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Picosecond Raman-induced phase conjugation in liquids and solids

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We have used the new Raman-induced phase conjugate (RIPC) technique to obtain strong Raman signals using picosecond laser pulses. We have obtained the picosecond RIPC spectra of carbon disulfide, benzene, nitrobenzene, and calcite. By delaying one of the interacting pump beams relative to the other pump and probe beams we were able to determine the intensities of the phase conjugate beams at the Stokes frequencies as a function of time with 20-ps resolution. These measurements show the potential of this technique to determine phonon relaxation times in condensed matter using shorter laser pulses.

I. Introduction

Phase conjugation allows the generation of a time-reversed replica of an optical wavefront using nonlinear optical effects.[1] Besides the multiple applications of phase conjugation in optical image processing, the availability of picosecond and femtosecond laser pulses has offered a new approach to studying ultrafast dynamic phenomena in liquids and solids.[2,3] Recently, Saha and Hellwarth[4] demonstrated a new coherent Raman spectroscopy technique using phase conjugation in which 2-single-pulse laser beams at w and $w - \Omega$ or $(w + \Omega)$ (where Ω corresponds to a vibrational frequency in a nonlinear medium) mix with a third laser beam to generate a fourth beam at $w - \Omega$ or $(w + \Omega)$, nearly phase conjugate to one of the beams at w. The resonance enhancement of the X^3 nonlinear coefficient generates the signals at the Stokes or anti-Stokes frequencies. According to Saha and Hellwarth[4] the main characteristics of this Raman-induced phase conjugation (RIPC) technique are a wide frequency range (thousands of cm^{-1}) and a broad acceptance angle for phase matching (40 mrad). For example, in identical conditions, the phase matching limited frequency range for RIPC is 1–2 orders of magnitude larger than the frequency range in CARS spectroscopy.[4] RIPC appears to be well suited to obtain broadband low resolution Raman spectra even for materials with unknown dispersion of the refractive index.

In this paper, we demonstrate the use of the RIPC technique to obtain picosecond Raman spectra covering a 1500-cm^{-1} range using a picosecond continuum, and investigate the suitability of the RIPC technique to measure relaxation times in liquids and solids using picosecond laser pulses. We have obtained the picosecond RIPC spectra of carbon disulfide, benzene, nitrobenzene, and calcite and were able to determine with picosecond resolution the intensities of the phase conjugate beams at the Stokes frequencies as a function of time.

II. Experimental Methods

A phase conjugation geometry was used in these experiments with one essential difference with previously reported setups[4]: one of the counter propagating beams was a broadband supercontinuum extending throughout the visible spectrum. The picosecond pulse continuum was produced by focusing the laser fundamental and its second harmonic into a 5-cm liquid D_2O cell.

The experimental setup is shown in Fig. 1. Two ~30-ps collinear single-laser pulses at 1064 and 532 nm were generated by a passive/active mode-locked Quantel Nd:YAG oscillator/amplifier laser system and a KDP crystal. The fundamental and harmonic were then separated by a beam splitter $BS1$. The second harmonic was then split into two beams by a 50/50 beam splitter $BS2$ which were directed through variable delay lines toward the sample. One beam was used as a probe (beam 1, pulse energy ~1.5 mJ), the other as one of the counterpropagating pump beams (beam 2, pulse energy ~1 mJ). The angle between pump and probe was ~6°. The 1.06-μm beam was used to generate the other counterpropagating super-

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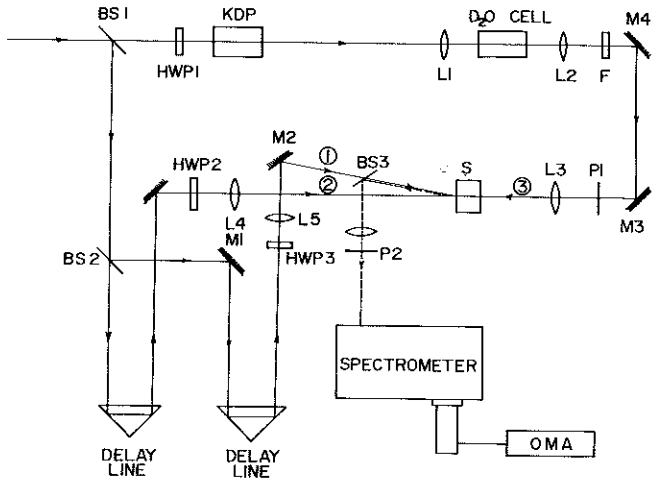

Fig. 1. Experimental setup for Raman-induced phase conjugation.

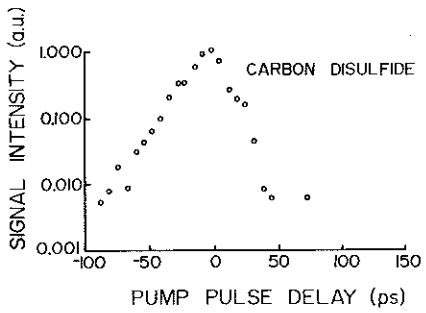

Fig. 2. Dependence of the degenerate phase conjugate signal intensity for CS_2 on the probe (1) pulse delay.

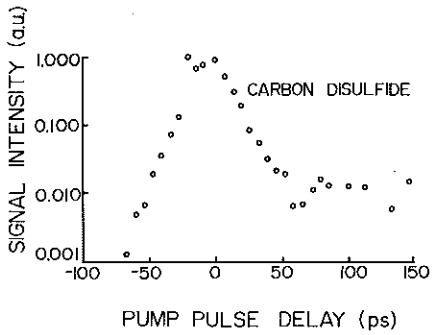

Fig. 3. Dependence of the degenerate phase conjugate signal intensity for CS_2 on the pump (2) pulse delay.

continuum pump (beam 3, pulse energy ~30 μJ). To increase the continuum intensity in the visible a second harmonic KDP crystal was placed in the path of the laser radiation, and both the 1064 nm and generated second harmonic beams were focused into a D_2O cell by lens $L1$.

The picosecond continuum was collimated by lens $L2$ and filtered using filters F to pass wavelengths >532 nm and extended from 550 to >800 nm, providing a broad band of light at the Stokes frequencies. Halfwave plates ($HWP1$, $HWP2$, $HWP3$) and polarizers ($P1$, $P2$) were used to control the relative polarization of all the interacting beams. All three beams were focused into the sample cell with 25–30-cm lenses ($L3$, $L4$, $L5$) so phase matching was possible within a 30-mrad spanning angle. The signal beam, phase conjugate to the probe beam, was directed by a wedge glass plate $BS3$ toward the entrance slit of a spectrometer. The spectra were recorded and analyzed with an optical multichannel analyzer (OMA). For the time-resolved measurements, the monochromatic pump beam (2) or probe beam (1) was delayed relative to the two other beams, and the intensity of the Raman-induced phase conjugate beam was measured for different delays. By delaying the probe beam (1) either the coherence or the intensity correlation of the exciting beam could be measured depending on the response time of the medium.[3,5] However, transient grating effects could be investigated with picosecond resolution by delaying the monochromatic pump beam (2).

To determine the time resolution of our apparatus, time-resolved phase conjugate measurements were carried out in CS_2. Figure 2 shows the normalized degenerate phase conjugate signal for CS_2 vs delay time between the probe beam and the two pump beams. Since in this case the duration of the laser pulse is much greater than the relaxation time of the medium, the response instantaneously follows the driving field. A plot of the detected conjugate signal as a function of the probe pulse delay corresponds to the intensity correlation of the laser pulse.[5] This measurement shows that the time resolution of the setup is ~10 ps. By delaying the monochromatic pump pulse (2) relative to the two other beams one can monitor the temporal decay of the grating created by the probe and continuum beams.[6] Figure 3 shows such a measurement for CS_2 at the degenerate frequency. This curve is identical to the curve of Fig. 2 except for a weak slow component which is of thermal origin. This shows that the grating relaxation is not resolved in this experiment as expected, since CS_2 molecular orientational relaxation times are much faster (<2 ps) than our resolution.

III. Results

Typical low resolution spectra of the RIPC signal at zero delay for nitrobenzene, carbon disulfide, and calcite at room temperature are shown in Figs. 4–6. The spectra cover a 1000-cm^{-1} range from 500 to ~ 1700-cm^{-1}.

The nitrobenzene spectrum (Fig. 4) shows three strong Raman lines at 1000, 1345, and 1585 cm^{-1}. These bands correspond to the strongest Raman lines in the spontaneous Raman spectrum. By slightly varying the crossing angle ($\Delta\theta \sim 30$ mrad) one can select any one of these lines. Figure 5 shows the case when optimum phase matching corresponds to the 1345-cm^{-1} vibrational mode. The carbon disulfide spectrum (not shown) had one strong band: the 656-cm^{-1} normal mode of CS_2.

A strong phase conjugated signal was obtained from a calcite crystal at 564 nm corresponding to the 1086-cm^{-1} optical phonon. The spectrum shown in Fig. 6 was obtained well below the damage threshold of the 1-

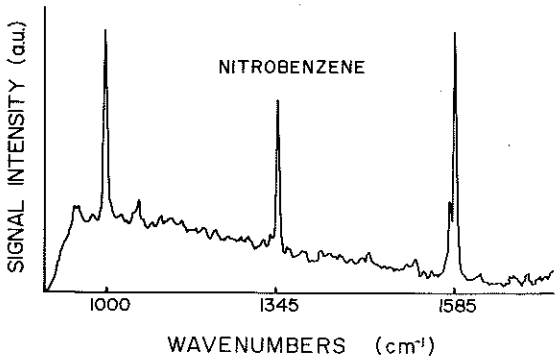

Fig. 4. Spectrum of RIPC signal for nitrobenzene at the zero delay time.

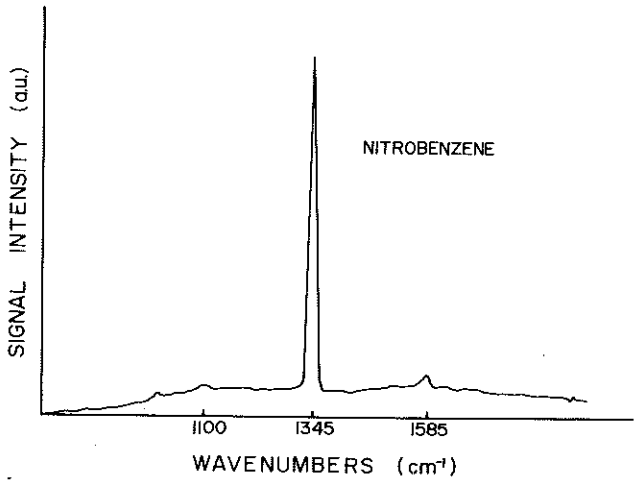

Fig. 5. Spectrum of RIPC signal for nitrobenzene at the zero delay. Optimum phase matching for the 1345-cm^{-1} vibrational mode of nitrobenzene on the pump pulse delay.

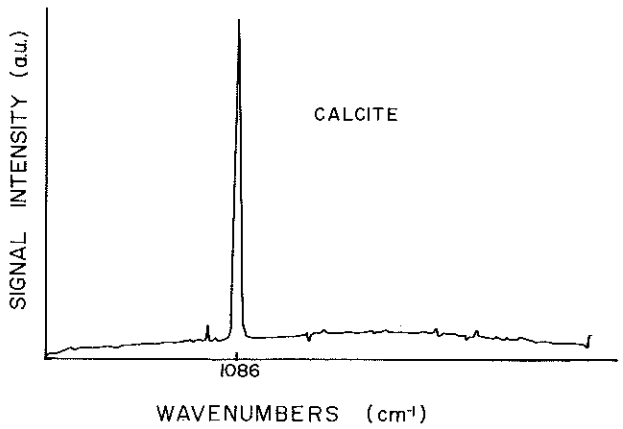

Fig. 6. Spectrum of RIPC signal for calcite at zero delay.

cm crystal used in our experiment. At high intensity (close to the damage threshold) stimulated backscattering of the narrowband pump beam appears. This can be eliminated by lowering the laser intensity. Contrary to earlier four-wave mixing techniques[7] careful phase matching alignment was not needed to generate a strong signal.

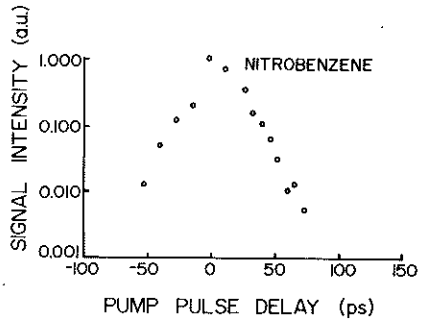

Fig. 7. Dependence of RIPC signal for the 1345-cm^{-1} vibrational mode of nitrobenzene on the pump pulse delay.

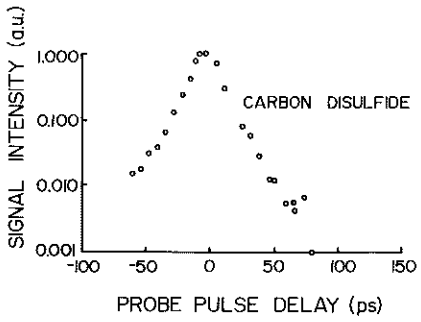

Fig. 8. Dependence of RIPC signal for the 657-cm^{-1} vibrational mode of carbon disulfide on the pump pulse delay.

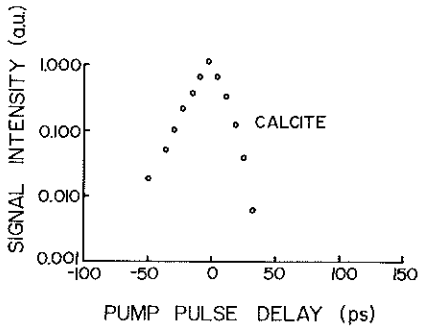

Fig. 9. Dependence of the RIPC signal for the 1086-cm^{-1} optical phonon of calcite on the pump pulse delay.

For all three samples the RIPC signal disappeared completely when any one of the three interacting beams was blocked and was nearly collinear to the degenerate phase conjugation beam. The spectra shown are averages of fifty laser shots. Different polarization schemes were tried, the nonresonant background, although always present, was relatively weak in all cases, and the spectra shown correspond to the case where all the polarizations were parallel. The RIPC signal was then the strongest. The SNR, limited by the continuum fluctuations, was $\sim 200/1$. The SNR could be improved by increasing the number of laser shots per spectrum.

We were able to determine with picosecond resolution the intensities of the phase conjugate beams at the Stokes frequencies as a function of time. As pointed out above a measurement of the signal intensity at

Stokes frequencies vs delay time between one of the pump beams (2) and the continuum and probe in a transparent medium should be a measure of the relaxation time of the laser-induced transient grating.[6,8] The grating is produced by the periodic changes in optical properties of the material in the overlap region of the probe and continuum beams. In RIPC experiments the modulation of the medium is considerably enhanced by the presence of the resonance Raman lines. For a delta-function excitation the transient grating should disappear with the relaxation of the vibrational mode, and the time-resolved RIPC experiment provides a direct measurement of the relaxation time of the excited vibrational modes or phonons.

Figures 7–9 show the normalized intensity of the RIPC signal vs delay time for the 656-cm^{-1} vibrational mode of carbon disulfide at the 1345-cm^{-1} vibrational mode of nitrobenzene and the W_p = 1086-cm^{-1} optical phonon of calcite. The RIPC signal could be followed over more than 2 orders of magnitude. The dynamic range in this experiment is limited by the continuum fluctuations. Although use of the picosecond continuum allows the simultaneous study of several Raman lines over more than 1500 cm^{-1}, the cost is a relatively modest (200/1) dynamic range. A better dynamic range can be achieved if tunable narrow bandwidth laser beams were used and the lines are studied one at a time as in time-resolved CARS. Comparison of the different decay curves shows that away from the maximum (>30 ps) the calcite curve decays faster than the CS_2 curve. The extracted decay times of 20 ± 10 and 10 ± 8 ps, for CS_2 and calcite respectively, correspond to expected values from previous CARS measurements. These measurements show that the time-resolved RIPC technique is potentially a powerful tool to determine relaxation times in liquids and solids. Experiments with a laser system capable of delivering shorter pulses (<5 ps) should be able to reveal the potential of the technique to accurately determine relaxation times.

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