Multiple coherent anti-Stokes Raman scattering due to phonon grating in $KNbO_3$ induced by crossed beams of two-color femtosecond pulses

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Multiple coherent anti-Stokes Raman scattering signals of the phase-matched SHG light were observed in $KNbO_3$, by using a pair of crossed beams of two near-infrared femtosecond pulses under the resonant pumping of a particular optical phonon. Angle-resolved spectroscopy reveals that the phonon grating induced by the crossed beams is responsible for the signals up to the eleventh order covering a broad wavelength region, with the intensities of the same order. A theoretical explanation for the present phenomenon is presented. The result is compared with similar but collinear ones due to vibration or rotation modes in molecular gases in literatures. The significance of the present work is discussed from the viewpoints of Raman coherence and of developing ultrafast pulses in a condensed matter.

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In the past decade, quantum control of radiation has been one of the main subjects in the field of quantum optics.[1–3] Among others, the control with use of Raman coherence based on a vibration or rotation state in molecules[4,5] has attracted much interest not only in physics, but also from the viewpoint of application, because it has the potential of generating ultrashort light pulses such as subfemtosecond (attosecond) pulses.[6–8] So, such research has been extensively done both experimentally and theoretically. It is noted that before the concept of the maximal coherence was first introduced in 1997,[4] generation of broadband higher-order stimulated Raman scattering with a combined use of pump laser and the first-order Stokes light collinear with the laser had already been well studied.[9–12]

Experimental works in terms of the control of Raman coherence have been performed in two regimes, i.e., one with the pulse width Δt for excitation being larger than the coherence time τ_c and the other with Δt smaller than τ_c. More specifically, nanosecond pulses with a very narrow spectral width are employed in the former, or the steady state, case,[5,6] whereas subpicosecond pulses are employed in the latter, or the transient, case.[8,13] Furthermore, the experiments have also been made in the so-called impulsive regime, where Δt is smaller than the inverse of the angular frequency of the relevant vibration, T_v; in this case Δt is typically a few tens of femtoseconds.[7] Those works have been performed mostly in a gaseous system. In other words, those works are based on Raman modes of isolated vibrational or rotational excitation in molecules; the only exceptional case is an experiment performed in solid hydrogen at low temperatures, where the vibration modes in isolated molecules are weakly coupled with each other.[14] However, it is noted that all those experiments were carried out with two collinear pumping lasers with the difference of their frequencies resonant with the frequency of the Raman mode.

In this paper, we report on the finding that a broadband of up to eleven orders of coherent anti-Stokes Raman scattering (CARS) radiations is observed in a condensed matter, i.e., $KNbO_3$ and $LiNbO_3$ single crystals, by using a pair of crossed beams of two-color femtosecond pulses. Those radiations arise as a result of multiple scattering of second-harmonic light (SHG) by a phonon grating, which is induced by resonant excitation of a particular Raman-active phonon mode. This is the first report, to our knowledge, on control of Raman coherence in a crystalline sample with use of crossed beams. In this paper, we describe mainly the result for $KNbO_3$.

The crystalline structure of $KNbO_3$ belongs to C_{2v} symmetry (orthorhombic) at room temperature, so that it lacks an inversion symmetry. Factor-group analysis reveals that 12 optical phonons at Γ point in the Brillouin zone (BZ) are classified into the following irreducible representations, i.e., $4A_1(z)+1A_2+4B_1(x)+3B_2(y)$, all being Raman active; the letter in the parenthesis denotes the polar crystallographic axis, since $A_1(z)$, $B_1(x)$, and $B_2(y)$ are polar modes (infrared active). Because of the polar nature, those are split into the transverse optical (TO) and longitudinal optical modes, respectively. In this work, we have focused on the TO_4 mode of A_1 symmetry with the highest frequency of 610 cm^{-1} among eleven TO modes in total. Based on Raman tensors R_{xx}, R_{yy}, and R_{zz}, this mode can be observed, for example, in $z(x,x)z$ geometry (in terms of Porto notation) in spontaneous Raman scattering, which we have reconfirmed.

A sample of $KNbO_3$ was prepared in a rectangular parallelepiped form with $6.5\times6.8\times8.3$ mm^3 in size. The surfaces of the sample for ingoing and outgoing light are such that the normal is perpendicular to the x axis and makes an angle of 32.8° with the z axis in the (yz) plane. Thereby the type-I phase matching (PM) for SHG can be attained approximately at the normal incidence for the incident beams used for exciting the CARS signal, which will be described below.

Two laser pulses of ~150 fs in pulse duration having near-infrared frequencies of ω_1 and ω_2 were employed to resonantly excite a particular phonon mode; that is, the frequency difference $\Delta\omega=\omega_1-\omega_2$ was set to be almost equal to the phonon frequency. The signal and idler output beams from an optical parametric amplifier (Spectra-Physics Inc., OPA-800) pumped by a regeneratively-amplified mode-

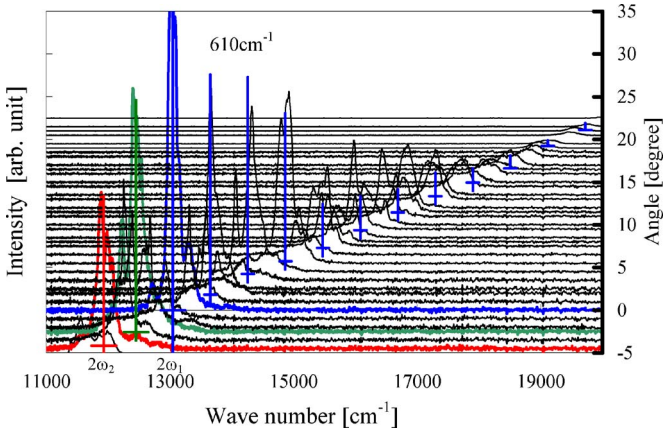

FIG. 1. (Color online) The angle-resolved spectra due to multiple CARS signals based on the SHG light observed in a $KNbO_3$ crystal under resonant pumping of $A_1(TO_4)$ mode at room temperature; excitation wave number was set to be 610 cm^{-1} using two laser beams with ω_1=6565 cm^{-1} and ω_2=5952 cm^{-1}, and with the power of 3.0 μJ/pulse, where both beams were polarized along the x axis. The angle is measured from the $\boldsymbol{k}_1$ direction and the spectrum is observed at every 0.5°.

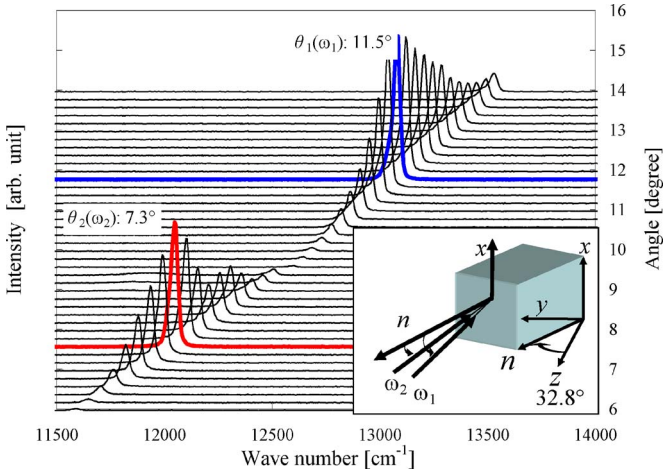

FIG. 2. (Color online) The SHG signals at $2\omega_1$ and $2\omega_2$ are observed in the directions of 11.5° and 7.3°, respectively, from the normal incidence on the yz plane. Note that the PM conditions are well satisfied and that the spectral width 200 cm^{-1} comes from the pulse width 150 fs.

locked Ti-sapphire laser were used as ω_1 and ω_2 pulses, respectively. Importantly, two beams being crossed with a small crossing angle $\Delta\theta°$ of typically 4.5° in air were focused onto a sample by using a lens with the focal length of 150 mm;[15] the relative time delay was varied to be within ±200 fs. The power density up to 2×10^{11} W/cm^2 was employed for excitation. The polarizations of incident pulses were chosen to be parallel to each other and to the x axis. As a consequence, not only the phase-matched SHG light can be generated, but also the A_1 phonon mode is allowed to be excited; more exactly, we adopted the PM angle at the nearly normal (7.3°) incidence for the ω_2 light. The scattered signals as well as the SHG light were picked up by an optical fiber head whose open window is about 3 mm in height and 0.5 mm in width. The fiber head attached to an electrically movable rotation stage was set about 25 mm apart from the sample and, thereby, angle-resolved spectra could be observed; actually the CARS spectra were measured at every 0.5° (0.2°) in the visible (near-infrared) region.[15,16] The signal light was detected with a fiber-multichannel spectrometer (Ocean Optics, Inc, USB400) with a CCD array detector, which covers 400 to 1000 nm in wavelength. A cooled InGaAs one-dimensional array detector (Roper Scientific, Inc. OMA-V) was also employed as an auxiliary detector together with a monochromator in the near-infrared region from 900 to 1600 nm. All experiments were performed at room temperature.

In Fig. 1 an example is shown of the successive angle-resolved spectra of the CARS signals, which were observed with $\Delta\omega$=613 cm^{-1} and the beam angle of 4.5°; ω_1 and ω_2 are 6565 and 5952 cm^{-1}, respectively, and their power is 3.0 μJ/pulse each. More detailed and expanded angle-resolved spectra in the SHG frequency region are presented in Fig. 2, which were also observed under the condition identical to the case in Fig. 1, concerning $\Delta\omega$, $\Delta\theta°$, and the power. First, it is seen in Fig. 2 that the PM angle θ_{PM} for the ω_1 beam deviates by 11.5° from the normal incidence, and also by 7.3° for the ω_2 beam. Second, note that in Fig. 1 many signals with the respective frequency shifts manifest themselves, particularly on the anti-Stokes side.

In Fig. 3 an example of analysis is presented which indicates that multiple CARS signals are observed from the third to ninth order with a frequency spacing of 610 cm^{-1}, where the fitted position of the frequency (energy in cm^{-1}) at a particular angle is marked with the cross bar in each case. A similar analysis reveals that multiple CARS signals stem from the PM-SHG lights, from the first to eleventh order with the frequency spacing of A_1 TO_4 phonon clearly observed, together with the first and the second Stokes signals. Notice that the frequency spacing is almost equal to $\Delta\omega$ of 610 cm^{-1}, not the double. The weak sub-bands may come from combinations of the Raman-active (195 cm^{-1}) mode which is impulsively excited.

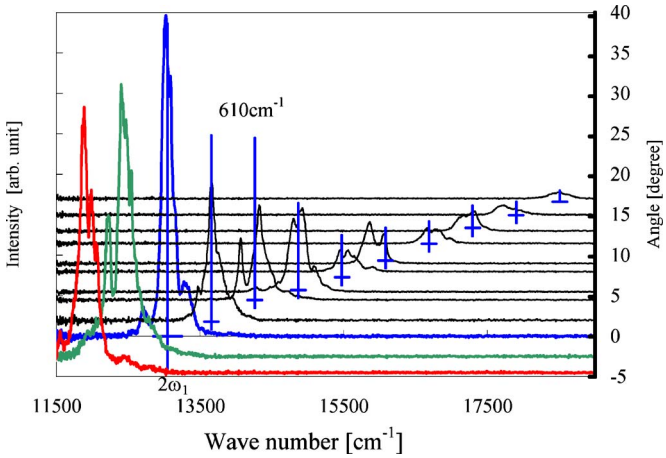

FIG. 3. (Color online) An example of analysis of the data shown in Fig. 1; notice that the angle-resolved CARS spectra contain the successive spectral lines due to the Raman-active mode with a frequency spacing of 610 cm^{-1}. For detail, see the text.

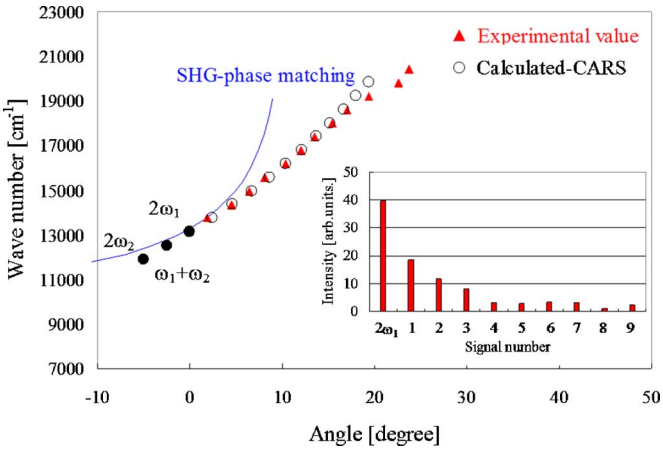

FIG. 4. (Color online) The wave numbers of the observed (triangles) and the calculated (open circles) CARS signals are plotted as a function of the observed direction (angle), together with the signals (closed circles) of sum-frequency generation and the SHGs; the theoretical curve on which the PM-SHG is satisfied is also shown by the thin curve. The inset shows the signal intensities of the nth order CARS signal relative to that of the SHG at $2\omega_1$.

In Fig. 4, the scattering-angle dependence of the CARS signals (closed triangles) is shown due to the TO_4 phonon, where for convenience the observed angle is relative to that of $2\omega_1$ light (PM-SHG). In Fig. 4 the positions of the first- and second-order Stokes Raman signal are also plotted, together with two PM-SHGs. The intensity of the respective signals relative to that of $2\omega_1$ light is plotted in the inset of Fig. 4, where the intensity is normalized by the wavelength-dependent sensitivity of the optical tools used including the detector and the monochromator. Notice that a total of powers converted to all CARS signals amounts to almost the same as that of the SHG at $2\omega_1$, which is estimated as around 48% (relative to the laser at ω_1).

Let us consider the mechanism of generating the present multiple CARS signals. At the first step, by resonant pumping with use of two intense pulsed beams a coherent phonon grating is produced with the wave vector given by $\Delta\boldsymbol{k}=\boldsymbol{k}_1-\boldsymbol{k}_2$, where $\boldsymbol{k}_1$ ($\boldsymbol{k}_2$) is the wave vector in the crystal of the ω_1 (ω_2) beam; $\boldsymbol{k}_1$ ($\boldsymbol{k}_2$) differs from $\boldsymbol{k}_1^0$ ($\boldsymbol{k}_2^0$) in air. Then the PM-SHG ($2\omega_1$) light is scattered by this dynamical phonon grating with the frequency $\omega_v=\omega_1-\omega_2$ and $\Delta\boldsymbol{k}$, causing the first-order anti-Stokes Raman radiation with the frequency $\omega_{+1}\equiv 2\omega_1+\omega_v$ and the wave vector $\boldsymbol{k}_{+1}\equiv\boldsymbol{k}^{2\omega_1}+\Delta\boldsymbol{k}$, where $\boldsymbol{k}^{2\omega_1}\cong 2\boldsymbol{k}_1$. Note that the quasi-phase-matching condition is fulfilled in this case. Therefore, the observed angle θ_{+1}^0 in air is expressed as $\sin^{-1}[\Delta\theta^\circ k_2^0/k_{+1}^0]$, considering Snell's law; see Fig. 5. Here it is noted that θ_{+1}^0 can be described in terms of the wave vectors k_2^0 and k_{+1}^0 and the crossing angle $\Delta\theta^\circ$ in air as long as we neglect the dispersion of the refractive index $n(\omega)$. Similarly, scattering of this first-order anti-Stokes radiation by the same phonon grating gives rise to the second-order radiation. Thus the higher-order (lth) anti-Stokes Raman radiation arises successively (l being the positive integer). The angle for the lth signal is given, in general, by $\theta_{+l}^0=\sin^{-1}[l\Delta\theta^\circ k_2^0/k_{+l}^0]$, with $k_{+l}^0=|\boldsymbol{k}^{2\omega_1}+l\Delta\boldsymbol{k}|$. See again Fig. 5. The data points (open circles) calculated in terms of this relation are also shown for comparison in Fig. 4. The agreement between the observed and the calculated is satisfying enough except for $l=10$ and 11. There signal frequencies are nearly equal to that of the third harmonics.

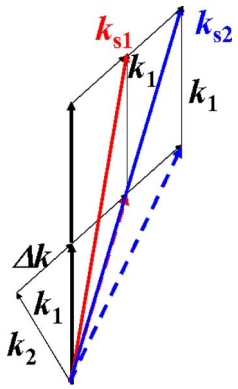

FIG. 5. (Color online) The quasi-PM condition is drawn for the first ($\boldsymbol{k}_{S1}$) and the second ($\boldsymbol{k}_{S2}$) CARS signals (thick lines) of the SHG at $2\omega_1$.

As for the intensity I_l of the lth order signal, it can be shown that I_l is given in terms of the lth order Bessel function. In this connection, it is remarked that the theoretical formulation is to a considerable extent in parallel to the one-beam excitation case in molecules. Here, as the depletion effect of pumping-light intensities can be practically neglected, I_l is known to be given by the lth order Bessel function.[17,18] However, in the present case, we find that the depletion effect is so significant that the respective intensities cannot be expressed in such a simple way as that in the above molecules; the details will be presented in a forthcoming paper. Interestingly, depending on the case, the intensity does not necessarily decrease monotonously with the increase of l, as shown in the inset of Fig. 4.

Now, let us discuss the present result. First, by resonant pumping with use of collinear beams of two-color laser pulses, coherent higher-order CARS radiations due to the vibration or rotation mode were observed in molecules such as H_2 in many groups. It is shown that in this collinear pumping case, the origin of those signals can be well interpreted as arising from the parametric process among the lth, $(l-1)$th, and $(l+1)$th order signals.[19] In the present work, we have shown that seemingly similar CARS signals were also observed due to a Raman-active optical phonon in a condensed matter by using a pair of crossed beams. However, we point out that for a few reasons the present origin is essentially different from the gaseous cases. (1) Because experimentally the present CARS signals have disappeared when the crossing angle approaches zero. Besides, (2) because, theoretically, the signals arise as a result of scattering of a probe light, or the third light (SHG in the present case) by a phonon grating.

Second, this is the first report, we believe, concerning observation of the multiple CARS signal using a pair of crossed beams. In this connection, we note our previous work on $KTaO_3$, which is similar to the present work in a sense that a phonon grating is responsible for the signals.[15,16] However, those signals are not the CARS, since all Γ-point

optical phonons are not Raman active in $KTaO_3$. There folding of the BZ- edge onto the Γ point was essential under strong pumping of a pair of phonons at the BZ- edge.

Third, we briefly mention the case where a non-PM SHG exists instead of the intense PM SHG, but, otherwise, the experiment is very similar to the present one. We have performed this kind of experiment for $LiNbO_3$ before. Similar to the present result of $KNbO_3$, a series of multiple CARS signals, which are considerably weak as they should be, based on scattering of $2\omega_1$ light (a weak SHG) by a phonon grating, were also observed. However, those lth order signals have turned out to be observed at such angle positions as cannot be explained in a way similar to the $KNbO_3$ case; the result due to another mechanism will be presented in a separate paper.

Finally, we would like to mention the possibility of generating ultrashort pulses such as subfemtosecond ones. As the present phenomenon is a coherent one, it is possible in principle. For this purpose, broader band signals than the present case are required. It should be possible by utilizing a Raman-active crystal with a large band gap, e.g., a diamond or AlN. From this point of view, use of a vibration mode in H_2 molecules in combination with a pair of collinear beams has an advantage, generally speaking, over the crystal, since no band gap exists in the latter. However, the fact that the repetition rate of short pulses becomes very fast due to the very large vibration frequency is a drawback in the case of H_2, in utilizing ultrashort pulses for application. In this connection, we note that, from the viewpoint of efficiency of signal generation, use of a phonon grating is advantageous to that of the vibration or rotation mode in molecules including H_2, since formation of the phonon grating benefits greatly by the classical phonon-wave formation due to the phonon condensation.

As a final comment, we remark that an intense PM SHG is not a requisite, but any intense pulse of an arbitrary wavelength, externally introduced as a probe light, should generate similar multiple CARS signals. Such an experiment is now in progress.

In summary, by using crossed beams of two-color femtosecond pulses, we have observed a broadband of multiple CARS signals in $KNbO_3$. Those are generated as scattered lights of the PM SHG by a phonon grating excited by the crossed beams. A mechanism causing this phenomenon is presented, which can explain well the angular distribution of the signals. The present phenomenon is compared to a broadband of CARS signals in molecules generated by using collinear pulse beams, where the PM of four-wave mixing is formidably forbidden. The potential of generating ultrafast pulses in the future based on the present outcome is also discussed.

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