Simultaneous measurements of global vibrational spectra and dephasing times of molecular vibrational modes by broadband time-resolved coherent anti-Stokes Raman scattering spectrography*

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In broadband coherent anti-Stokes Raman scattering (CARS) spectroscopy with supercontinuum (SC), the simultaneously detectable spectral coverage is limited by the spectral continuity and the simultaneity of various spectral components of SC in an enough bandwidth. By numerical simulations, the optimal experimental conditions for improving the SC are obtained. The broadband time-resolved CARS spectrography based on the SC with required temporal and spectral distributions is realised. The global molecular vibrational spectrum with well suppressed nonresonant background noise can be obtained in a single measurement. At the same time, the measurements of dephasing times of various molecular vibrational modes can be conveniently achieved from intensities of a sequence of time-resolved CARS signals. It will be more helpful to provide a complete picture of molecular vibrations, and to exhibit a potential to understand not only both the solvent dynamics and the solute-solvent interactions, but also the mechanisms of chemical reactions in the fields of biology, chemistry and material science.

Keywords: coherent anti-Stokes Raman scattering, photonic crystal fibre, supercontinuum, molecular vibrational spectrum, dephasing time, time-resolved measurement

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1. Introduction

Compared with other kinds of coherent anti-Stokes Raman scattering (CARS) techniques, the time-resolved CARS technique (T-CARS)[1] can provide a complete picture of molecule, not only the vibrational spectra reflecting the molecular structure and compositions, but also the dephasing time of various molecular vibrational modes reflecting the molecular response to the external micro-environment, which is especially favourable for the study of interactions between molecules and their micro-environment such as solute-solvent interactions,[2,3] molecular dynamics,[4−8] supramolecular structures[9] and excess energy dissipations in the fields of biology, chemistry and material science.[10−13] However, the traditional T-CARS can give only the dephasing times of a few particular molecular vibrational modes once because of the limitation of line-width of laser pulse. It is not adequate and efficient for the study of complicated interaction processes between molecules. With the advent and the progress of supercontinuum (SC) generated by photonic crystal fibre (PCF) pumping with ultrashort laser pulses,[14] the broadband T-CARS based on SC has been developed to simultaneously obtain CARS signals corresponding to various molecular vibrational modes in a broader spectral range and their intensity variations with time.[15,16] However, in a broadband T-CARS based on SC, the simultaneously detectable spectral range depends not only on the spectral coverage of SC, but also on the temporal distribution of various spectral components of SC.[17] During our work, in order to ensure the simultaneous measuring of the global molecular vibrational spectra and dephasing times of various molecular vibrational modes, the temporal distribution of various spectral components of SC is optimised by choosing the PCF with an appropriate microstructure and geometrical length, and selecting suitable parameters of the input seed pulse. Compared with the experimental results

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shown in the previous reports, the CARS signals with suppressed NRB noise in a broader spectral range can be detected in a single measurement. At the same time, the dephasing times of various molecular vibrational modes can be simultaneously measured.

2. Theoretical analysis

The CARS is a four-wave mixing process in which a pump pulse (E_p), a Stokes pulse (E_S), and a probe pulse ($E_{p'}$) with central frequencies ω_P, ω_S, and $\omega_{P'}$ respectively interact with molecules of a sample, thereby generating an anti-Stokes field E_{AS} at a frequency of $\omega_{AS} = \omega_P - \omega_S + \omega_{P'}$, which are corresponding to the specific molecular vibrational modes.[18] But, in order to obtain the global molecular vibrational spectra of various molecular vibrational modes, the bandwidth of incident laser pulse used in CARS must be broad enough, or, have to be adjusted frequently. In the broadband T-CARS based on SC, various spectral components in SC are used as the pump pulse and the Stokes pulse with central frequencies ω_{Pi} and ω_{Si} respectively, to simultaneously excite multiple molecular vibrational modes with wavenumber Ω_i. The delayed narrowband probe light with central frequency $\omega_{P'}$ probes these molecular vibrational modes to generate anti-Stokes signals at the blue-shifted frequency $\omega_{ASi} = \omega_{Pi} - \omega_{Si} + \omega_{P'}$ under the phase-matching condition.

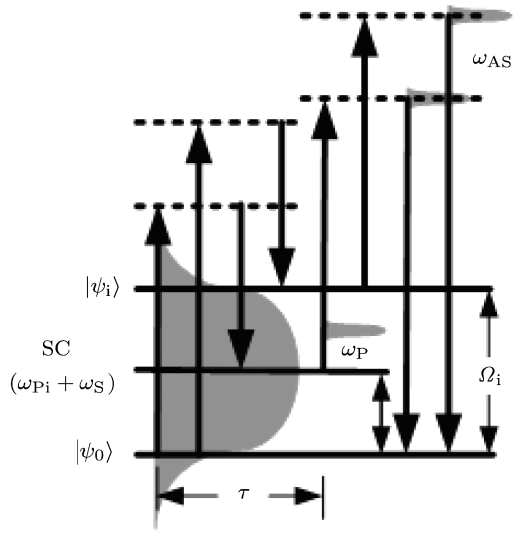


Fig. 1. Energy level diagram of CARS process in the broadband T-CARS.

Only when the frequency differences between the used various spectral components in SC are equal to the vibrational frequencies of various molecular vibrational modes, can the generated anti-Stokes signals be greatly and coherently enhanced. The energy level diagram of the CARS process in the broadband T-CARS is shown in Fig. 1.

Although the PCF can be used for the spectral broadening of low-power ultrashort laser pulses, the SC generally possesses a complex spectral phase that brings about a complicated temporal distribution of various spectral components in SC, referred to as the temporal-spectral structure of SC.[17] Therefore, the simultaneous measurements of the global molecular vibrational spectra and the dephasing times of various molecular vibrational modes with the broadband T-CARS based on SC are dependent not only on the roadwidth of SC but also on the continuity and the simultaneity of various spectral components in SC. As is well known, when a PCF is pumped by incident ultrashort laser pulse, the spectrum broadening and the temporal-spectral structure of SC rely on the properties of PCF, such as the geometric length and structure, and the parameters of the incident seed pulse, such as the peak power, central wavelength, pulse-width, polarisation, and chirping.[19] In order to seek the optimal parameters of the incident seed pulse for our existing PCFs, we carry out some numerical simulations by the split step Fourier method and the frequency-resolved optical gating method to analyse the influences of various parameters on spectrum broadening and temporal-spectral structure of SC. Some typical numerical simulation results are shown in Fig. 2 to reveal the influences of different parameters of seed pulse on SC, where a PCF with a zero-dispersion wavelength (ZDW) of 850 nm and geometric length of 180 mm is pumped by femtosecond laser pulses with a central wavelength of 783 nm, peak power of 20 kW, and pulse duration of 50 fs and 155 fs respectively. As the numerical simulation results show, when the pulse duration of seed pulse is 50 fs, the bandwidth of red-shifted spectral components in SC is not broad enough so as to meet the requirements for the coherent enhancement of all molecular vibrational modes at any delay time. On the contrary, when the pulse duration is 155 fs, the bandwidth, the continuity and the simultaneity of red-shifted spectral components in SC are obviously improved and can basically meet our requirements for SC.

By the above numerical simulations, we have gained the experimental conditions for improving the SC. Under the specific experimental conditions, the spectral broadening and temporal-spectral structure

of SC are codetermined and mutually restricted. In order to meet the requirements of the ultra-broadband T-CARS spectrography for bandwidth and temporal-spectral structure of SC simultaneously, the appropriate PCF and the pumping conditions should be elaborately selected. The central wavelength of the ultrashort laser pulse should be in the normal group velocity dispersion regime of PCF for weakening the influence of soliton-related propagation effects. But it is at the expense of a reduced spectral broadening of SC. In this case, the most direct method of increasing the extent of spectral broadening is to use the ultrashort laser pulse with higher peak power. When the peak power and the central wavelength of incident seed pulse are given, the input energy increases proportionally to the pulse duration. Because the extent of spectral broadening is increased with the pulse duration increasing and the temporal spectral structure becomes worse, the pulse duration about 100–200 fs is appropriate.

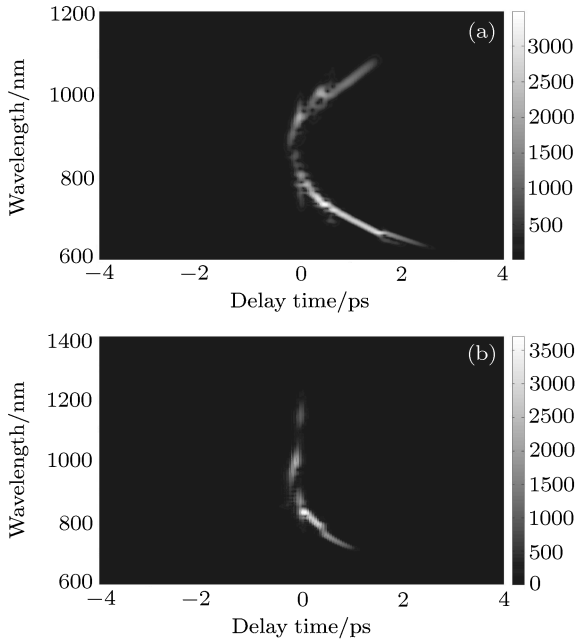


Fig. 2. Numerical simulation results of temporal-spectral structure of SC when using the femtosecond laser pulse with a central wavelength of 783 nm, peak power of 20 kW and pulse-width of 50 fs (a) and 155 fs (b) as seed pulse to pump a PCF with a ZDW of 850 nm and geometrical length of 180 mm.

3. Experimental setup

According to our numerical simulation results of SC, we have developed a broadband T-CARS based on the improved SC for efficiently detecting the global molecular vibrational spectrum and Raman free induction decay (RFID) of all molecular vibrational modes in a single measurement. The schematic of the broadband T-CARS spectrography is shown in Fig. 3. The femtosecond laser pulse with a pulse duration of 120 fs and central wavelength of 783 nm of a mode-locked Ti:sapphire laser oscillator (Mira900, Coherent) is split into two parts by a beam splitter. One beam of laser pulse with a peak power of 20 KW, whose pulse duration is broadened into 155 fs after passing through an optical isolator, is used as the seed pulse that is introduced into a PCF with a 0.68 NA aspherical lens. The geometric length and the ZDW of the PCF are 180 mm and 850 nm respectively. After passing through a long-pass filter with transmitting wavelengths of longer than 810 nm, the residual spectral components of SC are used as the pump and the Stokes light beams. Another beam is used as the probe light after passing through a narrow-band-pass filter with a bandwidth of 0.7 nm centred at 783 nm. Two laser pulse beams are collinearly introduced into a home-made microscope and tightly focused into samples with an achromatic microscopy objective (40×NA 0.75). The generated CARS signals in the forward direction are collected with the same microscope objective, filtered by 775 nm short-pass filters for eliminating the excitation light and auto-fluorescence and detected by a fibre spectrometer with a spectral resolution of 0.27 nm (Avantes, AvaSpec-2048TEC).

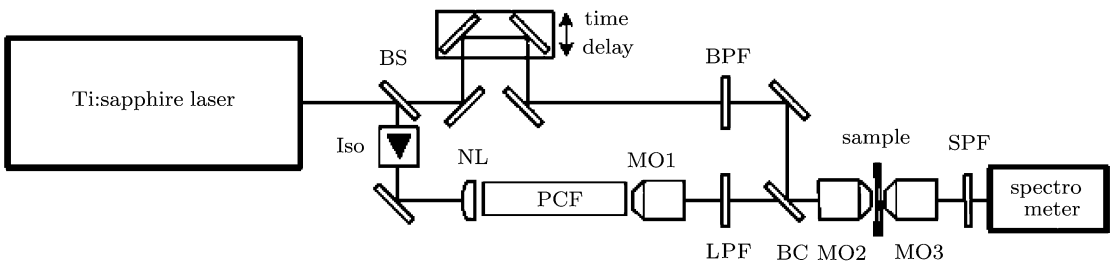


Fig. 3. Schematic of broadband T-CARS system. BS, beam splitter; Iso, optical isolator; NL, non-spherical lens; PCF, photonic crystal fibre; BC, beam combiner; MO1-3, microscopy objective; BPF, narrow-band-pass filter; LPF, long-pass filter; SPF, short-pass filter.

The delay time between SC and probe light can be accurately adjusted by a kit of time delay line. Pure liquid benzonitrile or benzonitrile-methanol-ethanol mixture solution is sandwiched between two cover glasses serving as samples.

4. Experimental results and discussion

In our experiments, the time-resolved measurement is achieved by adjusting the delay time between SC and probe light in steps of 0.12 ps and all the experimental results are obtained at the room temperature. The obtained intensities of CARS spectral signal for pure liquid benzonitrile (mass fraction > 98.5% and density 1.004 g/ml) against time by using our broadband T-CARS system are shown in Fig. 4. From the experimental results, the NRB noise can be effectively suppressed with the delay time increasing. Furthermore, the original CARS spectral profile of benzonitrile in 380–4000 cm^{-1}, when the delay time is 3 ps, is also shown therein. We can see the obvious peaks at wavenumbers of 1016 cm^{-1}, 1190 cm^{-1}, 1608 cm^{-1}, 2248 cm^{-1} and 3090 cm^{-1} corresponding to C–C–C trigonal breathing, C–H in plane bending, C–C in plane stretching, C≡N stretching, and C–H stretching vibrational modes respectively.[20] The molecular vibrational spectrum for pure liquid benzonitrile in the range of 380–4000 cm^{-1} can be simultaneously obtained without any tuning of laser frequency and system, and the spectral resolution, depending on the line-width of the probe pulse and spectral resolution of the spectrometer, is 14 cm^{-1}.

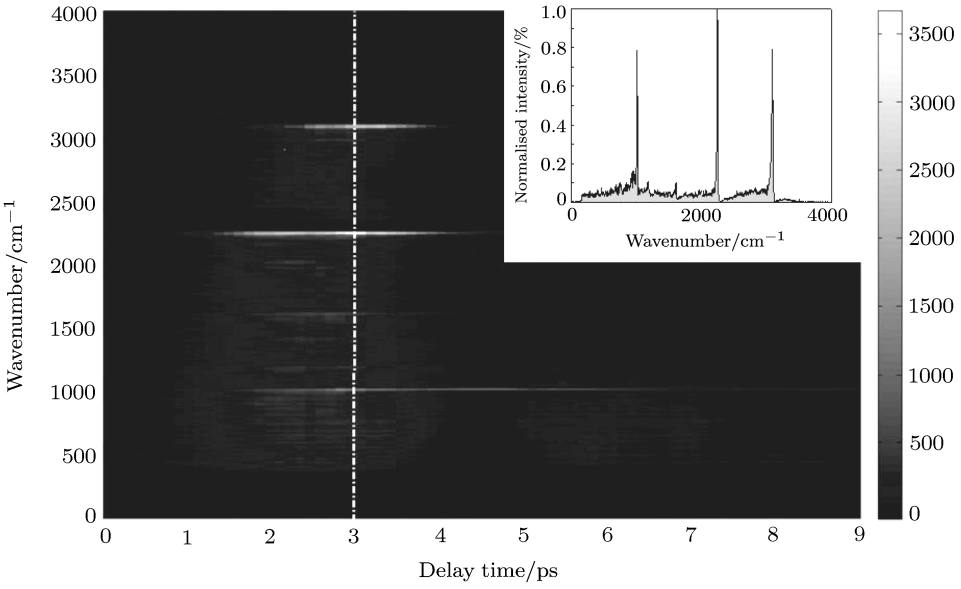


Fig. 4. Intensities of CARS spectral signals for benzonitrile versus delay time and the CARS spectrum with a delay time of 3 ps detected by our broadband T-CARS system.

By extracting the time evolution of CARS signals corresponding to the molecular vibrational modes for pure liquid benzonitrile, the RFID processes of various molecular vibrational modes can be measured at the same time. The dephasing times of various molecular vibrational modes can be obtained by fitting the data to a single exponential function as

$$I(\tau) = A_0 \exp(-2\tau/T), \quad (1)$$

where T is the vibrational dephasing time responding to each molecular vibrational mode; A is a constant; τ is the delay time. The normalised intensities of five typical peaks corresponding to typical molecular vibrational modes for benzonitrile at the wavenumbers of 1016 cm^{-1}, 1190 cm^{-1}, 1608‘cm^{-1}, 2248 cm^{-1} and 3090 cm^{-1} are plotted each as a function of τ and fitted to expression (1) in Figs. 5(a), 5(b), 5(c), 5(d) and 5(e) respectively.

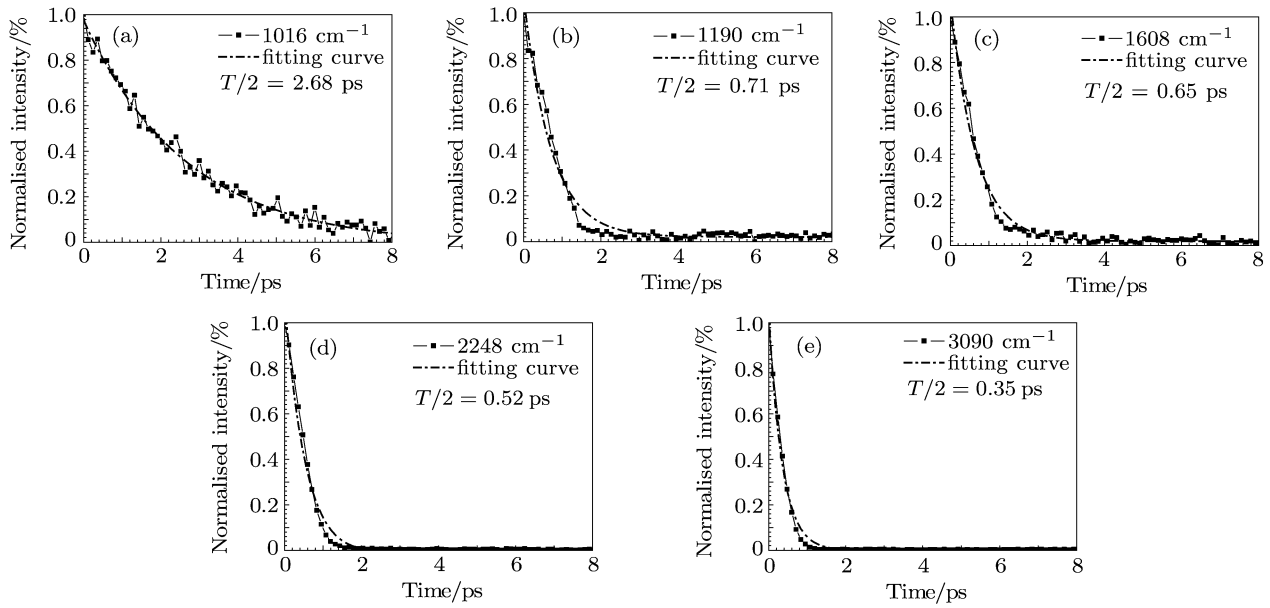


Fig. 5. Vibrational dephasing processes and their relevant dephasing times of various molecular vibrational modes for pure liquid benzonitrile shown in panels (a), (b), (c), (d) and (e) respectively, with the solid line corresponding to the change of CARS signal with delay time for molecular vibrational mode and the dash dot line representing the fitting curve to a single exponential function.

From the experimental results, the intensities of the CARS signals corresponding to different molecular vibrational modes attenuate exponentially against the delay time in a large dynamic range. By fitting the intensity data of the CARS signal to a single exponential function for the molecular vibrational mode at 1016 cm^{-1}, half of vibrational dephasing time $T/2$ of (2.68±0.12) ps can be worked out as shown in Fig. 5 (a), which accords well with the result given in Ref. [15]. After the same functional fitting as the above for other four molecular vibrational modes at 1190 cm^{-1}, 1608 cm^{-1}, 2248 cm^{-1} and 3090 cm^{-1} their values of half vibrational dephasing time $T/2$ are (0.71±0.02) ps, (0.65±0.02) ps, (0.52±0.02) ps and (0.35±0.01) ps respectively, which are also consistent with the previously published data.[21−23]

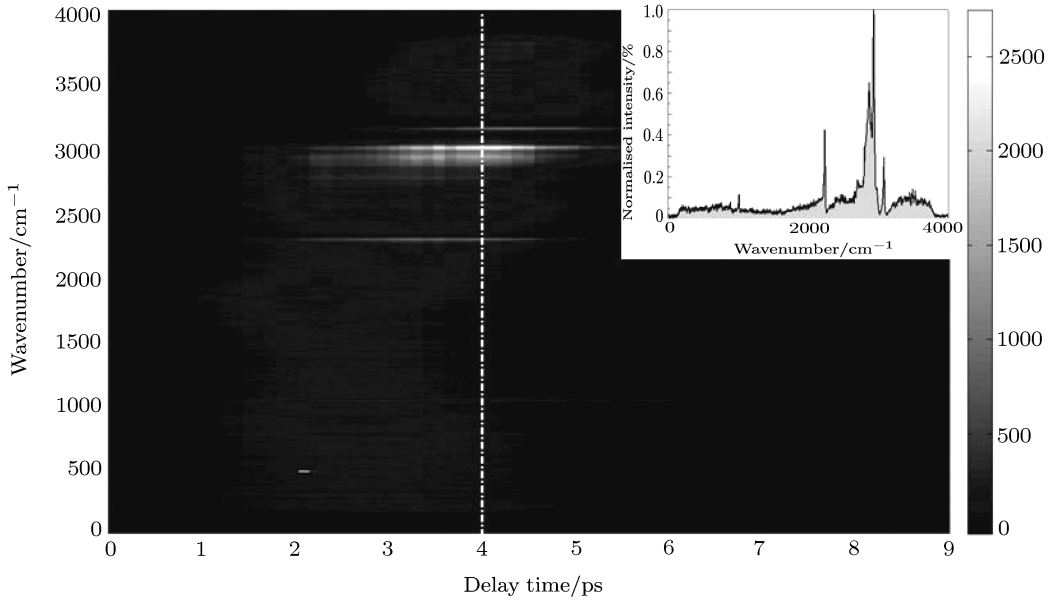


Fig. 6. Variation of CARS spectral signal for benzonitrile-methanol-ethanol mixture solution with delay time and the CARS spectrum with a delay time of 4 ps measured by our broadband T-CARS system.

Under the room temperature, we have carried out the same measurement for a benzonitrile-methanol-ethanol mixture solution in which the molarities of the benzonitrile, methanol and ethanol are 2.45×10^{-3} mol/ml, 4.95×10^{-3} mol/ml and 9.45×10^{-3} mol/ml respectively. The benzonitrile molecule is regarded as the target molecule. For the benzonitrile-methanol-ethanol mixture solution, the intensity change of CARS spectral signal of mixture solution with time and the original CARS spectral profile in 380–4000 cm^{-1} with a delay time of 4 ps are shown in Fig. 6. The NRB noise can be effectively suppressed with the delay time increasing. The peaks at wavenumbers of 1016 cm^{-1}, 2248 cm^{-1} and 3090 cm^{-1} corresponding to C–C–C trigonal breathing, C≡N stretching, and C–H stretching vibrational modes of benzonitrile respectively can be apparently seen.[18] Other peaks correspond to the typical molecular vibrational modes of methanol and ethanol. Therefore, we can conveniently distinguish the various compositions of a mixture based on the CARS spectrum.

The normalised intensities of three typical peaks corresponding to typical molecular vibrational modes for benzonitrile at the wavenumbers of 1016 cm^{-1}, 2248 cm^{-1} and 3090 cm^{-1} are plotted each as a function of τ and fitted to expression (1) in Figs. 7(a), 7(b), and 7(c) respectively. In this case, the values of half of vibrational dephasing times $T/2$ of three typical molecular vibrational modes for benzonitrile molecule at wavenumbers of 1016 cm^{-1}, 2248 cm^{-1} and 3090 cm^{-1} are (1.49±0.06) ps, (0.58±0.02) ps and (0.50±0.02) ps respectively.

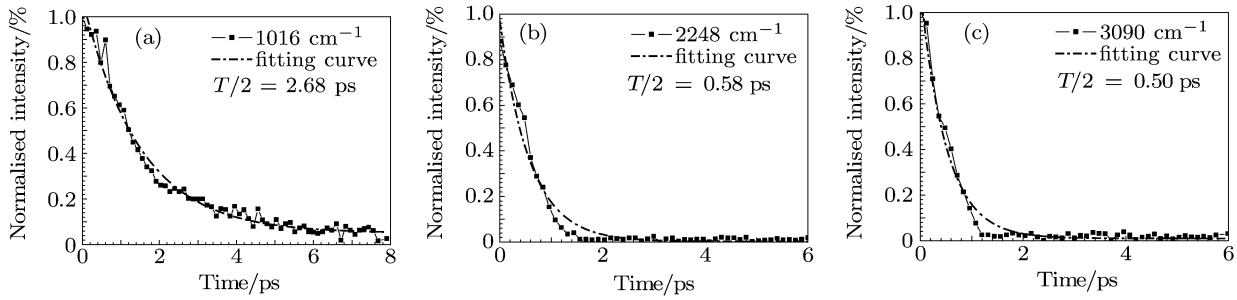


Fig. 7. Vibrational dephasing processes and their corresponding dephasing times of various molecular vibrational modes for benzonitrile in benzonitrile-methanol-ethanol mixture solution, shown in (a), (b) and (c) respectively, with solid line corresponding to the variation of CARS signal with delay time and the dash dot line showing the single exponential fitting curve.

In the benzonitrile-methanol-ethanol mixture solution, we can see that the dephasing time of coherently enhanced molecular vibrational mode for benzonitrile at 1016 cm^{-1} is shorter than that for pure liquid benzonitrile, while the dephasing time of the C≡N stretching vibrational mode of benzonitrile molecule at 2248 cm^{-1} is kept almost unchanged in two samples with different molarities of benzonitrile. But the dephasing time of C–H stretching vibrational mode of benzonitrile at 3090 cm^{-1} appreciably increases with the decrease of the benzonitrile molarity in the mixture solution. These results show that the influence of solvent on the property of solute is reflected not by the Raman peak position but by the variations of the vibrational dephasing times for different molecular vibrational modes. Therefore, we can conclude that our developed method and setup can be used to accurately measure the global molecular vibrational spectra and dephasing times of various molecular vibrational modes simultaneously.

5. Conclusions

A broadband T-CARS spectrography based on SC is developed and used to obtain the global molecular vibrational spectra in a wide spectral coverage with well suppressed nonresonant background noise in a single measurement. The obtained frequency-domain CARS signals have proved to possess the properties of excellent signal-to-noise ratio, significant chemical specificity and high spectral resolution. We have also demonstrated the measurements of dephasing times of multiple molecular vibrational modes from a sequence of time-resolved CARS signals and the comparison between the vibrational dephasing times for the same molecular vibrational mode in different environments. The method of measuring the vibrational spectrum and the dephasing time of multiple molecular vibrational modes exhibits the potential to understand not only both solvent dynamics and solute-solvent interactions, but also the mechanisms of a chemical reactions in the fields of biology, chemistry and material science.

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