-1}, which agrees very well with the frequency difference of aromatic CH stretching and the CH_2 antisymmetric stretching modes. We confirm that the two modes are coherently excited at the same time, and that the beat signal is ascribed to their interference. The dephasing times are $T_{2,a} = 1350$ fs and $T_{2,b} = 990$ fs. According to the intensities and the linewidths of the Raman peaks, as well as the ratio of A to B, we are able to assign the longer dephasing time to the CH_2 antisymmetric stretching mode and the shorter one to the aromatic CH stretching mode.

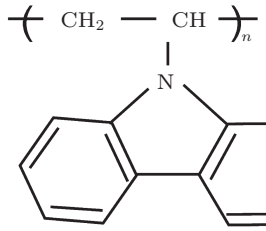


Fig. 3. The molecular structure of PVK.

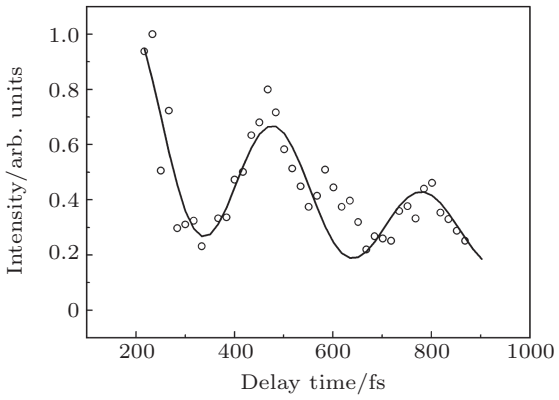


Fig. 4. A PVK film fs-CARS signal for a probe pulse delay time longer than 200 fs. The open circles show the experimental data and the solid line gives the fitting curve.

The fs-CARS experiments for liquid toluene and PVK film are performed under the same experimental conditions, and the aromatic CH stretching vibrational modes of the two samples display almost the same dephasing time.

4. Conclusion

In conclusion, we have demonstrated that a coherent coupling exists between the vibrational modes of the C–H chemical bonds at different positions in liquid toluene and PVK film by using the fs-CARS technique. Ultrabroadband WLC is used for the Stokes pulse. Owing to the chirp structure of the WLC, no complicated laser system is required for tuning the wavelength of the Stokes pulse, and we have achieved the selective excitation of the vibrational modes. In the fs-CARS signals of both samples, clear quantum beats are observed. The frequency of the beating pattern agrees very well with the energy difference between the simultaneously excited modes, and the dephasing times of the vibrational modes are obtained. This work has provided very valuable information on molecular dynamics, and is significant for the further study of molecular dynamic processes.

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