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Ultrafast multiplex CARS investigation of vibrational characteristics in chloroform and PMMA*

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This paper demonstrates the femtosecond time-resolved coherent anti-Stokes Raman scattering by using folded BOXCARS geometry where an ultrashort broadband coherent white light continuum was used as Stokes pulse, and carries out the non-contact detection at long distance. The CARS signal is so easy to be detected that it can be seen even by nude eye. The C–H bonds of chloroform or PMMA were detected and the vibration modes belonging to the side chain and the main chain in PMMA were also compared. Their vibrational characteristics involved decay process and quantum beating were discussed. This modified CARS experimental technique could make up the deficiency of traditional CARS technique.

Keywords: femtosecond, ultrafast, CARS, vibrational characteristics
PACC: 3310G, 3300, 3310, 3320F

1. Introduction

Femtosecond time-resolved CARS[1−4] technique has been extensively used in the investigation of the vibrational dynamic mechanism,[5,6] intramolecular energy migration process,[7] coherent control,[8] vibrational spectroscopy imaging,[9] and chemical reaction channels,[10] etc. Comparing with spontaneous Raman technique, we find that CARS signal level may exceed by a factor of 10^4-10^5.[3] The CARS technique is allowed to detect the signal far away from the sample, and it yields excellent signal-noise rate over fluorescence or thermal luminous background which may be extensively used in flames, discharges, or chemiluminescent samples.[3,11,12] Due to its extensive application in the domain of spectroscopy, it has attracted more and more attention. Its experimental setup is very complex, since it needs two colour pulses which are often supplied by two synchronous laser systems or optical parametric amplifiers.[7] People always try to simplify it and improve this technique in order to obtain more information on spectroscopy. In recent years, people have got much improvement[13,14] and have carried out the multiplex CARS technique, where an ultrashort broadband coherent white light continuum (WLC) was used as Stokes pulse, in the vibrational imaging domain.[4,15] In order to satisfy the phase matching, its experimental setup needs pulses arranged collinearly and tightly focalized by a short-focus microscope objective. Meanwhile, the CARS signal has to be separated from lasers pulses by spectral filters. Although this design is convenient for imaging, it also limits the application of the multiplex CARS in the domain of spectroscopy at the same time.

Here, we use the broadband coherent WLC as the Stokes pulse to perform time-resolved multiplex CARS measurement in the BOXCARS geometry for study of the chloroform and PMMA. They are common materials acting as the solvent and host polymer in industry and scientific research, which are used to disperse the sample. The vibrational characteristics of their C–H bonds on the electronic ground state have been detected, and the involved decay process and quantum beating were discussed. In addition, the vibration modes of C–H bonds belonging to the side chain and the main chain in PMMA were also compared. Understanding the vibration characteristic of them is useful to investigate the solute molecule and doped molecules, since their physical and chemical properties[16] are always influenced by the molecular motion of solvent and host molecule. All the re-

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sult suggests that the time-resolved multiplex CARS technique established here can be used in many areas of spectroscopy for study of the characteristics of molecule.

2. Experiment

Figure 1(a) shows a schematic diagram of the experimental setup. The laser pulse with 500 μJ is generated from a regenerative amplifier (1 kHz, Spectra-Physics, Spitfire) at 810 nm with full width at half maximum about 110 fs. The laser pulses are divided into three pulses, the Pu1 pulse, Pu2 pulse, and the third pulse by two beam splitters (BS). The third one focuses to a 1 mm Al_2O_3 crystal plate to produce a WLC pulse which is used as the Stokes pulse. Figure 1(b) shows that the Pu1, Pu2 and Stokes pulses are arranged in the folded BOXCARS configuration.

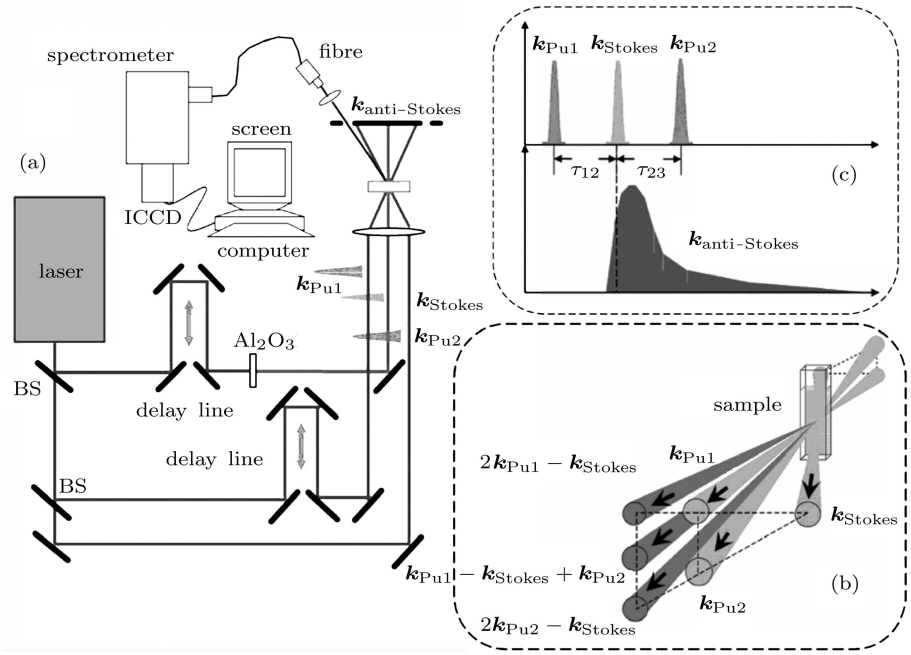


Fig.1. Experimental setup of the multiplex CARS. (b) The pulse configuration in the experiment. Three laser pulses with wave vectors: $\boldsymbol{k}_{\rm Pu1}$, $\boldsymbol{k}_{\rm Pu2}$, and $\boldsymbol{k}_{\rm Stokes}$ are focused in a right-angle triangular geometry into the sample. The CARS signals are in the phase matched directions of $2\boldsymbol{k}_{\rm Pu1}-\boldsymbol{k}_{\rm Stokes}$, $\boldsymbol{k}_{\rm Pu1}-\boldsymbol{k}_{\rm Stokes}+\boldsymbol{k}_{\rm Pu2}$, $2\boldsymbol{k}_{\rm Pu2}-\boldsymbol{k}_{\rm Stokes}$. (c) The time sequences of the pulse in the CARS experiment where the delay time between the three laser pulses are τ_{12} and τ_{23}.

The angles among them are less than 5 degree that makes the phase matching to be satisfied easily. A long-focus lens is used to focus the laser pulses. The pulse power of the Pu1 and Pu2 pulse ranges from 1 to 10 μJ and that of Stokes pulse is $\sim$1 μJ. The CARS signal was collected in the directions of $\boldsymbol{k}_{\rm s} = \boldsymbol{k}_{\rm Pu1} - \boldsymbol{k}_{\rm Stokes} + \boldsymbol{k}_{\rm Pu2}$, spatially isolated by irises, collected by the silica fibre, dispersed in the spectrometer (Bruker Optics 250 IS/SM) with spectral resolution about 0.1 nm and detected by an intensified CCD detector (IStar740, Andor). The timing orders among pulses can be tuned by means of Michelson-interferometer arrangements, which allow optical delays up to 333 ps with a minimal step size of 4.16 fs, and are controlled by a personal computer. Figure 1(c) shows that two delay times are involved: τ_{12} and τ_{23}. The former is the delay time between the Pu1 and Stokes pulse and the latter is that between the Stokes and Pu2 pulse. The position of Stokes pulse defines the temporal zero point in the experiment. The WLC spectrum is detected by spectrometer (Ocean Optics 2000) with a resolution of 2.0 nm in the range of 300 to 1100 nm and presented in Fig.2. In the experiment, the infrared component of WLC near the 1050 nm is used as Stokes light, which can make the frequency difference (FD) between $\omega_{\rm Pu1}$ and $\omega_{\rm S}$ to be automat-

ically resonant to the vibration Raman transition of sample. The vibration modes near the $3000\,\mathrm{cm}^{-1}$ are coherently excited.

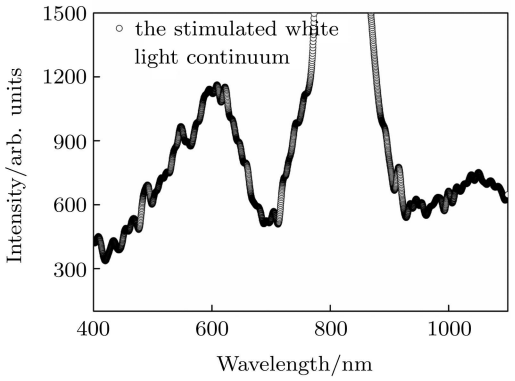


Fig.2. The spectral profile of the stimulated white light continuum and the 810 nm peak generated from a normal Al_2O_3 crystal. According to the Raman resonance, the range of detection is about $3000\,\mathrm{cm}^{-1}$.

The investigated materials are purchased and used without further purification. The chloroform is contained in a 1 mm thick quartz cell, its purity is 99.9% and the PMMA is prepared as a film by spin coating on normal glass substrate.

3. Result and discussion

Figure 3 shows the CARS signals of chloroform emitted in the phase-matching directions of $2\boldsymbol{k}_{\mathrm{Pu1}} - \boldsymbol{k}_{\mathrm{Stokes}}$, $\boldsymbol{k}_{\mathrm{Pu1}} - \boldsymbol{k}_{\mathrm{Stokes}} + \boldsymbol{k}_{\mathrm{Pu2}}$ and $2\boldsymbol{k}_{\mathrm{Pu2}} - \boldsymbol{k}_{\mathrm{Stokes}}$. Apparently, with the light of the folded BOXCARS configuration, the CARS signals are spatially separated from the three excitation beams $\boldsymbol{k}_{\mathrm{Pu1}}$, $\boldsymbol{k}_{\mathrm{Stokes}}$, $\boldsymbol{k}_{\mathrm{Pu2}}$

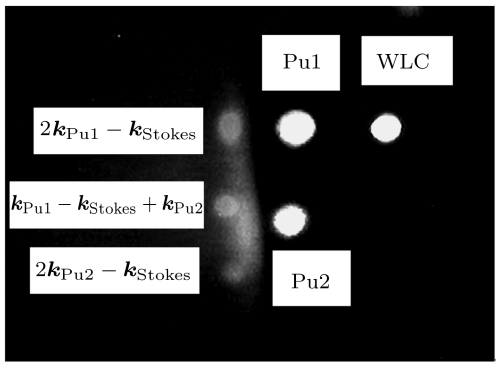


Fig.3. Three-pulse CARS signals in the phase matching directions $2\boldsymbol{k}_{\mathrm{Pu1}} - \boldsymbol{k}_{\mathrm{Stokes}}$, $\boldsymbol{k}_{\mathrm{Pu1}} - \boldsymbol{k}_{\mathrm{Stokes}} + \boldsymbol{k}_{\mathrm{Pu2}}$ and $2\boldsymbol{k}_{\mathrm{Pu2}} - \boldsymbol{k}_{\mathrm{Stokes}}$ for chloroform. In order to enhance the contrast, a filter is placed in the direction of incident pulses to weaken the intensity of the incident pulses ($\boldsymbol{k}_{\mathrm{Pu1}}$, $\boldsymbol{k}_{\mathrm{Pu2}}$, and $\boldsymbol{k}_{\mathrm{Stokes}}$).

and thus can be detected free from background light. Due to application of the long-focus lens, it is able to carry out the non-contact detection at long distance[17] and the signal may be collected by detector far away from the sample. This makes it useful even in domain of the inflammation diagnosis and gas detection, etc.

As shown in Fig.4, in the CARS process the Pu1 and Stokes pulses create a wavepacket of vibrational modes in the electronic ground state and establish a definite phase relationship (coherence) between these vibrational modes. Since the WLC pulse is much broad, multiple modes may be excited through Raman resonance. With the introduction of the Pu2 pulse, the dynamics of multiple excited vibrational modes can be obtained.

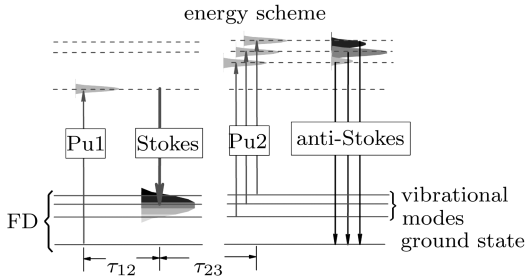


Fig.4. The schematic diagram of the energy levels and the vibrational modes in the ground state. The time ordering between the fields is defined by the two times τ_{12} and τ_{23}.

Figure 5 shows the three-dimensional and contour plots of the CARS signal of PMMA and chloroform in the phase matching direction of $\boldsymbol{k}_{\mathrm{Pu1}} - \boldsymbol{k}_{\mathrm{Stokes}} + \boldsymbol{k}_{\mathrm{Pu2}}$ versus τ_{23}, when $\tau_{12} = 0\,\mathrm{fs}$. Apparently, multiple vibrational modes of C–H bonds in PMMA have been detected as mentioned above. As noted, it can be observed from the contour map that the dynamic curves of these modes do not rise at the same time and have some difference. It results from the slight chirping of the femtosecond pulses and it commonly occurs in the laboratory.[18] Here multiple vibrational modes were detected simultaneously and the quantum beating was also observed clearly. In order to determine the multiple modes in the CARS signal of PMMA and chloroform, its transient spectrum was presented in the Fig.6. They are the projection of signals in the frequency domain, so that this may overcome the chirping effect of femtosecond pulse. There are four peaks and all of them are labelled with v_i according to their energy levels in the vibrational manifold (their positions in the spectra).

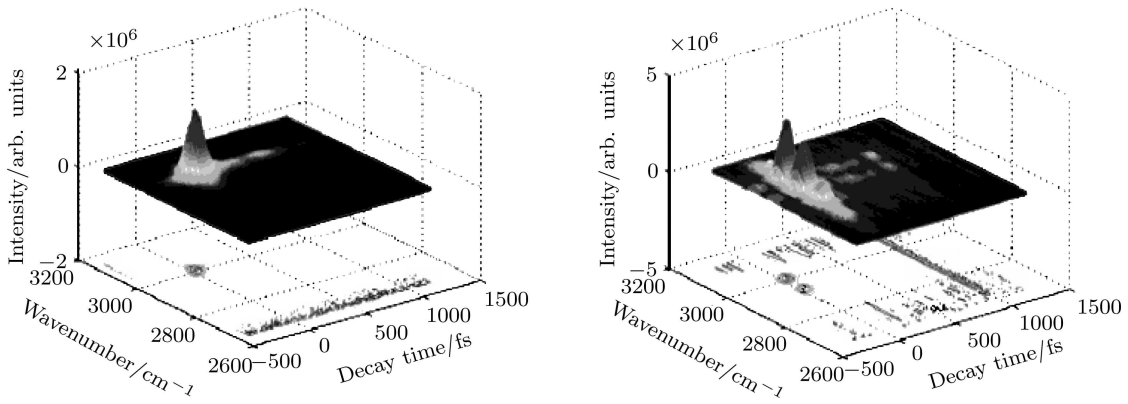


Fig.5. The three-dimensional and contour plot of CARS spectra of PMMA and chloroform in the phase matching direction of $\boldsymbol{k}_{\mathrm{Pu1}} - \boldsymbol{k}_{\mathrm{Stokes}} + \boldsymbol{k}_{\mathrm{Pu2}}$.

We determine the motion of the modes appearing in Fig.6 according to the calculation by Gaussian 98 and their energy levels in the vibrational manifold, and the results are summarized in Table 1. The mode v_4 is at 3064 cm^{-1} and represents the symmetry stretching vibration of C–H bonds in the group of '–O–CH_3', so it is the highest mode among them in the vibrational manifold. The mode v_1 is at 2870 cm^{-1} and reflects the stretching vibration of C–H bonds in the group of '–CH_2–' which is the lowest one in the spectrum. Apparently, for the same type of vibrational modes, the vibrational frequency of bonds in the side chain is higher than that in the main chain.

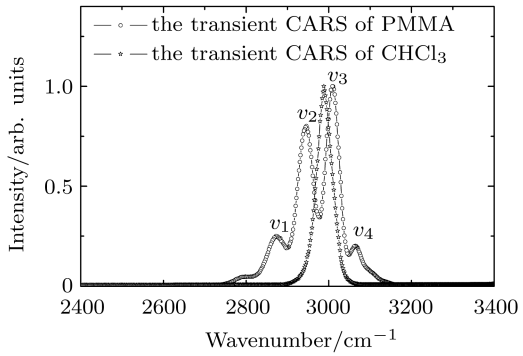


Fig.6. The transient CARS spectra of PMMA and chloroform. The corresponding modes in PMMA are labelled as v_i according to their energy level in the vibrational manifold.

Table 1. The number of modes, their position in the spectrum and the corresponding molecule motion.

Number	Wavenumber/ cm^{-1}	The vibration mode of C–H
v_4	3064	The symmetry stretching vibration in the group of –O–CH_3
v_3	3008	The in-symmetry stretching vibration in the group of –O–CH_3
v_2	2945	The stretching vibration in the group of –C–CH_3
v_1	2870	The stretching vibration in the group of –CH_2–

Figure 7 shows the decay curves of vibrational modes for PMMA and chloroform. There is quantum beating signal in the decay curve which has been initially observed in Fig.5. The quantum beats with period times at ∼200 fs are both observed in the dynamic process of modes in PMMA and chloroform which may be ascribed to the interference among the CARS polarization fields generated from different vibrational modes.[4] In the two-mode approximation, the periods of the quantum beating due to vibrational modes are calculated and the results are similar to that observed in our experiment. In addition, due to limitation of experimental condition, the differences among these periods were not detected, so the periods in Fig.7 are similar to each other.

All the dynamic curves may be fitted with a bi-exponential function. In Fig.7, these curves have been chirpily corrected. Generally speaking, the fast time component reflects the dephasing process and the slow one is originated from the population relaxation

process.[7] The corresponding formula is

$$I(t) = [A\exp(-t/\tau_{\rm de}) + B\exp(-t/\tau_{\rm po})] * G(t), \quad (1)$$

where $G(t)$, *, $\tau_{\rm de}$, $\tau_{\rm po}$, A, and B represent the instrumental function, the convolution integral operator, dephasing time, population relaxation time, and the corresponding percentages, respectively. A biexponential fit of the trace of chloroform indicates lifetimes of a 96.3 fs and 940.2 fs, and the fitted results of PMMA are summarized in Table 2.

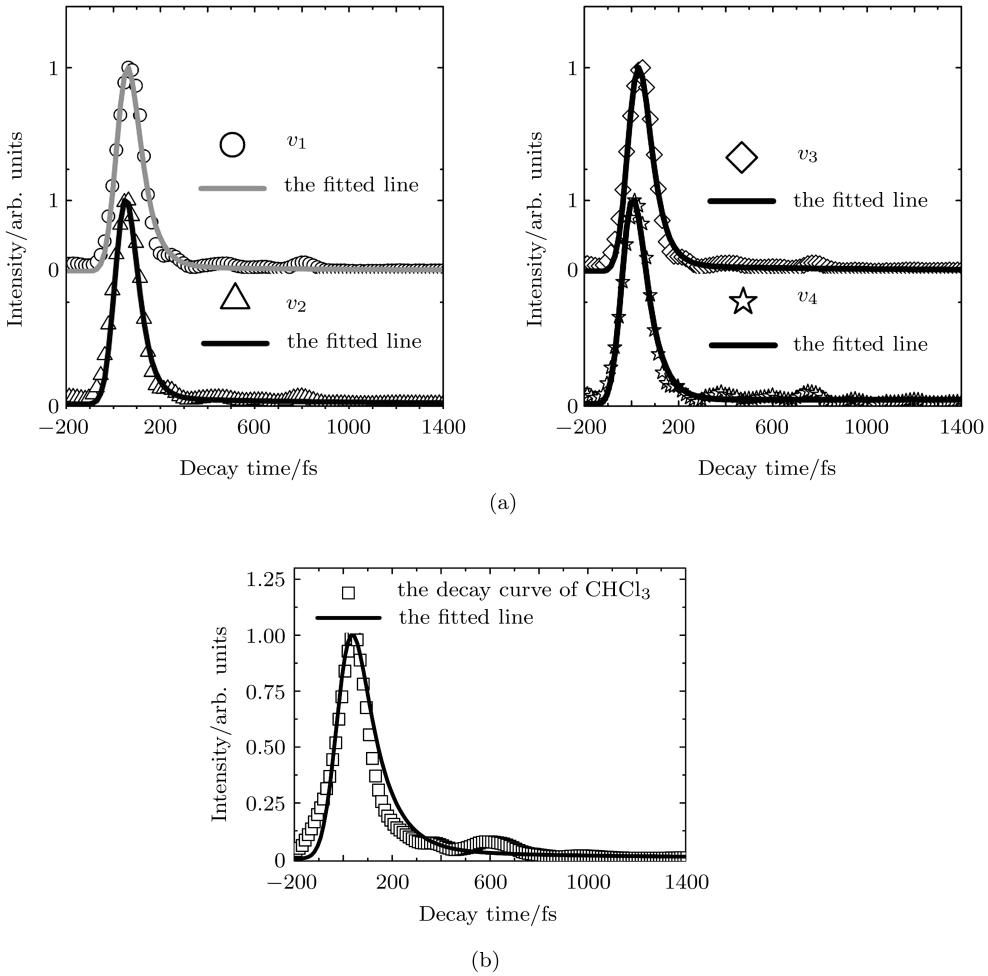


Fig.7. (a) The dynamic curves and the corresponding fitted lines of the modes in PMMA. (b) The decay curve and the fitted line of $CHCl_3$.

Table 2. The fitted results of all the decay curves. The dynamic process is fitted by biexponential fit convoluted with a Gaussian instrumental response.

Wavenumber/ cm^{-1}	Dephasing time/fs	Population relaxation time/fs
3064	59	2742
3008	56	1184
2945	47	782
2870	51	1130

Upon illustration, it is found that the intensities of CARS signal of C–H vibrational modes all decay very quickly in the initial time of about 400 fs and relax to zero in 1.2 ps after excitation. It is expected that the vibrational modes in the electronic ground state is so easily influenced by the thermal bath in the surrounding environment that their dephasing processes decay very fast. For the C–H modes in the electronic ground state,

all of the dynamic processes are likely to follow this tendency, since the kinetic trace of C–H mode in chloroform is very similar to those of PMMA. As seen in Table 2, the dephasing time (59 fs and 56 fs) and the population relaxation time (2742 fs and 1184 fs) of C–H modes in the group of '–O–CH_3' are longer than those (47 fs, 51 fs and 782 fs, 1130 fs) of C–H modes around the main chain.

Actually, the vibrational modes of C–H bonds in different parts of PMMA may be influenced by the main chain (C–C bonds) and the intensity may weaken with the distance between the probed bonds and the increase of main chain. Since '–O–CH_3' group is far away from the main chain in comparison with the '–C–CH_3' and '–CH_2–' groups, the influence originating from the atoms of main chain may be not very strong. As a result the dephasing time and the population relaxation time of C–H modes in the side chain become longer.

The experimental data suggest that the relaxation processes of vibrational modes of C–H bonds are similar to each other. Comparing with vibrational modes of C–H bonds in chloroform and PMMA, we find that the intensities all decay very fast and their dephasing times are less than one hundred femtoseconds. It suggests that all the vibrational modes of C–H bonds in the electronic ground state may be easily influenced by the thermal bath in the surrounding environment, even though these C–H bonds are in the different molecules. However, due to the difference of molecules, their relaxation processes still have a little change.

4. Conclusion

We have investigated the multiplex fs-CARS with WLC and applied it to the study of the characteristic of C–H vibrational modes of PMMA and chloroform involving the relaxation process, and the quantum beating, etc. All the results may be useful to facilitate the investigation on the properties of solute molecule in chloroform or doped molecule in PMMA as mentioned above. In addition, the experimental setup has been simplified very much, meanwhile it is still able to probe the multiple vibrational modes simultaneously which may offer much more information for the investigation on the spectroscopy. This modified CARS experimental technique could make up the deficiency of traditional CARS technique in other domain.

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