Ultrafast Raman Echoes in Liquid Acetonitrile

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(Received 3 September 1991)

Raman echoes are observed for the first time in the liquid phase. The symmetric methyl stretch of acetonitrile is shown to be homogeneously broadened, in disagreement with time-resolved coherent Raman scattering experiments and recent theory, but in agreement with line-shape studies and computer simulations. The vibration interacts primarily with rapid, collisional solvent motions, not with long-lived structural features.

PACS numbers: 78.47.+p, 33.70.Jg, 42.50.Md, 42.65.Re

Vibrational dephasing is an important probe of the molecular dynamics in liquids and of the influence of those dynamics on intramolecular coordinates. Vibrational dephasing has been extensively studied through analysis of isotropic Raman line shapes [1-6], as well as by time-resolved coherent Raman scattering (TRCRS) [7-9]. However, with these experiments, it is difficult to unambiguously determine the extent of inhomogeneous broadening of the line. This determination is critical for interpretation of the dephasing data and the underlying molecular processes causing the dephasing. We present the first results from liquid-phase Raman-echo experiments [10], which can unambiguously determine the homogeneity of vibrational lines [11].

In the absence of very rapid population relaxation or strong intermolecular resonance coupling, isotropic Raman line shapes are determined by the strength and correlation time of solvent-induced frequency perturbations [1,12]. Perturbations with correlation times long compared to their strength (typically on the order of 1 ps) cause inhomogeneous broadening of the line, and the linewidth is determined by the distribution of perturbations. Perturbations with correlation times short compared to their strength cause homogeneous broadening, and the width is determined by a dephasing time.

The common arguments over the degree of inhomogeneous broadening of vibrational lines are well illustrated by the symmetric methyl stretch of acetonitrile (ν_1, 2945 cm^{-1}), which has been extensively studied with contradictory conclusions. Based on detailed comparison of the Raman line-shape to Kubo line-shape [12] theory, a homogeneously broadened line has been found [2,3]. This is a difficult experiment, because the effects of weak hot bands, combination bands, and collision-induced processes in the wings of the line are difficult to completely eliminate. In addition, this method relies on the assumption of a Gaussian distribution of frequency perturbations. Although Gaussian inhomogeneous broadening of spectral lines is observed in many contexts, plausible mechanisms exist for non-Gaussian inhomogeneous broadening [13-15].

Several Raman studies have found that the behavior of the linewidth with temperature and pressure can be adequately explained by theories of homogeneous broadening due to rapid, binary collisions [2-5]. However, the same theory has also been used to justify substantial inhomogeneous broadening of the line [6].

Time-resolved coherent Raman scattering experiments have been proposed as a method of distinguishing homogeneous and inhomogeneous broadening [7]. Results indicating significant inhomogeneous broadening were found in many liquids [7-9]. For acetonitrile, the homogeneous contribution to the linewidth as measured by TRCRS was 2.8 cm^{-1} compared to the total isotropic Raman linewidth of 6.5 cm^{-1}. However, further work has concluded that under simple conditions, the TRCRS decay is exactly the Fourier transform of the isotropic Raman line and gives no information on the relative contributions of homogeneous and inhomogeneous broadening [11,16]. An analysis of additional effects occurring with high intensities indicated that propagation effects could cause an effective discrimination between homogeneous and inhomogeneous broadening [17,18]. This analysis has been criticized theoretically [11] and has not been further verified experimentally.

Support for inhomogeneous broadening has come from a theory developed by Schweizer and Chandler [19] from an idea introduced by George, Auweter, and Harris [8] that inhomogeneous broadening is caused by coupling of the vibration to long-lived fluctuations in the local density. Calculations by George, Auweter, and Harris using Schweizer-Chandler theory predict substantial inhomogeneous broadening in acetonitrile as well as other simple liquids [9,20]. However, the assumptions of this theory have been challenged by recent computer simulations of acetonitrile [15].

Loring and Mukamel have shown that an unambiguous determination of the extent of inhomogeneous broadening can only come from a higher-order nonlinear experiment [11]. Specifically, they demonstrated that the Raman-echo experiment can resolve the current controversy. Closely related to the spin echo of NMR [21] and the photon echo of electronic spectroscopy [22], the Raman echo [10] shows qualitatively different results for homogeneously and inhomogeneously broadened lines under very general assumptions.

The Raman echo has a low cross section as it first appears in seventh-order perturbation theory and corresponds to a $\chi^{(7)}$ process. It involves the synchronized application of five subpicosecond light pulses with two different frequencies at angles satisfying the phase-matching condition

$$\mathbf{k}_e = \mathbf{k}_{L3} + 2(\mathbf{k}_{L2} - \mathbf{k}_{S2}) - (\mathbf{k}_{L1} - \mathbf{k}_{S1}),$$

where $\mathbf{k}_e$ is the wave vector of the echo signal, $\mathbf{k}_{L1}$, $\mathbf{k}_{L2}$, and $\mathbf{k}_{L3}$ are the wave vectors of the higher-frequency pulses, and $\mathbf{k}_{S1}$ and $\mathbf{k}_{S2}$ are the wave vectors of the lower-frequency pulses. These technical difficulties have led one group to conclude that the Raman echo is impossible in small-molecule liquids [23]. We report here the first successful Raman echo in the liquid phase.

The experiment was performed with a pair of synchronously pumped dye lasers; one operating in the yellow at 570 nm and one operating in the red at 685 nm. To provide good synchronization, both dye lasers were pumped by a single cw mode-locked Nd-doped yttrium-aluminum-garnet (Nd:YAlG) laser whose output was compressed to 2 ps [24] before frequency doubling. The dye-laser pulse widths were broadened by the tuning elements to 450 fs for the yellow and 850 fs for the red. The time resolution of the experiments was determined by the shorter yellow pulse. The dye-laser pulses were amplified in two amplifier chains pumped by the second harmonic of a single Q-switched Nd:YAlG laser to typical powers of 0.55 mJ for the yellow pulse and 0.15 mJ for the red pulse.

The yellow pulse was split into three portions and the red into two. A yellow and a red pulse were combined collinearly and overlapped in time to form excitation pulse I, which coherently excited the sample by stimulated Raman scattering. A second pair of red and yellow pulses was similarly combined and synchronized to form excitation pulse II. Brought to the sample at a 125-mrad angle to and at a variable delay from excitation I, excitation II induced a rephasing of any inhomogeneous processes.

The remaining yellow pulse detected the amount of vibrational coherence at a variable time after this pulse sequence by anti-Stokes coherent Raman scattering. The probe was brought in at 125 mrad to excitation II, and anti-Stokes light was generated nearly collinearly with the probe. The 488-nm anti-Stokes light was isolated with interference filters and a pinhole before detection by a photomultiplier. The probe pulse was polarized perpendicular to the excitation pulses to avoid artifacts when the pulses overlapped. The signal was identified as the Raman echo by its appearance at the correct phase-matching angle and by its disappearance when any of the five pulses was blocked.

The pulses were focused to a diameter of 0.5 mm at the sample, which consisted of a 1-mm path-length cell of acetonitrile. The resulting intensity was just below the level where self-focusing caused severe distortion of the beams. From the amount of energy deposited in the sample, the pulse area is calculated to be very small, indicating that perturbation theory is adequate.

In a different experiment, simultaneous red and yellow pulses at an angle of 32 mrad excited a vibrational coherence which could be observed without a rephasing pulse. The coherence was measured by coherent scattering from a yellow probe pulse at 84 mrad from the yellow excitation pulse. The decay of this coherence is analogous to a free induction decay (FID). The intensity of the anti-Stokes light S_{FID} as a function of probe delay time τ is exactly the Fourier transform of the isotropic Raman line shape $\hat{L}$ and responds equivalently to the homogeneous, $\exp(-\tau/T_2)$, and inhomogeneous $\hat{L}_{\mathrm{inh}}$ portions of the line-shape transform:

$$S_{\mathrm{FID}}(\tau) = L^2(\tau) = \exp(-2\tau/T_2) L_{\mathrm{inh}}^2(\tau).$$

The FID for acetonitrile has been previously measured by Gale, Guyot-Sionnest, and Zheng [25]. Figure 1 shows the agreement between our measurement of the FID decay and the decay predicted from the line shape. In acetonitrile, the line shape is very close to Lorentzian [2], so the decay reduces to $S_{\mathrm{FID}}(\tau) \sim \exp(-2\Gamma\tau)$, where $\Gamma/\pi c$ is the measured full width at half maximum of 6.5 cm^{-1} [2]. The instrument response function has been represented by convolving a Gaussian with the decay. The zero time of the decay was independently determined by cross correlation measurements of the pulses in a second-harmonic crystal.

In contrast to the FID and line-shape measurements, the Raman-echo intensity S_{RE} responds differently to homogeneous and inhomogeneous broadening as τ_1, the time between excitations I and II, and τ_2, the time between excitation II and the probe, are varied [22]:

$$S_{\mathrm{RE}}(\tau_1, \tau_2) \sim \exp[-2(\tau_1 + \tau_2)/T_2] L_{\mathrm{inh}}^2(|\tau_1 - \tau_2|).$$

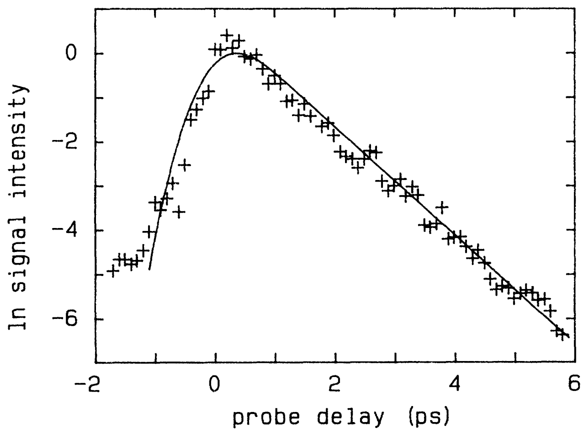

FIG. 1. Points: Logarithm of the Raman free-induction-decay intensity vs delay between excitation and probe. Line: Decay predicted from the isotropic Raman line shape.

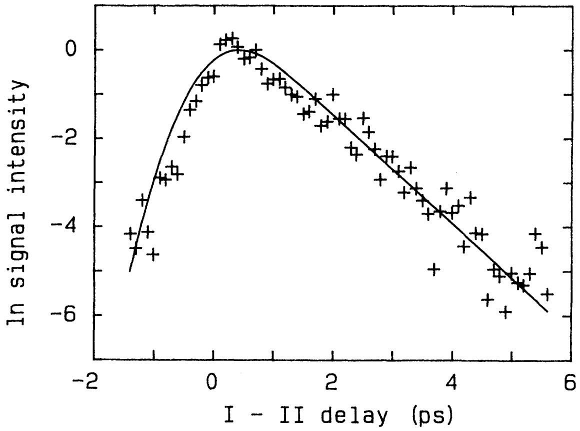

FIG. 2. Points: Logarithm of the Raman-echo intensity vs τ_1 with $\tau_2 = 1$ ps. Line: Decay predicted from the isotropic Raman line shape.

If τ_2 is held constant, and τ_1 is varied, the Raman-echo decay will exactly match the FID decay. This is demonstrated in Fig. 2 for $\tau_2 = 1$ ps.

If τ_1 is held constant and τ_2 is varied, the result depends on the amount of inhomogeneous broadening and the value of τ_1. If $\tau_1 = 0$, the decay will always exactly match the FID. If there is no inhomogeneous component to the line, increasing τ_1 will leave the decay in τ_2 unchanged.

Figure 3 shows that this case describes the experimental results exactly. As τ_1 increases from 0 to 4 ps, there is no change in the form of the decay with τ_2. In each case, the decay also duplicates the decay seen in the FID and in the Fourier transform of the line shape. Thus the symmetric methyl stretch is homogeneously broadened.

If a significant inhomogeneous component had been present, the decay would have been broadened and delayed as τ_1 increased. For example, if the inhomogeneous distribution in frequency is taken as a Gaussian with a standard deviation of Δ, the Raman-echo signal would be [22]

$$S_{\mathrm{RE}}(\tau_1,\tau_2) = \exp[-2(\tau_1+\tau_2)/T_2] \times \exp[-\Delta^2(\tau_2-\tau_1)^2] .$$

The dashed lines in Fig. 4 show the signal predicted for an inhomogeneous width of 5 cm^{-1} as suggested by TRCRS experiments [9]. Notice that for these parameters, which are typical of values expected in many systems, the signal is not expected to form a sharp, time-delayed echo. Rather, for modest amounts of inhomogeneous broadening, the decay is delayed and broadened for increasing values of τ_1. In contrast, a homogeneous line shows a prompt and unchanging decay for all values of τ_1.

Clearly, a significant inhomogeneous broadening is not present. Even an inhomogeneous component of only one-third of the total linewidth would have been readily detected, as shown by the solid line in Fig. 4. The range of values predicted using Schweizer-Chandler theory [9] is clearly inconsistent with the Raman-echo results. Either coupling to density fluctuations is weaker than predicted or the lifetime of the fluctuations is much shorter than assumed.

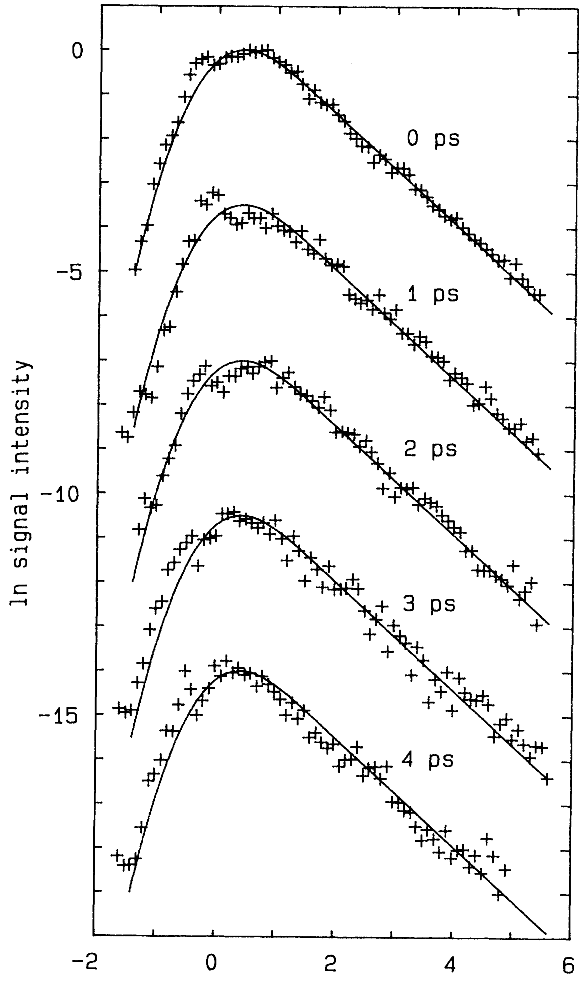

FIG. 3. Points: Logarithm of the Raman-echo intensity vs τ_2 for various values of τ_1. Lines: Identical decays predicted for a homogeneous vibrational line.

In conclusion, we have demonstrated that the Raman echo is a viable technique for determining the time scale of solvent perturbations of vibrations. In the case of the symmetric stretch of acetonitrile, the Raman line is entirely homogeneous, implying that the solvent perturbations have a lifetime much shorter than the 1.6-ps homogeneous dephasing time. The vibration does not couple significantly to any long-lived features of the liquid structure.

This work was supported by the National Science

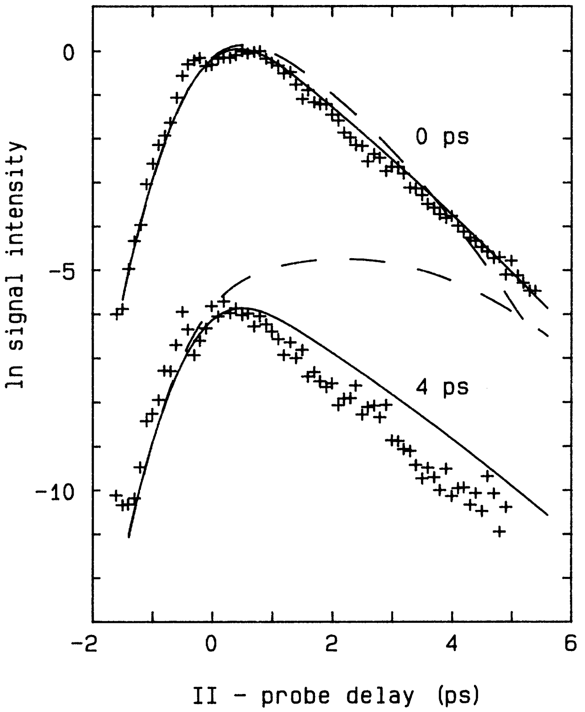

FIG. 4. Points: Logarithm of the Raman-echo intensity vs τ_2 for $\tau_1=0$ and 4 ps. Dashed lines: Predicted decays for a vibrational line with a substantial inhomogeneous broadening ($T_2=3.4$ ps, $\Delta=5.0$ cm^{-1}) typical of theoretical predictions [9]. Solid lines: Predicted decays for a vibrational line with 35% inhomogeneous broadening ($T_2=1.9$ ps, $\Delta=1.3$ cm^{-1}) indicating the sensitivity of the technique.

Foundation (CHE-8806381). M.B. is a Presidential Young Investigator. L.J.M. is a National Physical Science Consortium Fellow.

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