

Real-time measurements of phonon lifetime using a streak-camera-Raman-induced phase-conjugation method

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A novel real-time technique to measure phonon dynamics using the Raman-induced phase-conjugation method in combination with streak-camera technology is described. The technique is used to determine vibrational and optical phonon dephasing kinetics of CS₂, calcite, and LiNbO₃ with a temporal resolution of 3 psec.

Since the early 1970's the study of vibrational kinetic processes in solids and liquids has been made possible by several new ultrafast experimental techniques for the excitation and probing of molecular and lattice vibrations.¹⁻⁸ These techniques include coherent excitation by stimulated Raman scattering and by coherent anti-Stokes Raman scattering (CARS) and incoherent excitation by resonant infrared absorption.¹⁻⁶ Recently the Raman-induced phase-conjugation (RIPC) technique was shown to be suitable for measuring vibrational relaxation times.^{7,8} RIPC is characterized by a wider frequency range and a broader acceptance angle for phase matching than CARS.⁷ In all these techniques the time information is obtained by delaying in time a probe beam relative to the excitation beam(s). The kinetic information is obtained on a picosecond time scale by using a slow detector from the convolution of the probe pulse shape with the response function of the material.

In this Letter, we demonstrate a novel technique that combines the RIPC geometry with streak-camera techniques to determine the phonon and vibrational dephasing times in real time. This is the first time to our knowledge that optical phonon and molecular vibration kinetics have been measured in real time. In this new method, the phase-conjugated pulse generated using RIPC is passed into a streak camera and a video computer system to record its time profile. The rise and decay times of the generated pulse are directly related to the phonon formation and dephasing times. The technique was used to determine phonon and vibrational dephasing times in CS₂, LiNbO₃, and calcite at room temperature and to test the new method. The measured times agree well with earlier measurements made using different excite-and-probe Raman techniques.

The RIPC setup was previously described in detail.⁸ In the technique, three pulses of different frequencies, one derived from a nonlinear supercontinuum⁹ at $\omega - \Omega$ (where Ω corresponds to a vibrational frequency) and two laser pulses at ω (where ω is the second harmonic of a Nd:YAG laser), interact in the nonlinear medium to generate a fourth beam nearly phase conjugate to one of the laser beams at ω . The picosecond

pulse continuum was produced by focusing the laser fundamental and its second harmonic into a 5-cm liquid D₂O cell. The supercontinuum source has the advantage that it can couple to all Raman-active phonon modes that lie within the frequency bandwidth, which can typically be 3000 cm⁻¹. Thus, with a single laser pulse, Raman spectra spanning the continuum bandwidth can be obtained. The phonon dephasing time can be determined by delaying one of the interacting beams relative to the other two. With this method we showed previously that the resolution of this technique is >10 psec with a Quantel 30-psec laser system. By using shorter pulses, dephasing times can be measured more accurately.⁸

Recently we demonstrated¹⁰ that if narrow-band filters are used to spectrally select a 10-nm window within the continuum, laser pulses of less than 3 psec can be generated between 460 and 600 nm from a supercontinuum generated in D₂O by a 25-psec laser pulse. Therefore the continuum beam at a given wavelength is much shorter than the second-harmonic beam. Since the nonlinear material is coherently driven only when both the second-harmonic laser pulse and the continuum pulse are present, the excitation lasts for only 2 to 3 psec, which is the duration of the continuum pulse. Once the excitation has ended, the sample relaxes according to its characteristic dephasing time, which for most samples is of the order of a few picoseconds (<2-20 psec).

In this work, we monitor directly in real time the intensity of the phase-conjugate signal as a function of time, using a Hamamatsu Model C1587 2-psec-resolution streak camera and a temporal analyzer. With this method, the resolution is determined by the duration of the short-continuum pulse and the streak-camera resolution (3 psec). The difference between this novel technique and previous methods can easily be illustrated if we consider the formula describing the phase-conjugate field in the adiabatic approximation in a nonlinear medium^{11,12}:

$$E_{pc} \sim E_{pr}(t + \tau_{del}) \int_{-\infty}^t E_p(t') E_c(t') Q(t - t') dt', \quad (1)$$

where E_{pc} is the phase-conjugate field, E_p and E_c are

the pump and the continuum fields, respectively, E_{pr} is the probe pulse, Q is the nonlinear response function of the medium, and τ_{del} is the delay between the probe and the two other beams. We have assumed a thin sample and neglected geometrical effects. There is no delay between the pump and continuum pulses.

In the case of a pump-and-probe experiment the intensity of the phase-conjugate pulse is detected by a slow detector and is proportional to

$$I_{pc}(\tau_{del}) \sim \int_{-\infty}^{+\infty} |E_{pc}|^2 dt \sim \int_{-\infty}^{+\infty} |E_{pr}(t - \tau_{del}) \int_{-\infty}^t E_p(t') E_c(t') \times Q(t - t') dt'|^2 dt. \quad (2)$$

In our case, the phonon response function has an exponential form:

$$Q(t) = Q_0 \exp(-t/\tau), \quad t \geq 0, \quad (3)$$

where τ is the phonon dephasing time. Assuming a very short continuum [$E_c(t') \approx \delta(t')$] and a very long pump [$E_p(t') \approx E_{po} = \text{constant}$], the phase-conjugate intensity as a function of delay is given by

$$I_{pc}(\tau_{del}) \sim \int_{-\infty}^{+\infty} |E_{pr}(t - \tau_{del}) E_{po} Q_0 \exp(-t/\tau)|^2 dt, \quad (4)$$

and the dependence of the phase-conjugate pulse intensity on the delay time is determined by the convolution of the probe pulse shape with the response function of the material.

When the phase-conjugate signal is detected in real time with an ultrafast streak camera the situation is quite different. Under the same assumptions as above and with $\tau_{del} = 0$ (all three beams coincide at the sample site), the intensity of the signal reaching the streak camera at time t is given by

$$I_{pc}(t) = |E_{pc}(t)|^2 \sim |E_{pr}(t) E_{po} Q_0 \exp(-t/\tau)|^2 \sim I_{pr}(t) e^{-2t/\tau}. \quad (5)$$

For a long probe pulse ($>\tau$) of any shape the medium's

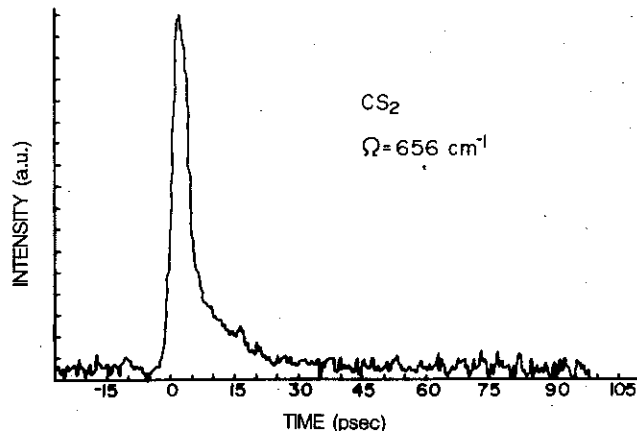


Fig. 1. Real-time single-shot time-resolved measurement of the 656-cm^{-1} vibrational mode in CS_2 .

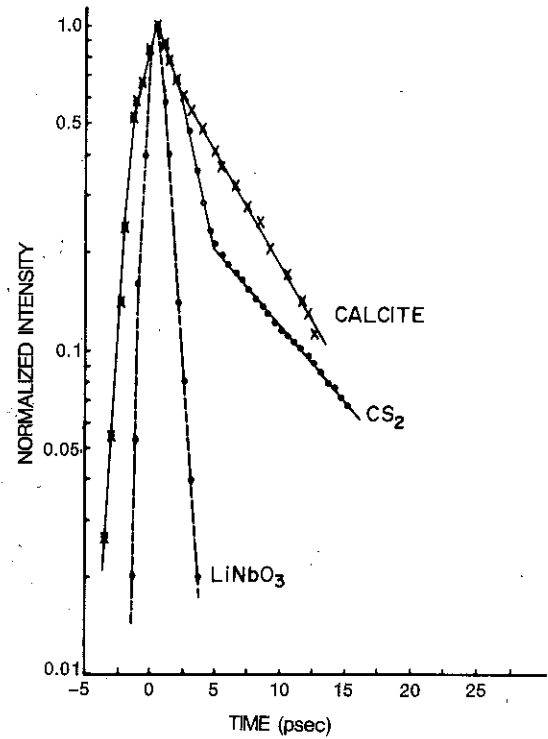


Fig. 2. Semilogarithmic plot of single-shot real-time RIPC pulse shapes obtained from CS_2 , calcite, and LiNbO_3 . The values of the phonon dephasing times calculated from these curves using expression (5) are 8 and 20 psec, respectively, for CS_2 and calcite.

response function is obtained by dividing the phase-conjugate signal by the probe intensity. Expression (5) shows that when the nonlinear phonon response of a material is studied by using a fast detector, the temporal shape of the phonon response function of the material can be obtained in real time. Under our experimental conditions, with a 3-psec-continuum pulse, 25-psec probe and pump pulses, and a 2-psec-resolution streak camera, expression (5) should be quite accurate for phonon and vibrational relaxation times longer than 3 psec and smaller than 20 psec. To measure shorter dephasing times, a shorter-continuum pulse and a faster streak camera are necessary.

Measurements of vibrational and phonon dephasing times have been attempted in three materials to verify the new real-time streak-camera-RIPC technique. For two samples, CS_2 and calcite, the dephasing times were known to fall within the range of our laser system (3–20 psec).^{1,3,13,14} For the third sample, LiNbO_3 , no direct measurements in the time domain were available, but phonon relaxation processes were projected from linewidth measurements to be very fast.¹⁵ The measurements on LiNbO_3 were used to determine the system's resolution.

Figure 1 shows a typical single-shot real-time streak-camera measurement of the 656-cm^{-1} vibrational mode of CS_2 , which exhibits a fast electronic component and a slower exponential phonon decay. The rise time is <3 psec, and an exponential fit to the tail of the scattered pulse envelope yields a dephasing time of 20 ± 1 psec, in excellent agreement with previ-

ous measurements using standard pump-probe techniques and linewidth measurements.^{16,17}

The new technique was also used to measure the dephasing of the 1086-cm⁻¹ line in calcite. Figure 2 shows the calcite phase-conjugate pulse envelope obtained from a streak-camera's single shot plotted using a logarithmic intensity scale, together with the 656-cm⁻¹ CS₂ curve and the 630-cm⁻¹ phonon dephasing curve of LiNbO₃. The LiNbO₃ 630-cm⁻¹ phonon line was used to determine the resolution of the experimental setup. This line exhibits rapid rise and decay with no exponential tail and a full width at half-maximum of approximately 3 psec. The single pulse displayed corresponds to a shorter-than-average-continuum pulse and has a slightly faster rise time than the two other curves in the figure. The calcite curve shows a fast rise time and electronic response followed by a slow exponential phonon decay. The average value obtained from 10 laser shots yields a phonon dephasing time of 9 ± 1 psec. For a homogeneously broadened line of Lorentzian shape this value corresponds to a spontaneous Raman linewidth given by

$$\delta\nu = (\pi c\tau)^{-1} = 1.17 \text{ cm}^{-1},$$

in excellent agreement with linewidth measurements at room temperature by Park.¹⁸

In summary, we have described a new technique to determine the phonon and vibrational dephasing times in solids and liquids in real time. This technique, in which a phase-conjugate signal is studied using a 2-psec streak camera, was shown to measure accurately the dephasing times in CS₂ and calcite.

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References

1. A. Laubereau and W. Kaiser, *Rev. Mod. Phys.* **50**, 607 (1978).
2. R. R. Alfano and S. L. Shapiro, *Phys. Rev. Lett.* **20**, 1247 (1971).
3. C. H. Lee and D. Ricard, *Appl. Phys. Lett.* **32**, 168 (1978).
4. K. P. Cheung and D. H. Auston, *Phys. Rev. Lett.* **55**, 2152 (1985).
5. S. De Silvestri, J. G. Fujimoto, E. P. Ippen, E. B. Gamble, Jr., L. R. Williams, and K. A. Nelson, *Chem. Phys. Lett.* **116**, 146 (1985).
6. R. Leonhardt, W. Holzappel, W. Zinth, and W. Kaiser, *Chem. Phys. Lett.* **133**, 373 (1987).
7. S. K. Saha and R. W. Hellwarth, *Phys. Rev. A* **27**, 919 (1983).
8. R. Dorsinville, P. Delfyett, and R. R. Alfano, *Appl. Opt.* **26**, 3655 (1987).
9. R. R. Alfano and S. L. Shapiro, *Phys. Rev. Lett.* **24**, 584, 592, 1217 (1970).
10. R. Dorsinville, P. Delfyett, and R. R. Alfano, "Generation of 3-psec pulses by spectral selection of the supercontinuum generated by a 25-psec second-harmonic Nd:YAG laser pulse in a liquid," submitted to *Appl. Opt.*
11. J. M. Buchert, R. Dorsinville, P. Delfyett, and R. R. Alfano, in *Proceedings of the International Conference on Lasers '85* (STS, McLean, Va., 1986), p. 340.
12. M. A. Vasil'eva, J. Vischakas, V. Kabelka, and A. V. Masalov, *Opt. Commun.* **53**, 412 (1985).
13. A. Laubereau, in *Semiconductors Probed by Ultrafast Spectroscopy*, R. R. Alfano, ed. (Academic, New York, 1984), Vol. 1, Chap. 8.
14. A. Laubereau, G. Wochner, and W. Kaiser, *Opt. Commun.* **14**, 75 (1975).
15. A. S. Barker and R. Loudon, *Phys. Rev.* **158**, 433 (1967).
16. J. P. Heritage, *Appl. Phys. Lett.* **34**, 470 (1979).
17. W. R. L. Clements and B. P. Stoicheff, *Appl. Phys. Lett.* **12**, 246 (1968).
18. K. Park, *Phys. Lett.* **22**, 39 (1966).