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Influence of geometrical configuration on molecular vibrational dynamics in BBO crystals studied by femtosecond CARS

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ABSTRACT

Femtosecond time-resolved coherent anti-Stokes Raman spectroscopy is utilized to study the ultrafast vibrational dynamics in BBO crystals at room temperature. The beat wavenumbers between Raman modes and coherence decay rates of Raman modes (at 1214 cm^{-1} and 1437 cm^{-1}) in BBO crystals are excited and detected. The intensities of vibrational modes in BBO crystals are found that they can be controlled by geometrical configuration.

1. Introduction

Femtosecond time-resolved coherent anti-Stokes Raman spectroscopy (CARS) is widely accepted as a powerful spectroscopic tool for studying the vibrational dynamics of Raman modes in time domain due to its high spatial resolution, good temporal resolution and high sensitivity since 1980s for some decades [1–3]. Since then femtosecond time-resolved CARS technique has been successfully applied to different samples in condensed phases to study vibrational dephasing and relaxation in the ultrafast time regime, such as polydiacetylene [4,5], graphene [6], polyvinyl alcohol [7], and poly methyl methacrylate [8] etc. Furthermore, there are some advances in femtosecond time-resolved CARS, such as single-shot [9], hybrid fs/ps [10,11] and in situ heterodyne detection [12].

Recently some scientists used the femtosecond time-resolved CARS to study the coherent vibrational process in crystals [13–15]. The β phase barium metaborate crystals (BBO crystals) have a remarkable nonlinear coefficient, a wide transmission range and a high damage threshold. It is often used for generating laser with different wavelength in ultrafast domain. The research of BBO crystals focuses on its applications in laser generation. Liu et al. [16] gained as broad as 12,000 cm^{-1} CARS signal in BBO crystals using two crossing femtosecond laser pulses. Liu et al. [17] gained multicolor femtosecond laser pulses in BBO crystals using continuum white light and 800 nm fundamental pulses. Wang et al. [18] reported that a visible colored crescent was gained in a bulk BBO crystal at certain incident angles. BBO crystals have previously been investigated extensively by spontaneous Raman spectroscopy [19,20]. However, a little is known about their time-resolved CARS spectra [21].

In the present work, we report the application of femtosecond time-resolved CARS on the investigation of the dynamics of coherently ground states in BBO crystals. A commercial regenerative amplifier and two optical parametric amplifiers provide the laser pulses. CARS signal beats between the vibrational modes (from 1200 cm^{-1} to 1600 cm^{-1}) in BBO crystals are obtained at room temperature by Fourier transformation and biexponential fit. The intensities of vibrational modes were controlled by the geometrical configurations. Two-beam CARS is used to get duration of the laser beams by changing the delay time of Stokes pulses.

2. Experimental

The experimental setup of our femtosecond time-resolved CARS is similar to that described previously [21]. In the following, the experimental setup and methodology are described briefly. The experimental setup used for femtosecond time-resolved CARS scheme is shown in Fig. 1. A commercial Ti: sapphire regenerative amplifier is used to pump one or two optical parametric amplifiers (OPA). If one OPA is needed, the output of the Legend is split into two parts. The first part, taking 90% of the total optical power, is

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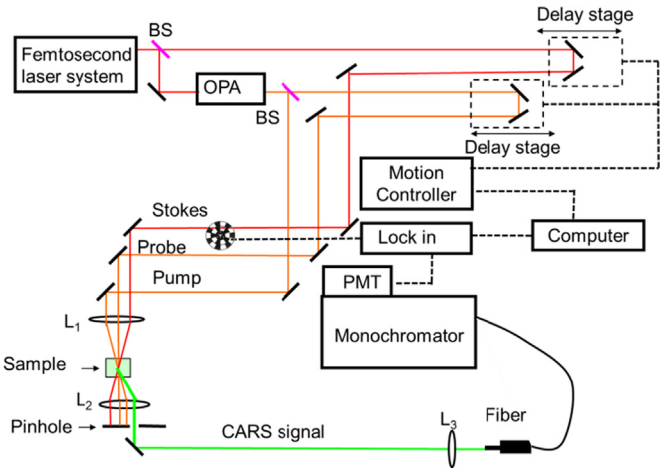

Fig. 1. Femtosecond time-resolved CARS experimental setup (BS, beam splitter).

fed to an OPA. The output of OPA is split into two parts (by a 1:1 beam splitter) to obtain the pump (λ_{pu}, $\mathbf{k}_{pu}$) and probe (λ_{pr}, $\mathbf{k}_{pr}$) beams. The second part of the amplifiers beam serves as the Stokes beam (λ_{st}, $\mathbf{k}_{st}$). If two OPAs are needed, the output of the Legend is divided into two parts (by means of by a 50% beam splitter) to pump two OPAs. The first OPA output is split into two parts providing the pump and probe pulses. The second OPA output serves as the Stokes pulses. All laser polarizations are parallel to each other.

The generation of CARS signal requires temporal and spatial overlap of the beams in the samples. The relative timing among the different beams is varied by computer controlled delay stages (Sigma Koki, SGSP20-85 with a minimal step size of 6.7 fs). The delay time between the pump and Stokes pulses defines as T_{12}. The delay time between the probe and pump pulses defines as T_{13}. The temporal overlap of the beams is examined by self-diffraction methods (in coverslip). After the three beams passed through the lens L_1 with a 200 mm focal length, they are focused onto the sample. This folded BOXCARS beam geometry ensures that the CARS signal propagates in a direction ($\mathbf{k}_{CARS}=\mathbf{k}_{pr}-\mathbf{k}_{st}+\mathbf{k}_{pu}$) different from the incoming beams and can therefore be background-free collected.

The signal is then collimated by the lens L_2 of focal length 200 mm. The spatially separated CARS signal beam is filtered by a spatial filter which is detected in detection system. It is spectrally dispersed in the monochromator (Newton, Andor) and detected by a photo multiplier tube (PMT) with a lock-in amplifier (SR830, Stanford Research Systems). A 0.1-mm-thick BBO crystal ($\theta=29.5^\circ$) is used as the sample. Depending on the sample, the average power of three beams is attenuated by a variable neutral-density filter. A large dynamic range, which is required in our measurements, is achieved by variable attenuation of the signal beam.

3. Results and discussion

3.1. Quantum beats in BBO crystals

The vibrational relaxation process can be monitored in real time by changing the delay time T_{13}. Raman transitions are coherently driven by pump and Stokes beams. Subsequently vibrational coherence due to Raman transition is probed by the probe beam, giving rise to a CARS signal [22].

Fig. 2(a) shows the time-integrated CARS intensity (a logarithmic scale) of BBO crystals as a function of delay time T_{13}. In this measurement, the pump pulses and the Stokes pulses are coincident in time. 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. The typical selective exciting transients in BBO crystals is obtained for a pump of wavelength $\lambda_{pu}=\lambda_{pr}=548$ nm and a Stokes wavelength $\lambda_{st}=589$ nm, detecting the time-resolved CARS signal at $\lambda_{CARS}=510$ nm. This is a result of time-resolved femtosecond CARS measurements for vibrational mode in BBO crystals at Raman shift of 1300 cm^{-1}.

The quantum beats seen on the CARS transients is due to the beating of the different vibrational modes are excited simultaneously because of the large spectral bandwidth of the femtosecond laser pulses and the close gap of neighboring Raman levels. In order to analyze the experimental data, Fourier transformations of the time domain signal were employed. Fourier transformations of the time-resolved CARS signals allows a clear identification of the excited Raman modes (the frequency components contributing to the CARS signal beats) when compared with results on the wavenumber of Raman modes from Raman spectroscopy. In order to eliminate the strong nonresonant four-wave mixing (FWM) signal (the almost instantaneous response from residual non-Raman resonant scattering contributions) in studying the quantum beats, we only analyze the data of the time delay T_{13} larger than 200 fs.

The fast Fourier transform (FFT) power spectra of the time-resolved CARS signal from Fig. 2(a) is exhibited in Fig. 2(b). From the results shown in Fig. 2(b), we infer that the CARS signal beats come from the interference predominately between the two components at 0 and 241 ± 10 cm^{-1}. It means that two vibrational modes are coherently excited at the same time. The Raman spectrum of BBO crystals in this wavenumber range can be found in several publications [19,20]. This corresponds to the Raman modes of B–O stretching vibrations at 1437 cm^{-1} and 1214 cm^{-1} in BBO crystals. Therefore, CARS signal beats for Raman modes originate predominantly from interference between stretching vibrations of intra-ring B–O bonds (E) and stretching vibrations of extra-ring B–O′ bonds (E′).

Du et al. [23] present a theoretical description of the femtosecond time-resolved CARS in crystals. The formula of time-integrated CARS signal for the case of two excited vibrational modes (Eq. (9) in Ref. [23]) is similar to function (1) in Ref. [24]. The formula is suitable for fitting femtosecond CARS signals of BBO crystals. The frequency difference $\Delta\omega$ of the vibrational modes and their respective dephasing times can be obtained from the quantum beats. The oscillations also can be fit with function (1) in Ref. [24]. The fitting results are $T_1=160\pm6$ fs, $T_2=23\pm2$ fs. The dephasing times for the two vibrational modes are determined to be 160 ± 6 fs and 23 ± 2 fs, respectively.

3.2. The influence of geometrical configuration

By varying the polarization of the laser pulses, different dynamics are coherently excited and probed by the nonlinear spectroscopy [25]. Therefore, the angle between the crystal axis and the polarization (geometrical configuration) will influence the intensity of the vibrational mode. Zero degree is the best angle for second harmonic generation in BBO crystals. Fig. 3(a) shows the time-integrated CARS intensity (a logarithmic scale) of BBO crystals with the different geometrical configurations as a function of delay time T_{13}. The typical selective exciting transients in BBO crystals is obtained for a pump of wavelength $\lambda_{pu}=\lambda_{pr}=714$ nm and a Stokes wavelength $\lambda_{st}=800$ nm, detecting the time-resolved CARS signal at $\lambda_{CARS}=645$ nm. This is a result of time-resolved femtosecond CARS measurements for vibration mode in BBO crystals at Raman shift of 1500 cm^{-1}. In order to eliminate the strong nonresonant FWM signal in studying the quantum beating, we only analyze the data of the T_{13} larger than 200 fs.