High Time Resolution with Incoherent Light in the Raman-Fringe Decay

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In this Letter a new technique for measuring ultrafast vibrational dephasing is introduced that depends on the measurement of the decay of Raman interference fringes. The technique has been applied to the 524-cm^{-1} mode of liquid CH_3I and the 656-cm^{-1} mode of liquid CS_2, and the results are found to be in excellent agreement with previous experimental studies and with theory.

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Over the years, many time-resolved four-wave-mixing experiments have been undertaken, using coherent light pulses from either low- or high-repetition-rate lasers. The time resolution obtained in these experiments is determined by the duration of the pulses. However, a number of recent studies by various groups has shown that the time resolution in time-resolved degenerate four-wave mixing[1] and coherent Stokes Raman scattering[2,3] (CSRS) is determined by the coherence time of the pulses involved rather than their widths. Most of these studies have been performed only with low-repetition-rate lasers[4] and a careful comparison with theory is needed to determine the relevant physical parameters.

In this Letter the use of a new method to measure vibrational dephasing, the Raman-fringe decay (RFD), is proposed that can be used with high-repetition-rate unamplified stochastic dye-laser pulses. The advantages of the method are a higher signal-to-noise ratio compared to low-repetition-rate experiments and a signal that decays with the vibrational dephasing time T_2 rather than $T_2/2$.

The difference between CSRS and the method discussed in this Letter is that here *both* the excitation and the probe pulse pairs consist of a Stokes and a laser pulse (see Fig. 1). After laser and Stokes pulses have been made (nearly) resonant with the Raman active vibrational mode of interest and the probe pulse pair has been passed through a variable delay over a time interval τ, probe and excitation beams are made collinear and focused into the sample. The signal is then detected at the anti-Stokes frequency. Since the probe pulse pair is an exact replica of the excitation pulse pair, the electromagnetic field is of the form

$$[E_i(t)+E_i(t-\tau)e^{+i\omega_i\tau}]e^{-i\omega_i t}+\text{c.c.}, \tag{1}$$

where i can denote either a laser or Stokes pulse and $E_i(t)$ is a (stochastically fluctuating) slowly varying pulse envelope. Applying third-order perturbation theory leads to an expression for the anti-Stokes intensity that, in the rotating-wave, slowly-varying envelope, and dipole approximation,[5] has fourteen terms that do not oscillate at optical frequencies. Of those terms, ten correspond to ordinary coherent anti-Stokes Raman scattering (CARS). The remaining terms oscillate with $\omega_L-\omega_S$ as a function of the delay τ. These oscillations will be referred to as Raman fringes henceforth.

Now it is possible to discern two extreme cases. In one extreme, the pulses are much longer than the dephasing time but their coherence time is shorter. If the assumption is made that the Stokes field is coherent and cw, that the laser field is a stochastic function with autocorrelation function

$$\langle E_L(t)^* E_L(t')\rangle = \exp(-\Gamma|t-t'|), \tag{2}$$

and that laser and Stokes pulses are two-photon resonant with the vibrational mode, the amplitude of the oscillating part of the anti-Stokes intensity $I(\tau)$ (cf. Ref. 2) is found to be given by

$$I(\tau)=e^{-\gamma|\tau|}\frac{\Gamma(\Gamma+3\gamma)}{\gamma(\Gamma+\gamma)^2(\Gamma-\gamma)} +e^{-\Gamma|\tau|}\frac{\Gamma^2-\Gamma\gamma-4\gamma^2}{\gamma(\Gamma+\gamma)^2(\Gamma-\gamma)}, \tag{3}$$

where $\gamma=T_2^{-1}$ is the dephasing rate. If laser and Stokes pulses are not two-photon resonant, the equation for the anti-Stokes intensity becomes much more elaborate and exhibits beats at the two-photon detuning frequency (i.e., $\omega_L-\omega_S-\Omega_2+\Omega_1$). Equation (3) is very similar to the

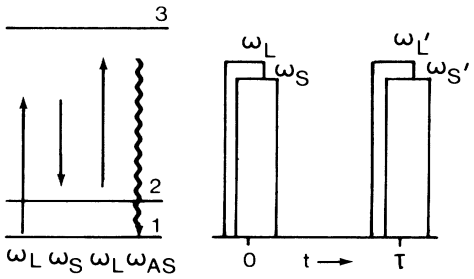

FIG. 1. The anti-Stokes field is generated by a CARS process in which the laser and Stokes pulses are nearly two-photon resonant. The inclusion of a Stokes pulse in the probe induces the Raman fringes discussed in text.

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main equation of Ref. 2 for the "off-resonance" case, except that it is much simpler. Note that the signal decays with the vibrational dephasing time T_2 whereas the stochastic CSRS intensity decays twice as fast; furthermore, the signal has no prominent coherence spike term and no background.

In the other extreme the (transform limited) pulses are shorter than the dephasing time of interest. An explicit calculation with two-sided exponential pulses shows that the form of the signal is very much the same as in the incoherent case, except that now the time resolution is determined by the pulse widths.

The above-described experiment has been performed on the 524-cm^{-1} mode in CH_3I and the 656-cm^{-1} mode in CS_2 with the experimental setup shown in Fig. 2. A cw mode-locked Ar-ion laser (Coherent CR10) synchronously pumps two dye lasers using rhodamine 6G, producing a laser and a Stokes beam with 55- and 35-mW power, respectively. The Stokes dye laser is always equipped with a three-plate birefringent filter resulting in 15-ps FWHM transform-limited pulses whereas the other dye laser is equipped with a single-plate birefringent filter leading to an autocorrelation trace with a 500-fs FWHM spike superimposed on a 15-ps FWHM background. After both laser and Stokes beams are split and recombined to form the excitation and probe pulse pairs, all beams are made collinear with a precision of 0.8 mrad and focused with a 5-cm lens into the sample. Two delay lines, with stepper motors having an accuracy of 1 μm, are used to delay the Stokes pulse with respect to the laser pulse and the probe pulse pair with respect to the excitation pulse pair. Cross correlation in a KDP (potassium dihydrogen phosphate) crystal is used to make all the pulses coincident. The anti-Stokes beam is separated from the other beams with a direct-vision prism and a grating monochromator and detected with a photomultiplier–photon-counting system. The samples are contained in a 1-cm quartz cuvette and consist either of CH_3I or CS_2, both of spectral quality and kept at a temperature of 293 ± 1.5 K (CH_3I is photochemically unstable and was therefore refreshed before each run).

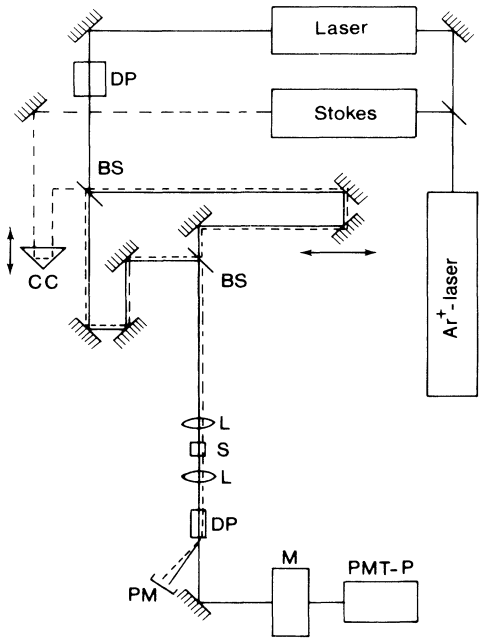

FIG. 2. Experimental setup for the measurement of the Raman-fringe decay. Note that the laser delay consists of mirrors mounted on a variable delay. The following symbols are used: BS, beam splitter; CC, corner cube; DP, direct-vision prism; L, lens; PM, power meter; S, sample; M, monochromator; PMT-P, photomultiplier-tube–photon-counter system.

With this setup the signal drowned in a huge background of spontaneous emission from the dye laser. Therefore, all experiments were performed with a RG600 low-pass colored glass filter in the Stokes beam (preserving its tunability) and a direct-vision prism in the laser beam. With the monochromator set at a resolution of 7 cm^{-1} (and an interference filter) this resulted in a signal intensity of 5000 photons/s on a small (100 Hz) background of residual spontaneous emission. The direct-vision prism has unfortunately the effect of limiting the effective bandwidth of the laser pulses resulting in a coherence time of 1.2 ps.

The inset of Fig. 3 shows the raw data obtained by scanning the probe pulse pair relative to the excitation pulse pair. The observed oscillations are not due to any mechanical instabilities since the oscillating part of the signal does depend on all four beams and the oscillation frequency changes from 656 to 524 cm^{-1} when the sample is changed from CS_2 to CH_3I. The raw data are digitally filtered by a broad-band fast Fourier filter to remove the high-frequency noise and the zero-frequency (i.e., not oscillating with frequency $\omega_L - \omega_S$) CARS sig-

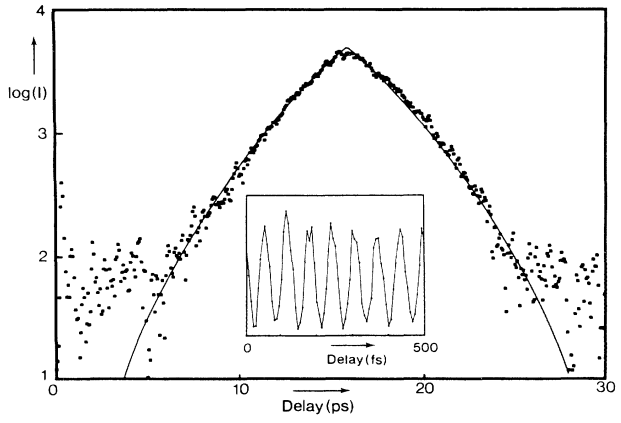

FIG. 3. The Raman-fringe decay in room-temperature CH_3I with incoherent laser pulses and two-photon resonance at 524 cm^{-1}. The smooth curve is a least-squares fit with the theory with $T_2 = 2.4$ ps. Inset: part of the raw data.

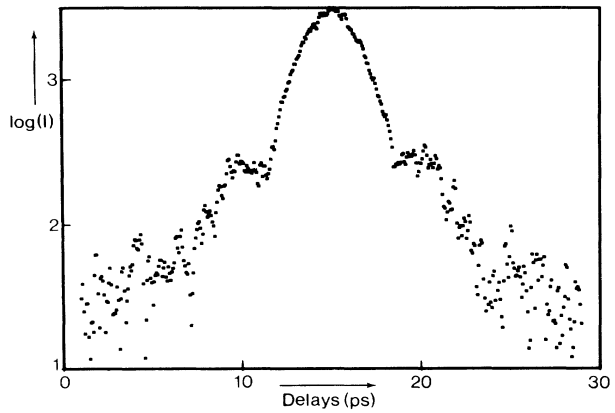

FIG. 4. The Raman-fringe decay in room-temperature CH_3I with incoherent laser pulses and two-photon detuning from 524 to 520 cm^{-1}.

nal. The fringe amplitude, averaged over 10-μm delay (which corresponds to 66.7 fs), is then determined as a function of delay.

Figure 3 shows the RFD measured in CH_3I with incoherent laser pulses. Although the coherence time of the laser pulses is only half as short as the vibrational dephasing time of CH_3I, it is found unambiguously that the signal decays with the expected[6,7] $T_2=2.4$ ps. The solid line in Fig. 3 is a least-squares fit of Eq. (3) to the data and yields the expected dephasing and coherence time. It should be noted that the interpretation is not hampered by a prodigious coherence spike as in incoherent CSRS[2] and that no baseline had to be subtracted.

If laser and Stokes pulses are slightly detuned from 524 to 520 cm^{-1}, the result of Fig. 4 is obtained which shows a beat with a period of 8 ps. This beating phenomenon, which is also predicted by the theory, can be seen much clearer in CS_2 due to its longer dephasing time. However, since the dephasing time in CS_2 is longer than the pulse widths ($T_2=20$ ps),[8] the interpretation is much harder.

Preliminary experiments have been performed in which the excitation and probe pulses are orthogonally polarized. As expected from theoretical considerations, the signal becomes asymmetric and decays much faster for negative delay if the signal is detected in the polarization directions of the probe pulse. In the same fashion it is expected that if the laser and Stokes pulses are orthogonally polarized, the signal decays with the rotational diffusion time rather than the vibrational dephasing time. Since the time resolution is, however, impaired by the direct-vision prism in the laser beam, it is as yet impossible to detect this very fast ($\cong 1.4$ ps)[6] relaxation.

The above-described technique is quite similar to time-resolved stimulated Raman scattering[8,9] and Fourier-transform coherent Raman spectroscopy.[10] However, the former technique relies on an expensive apparatus to extract the signal from an enormous background and the latter has again only been used with low-repetition-rate nanosecond lasers (and low-frequency rotational transitions).

In conclusion, it has been shown in this Letter that it is possible to perform experiments using incoherent pulses with cw mode-locked lasers in Raman scatterers without resonance enhancement. The described method pairs a high signal-to-noise ratio to high time resolution.

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