Ultrafast Raman Echo Measurements of Vibrational Dephasing and the Nature of Solvent−Solute Interactions

MARK BERG* AND
DAVID ANTON VANDEN BOUT

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

Received June 17, 1996

Since the first quantitative spectroscopic measurements were made, it has been clear that the states of molecules in solution are significantly perturbed by interactions with the solvent. In the case of vibrational states in solution, the spectroscopic transitions have an intrinsic width on the order of 1−10 cm^{-1}, several orders of magnitude broader than for isolated molecules. The general connection between line broadening and environmental perturbations was made in early work on spin resonance spectroscopy.[1−3] In the specific case of isotropic Raman transitions, the line is broadened because the solvent alters the vibrational motion.[4] The resulting line width is inversely related to the vibrational dephasing time, the time needed to randomize the phase of the vibrational motion. Given the line widths observed, typical solvent interactions are strong enough to randomize vibrational motion in solution within a few picoseconds.

Beginning in the early 1970s and continuing to the present, measurements of vibrational dephasing have been used as a window through which solvent−solute forces can be observed.[5,6] The need to understand these forces is growing as chemical physics attempts to treat solvent effects on chemical reactions in greater detail. Vibrational motion is a subset of the broader class of nuclear motions, which also includes the movement along the reaction coordinate for many reactions. The solvent interactions which cause vibrational dephasing are the same interactions which cause friction on reaction surfaces and alter the rates of reaction. Thus, a better understanding of the vibrational dynamics will contribute to a more complete understanding of solution-phase reaction dynamics.

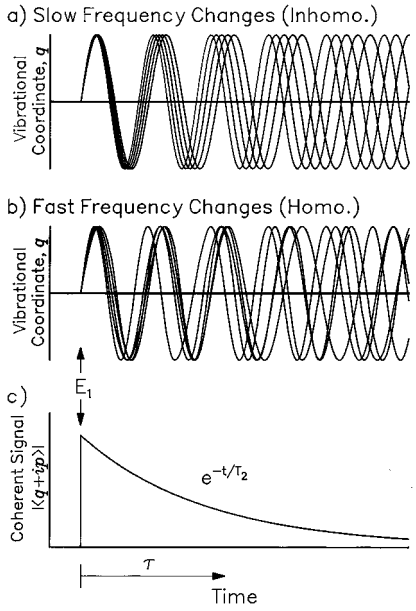

FIGURE 1. A schematic illustration of vibrational dephasing and the Raman free-induction-decay (FID) experiment. The excitation E_1 excites all the vibrators with the same phase. In (a), the solvent-induced frequency perturbations are long-lived. The individual oscillators get out of phase (a), and the net coherent signal (c) decays with the vibrational dephasing time T_2. In (b), the distribution of the frequency perturbations is twice as large as in (a), but the perturbation of each molecule changes quickly. The dephasing time T_2 and line width $\Gamma = (\pi T_2)^{-1}$ are similar to those in (a). Different combinations of perturbation strength and perturbation lifetime give qualitatively similar results in a Raman FID or line shape experiment.

A central quantity in vibrational dynamics is the vibrational dephasing time, which can be defined in the context of a classical vibration with the help of Figure 1. Imagine that the vibrations in a sample are excited such that every molecule has not only the same amplitude, but also the same phase of oscillation (Figure 1a,b). The energy of the vibration oscillates between the vibrational coordinate q and the vibrational momentum p, but the magnitude of the combined quantity $|q + ip|$ is constant for an individual, isolated molecule. To measure the coherence of the sample, $q + ip$ is averaged over all molecules before taking the magnitude; i.e., the coherence is $|\langle q + ip\rangle|$ (Figure 1c). Initially, all the molecules vibrate in phase, the terms in the average add constructively, and the coherence is large. With time, the molecules get out of phase with each other, there is cancellation between the different terms in the average, and the coherence decays. The time constant for this decay is the vibrational dephasing time T_2. If the decay is exponential, the

Mark Berg was born in Minnesota in 1958. He received a B.S. in chemistry from the University of Minnesota in 1979 and a Ph.D. in Chemistry in 1985 from the University of California at Berkeley, under the direction of Professor Charles B. Harris. He spent two years working as a postdoc with Professor Michael Fayer at Stanford University. In 1987, he joined the faculty at the University of Texas at Austin and, in 1994, moved to the University of South Carolina, where he is currently an Associate Professor. He has received the Dreyfus Distinguished Young Faculty, NSF Presidential Young Investigator, and Sloan Foundation Awards. His research centers on developing and applying new time-resolved spectroscopies to understanding molecular motions and interactions in liquids.

David Anton Vanden Bout was born in New York in 1968. He received his B.S. in chemistry from Duke University in 1990 and a Ph.D. in chemical physics in 1995 from the University of Texas at Austin, under the direction of Professor Mark Berg. He is currently working at the University of Minnesota as a National Science Foundation postdoctoral research fellow in Chemistry under the direction of Professor Paul F. Barbara. His research involves using high spatial resolution microscopy and spectroscopy to study the electronic and optical properties of heterogeneous materials.

* To whom correspondence should be addressed. Phone: (803) 777-1514. Fax: (803) 777-9521. E-mail: berg@psc.sc.edu.

(1) Anderson, P. W.; Weiss, P. R. *Rev. Mod. Phys.* **1953**, *25*, 269−276.
(2) Anderson, P. W. *J. Phys. Soc. Jpn.* **1954**, *9*, 316−339.
(3) Kubo, R. In *Fluctuation, Relaxation and Resonance in Magnetic Systems*, ter Haar, D., Ed.; Oliver and Boyd: London, 1962; pp 23−68.
(4) Gordon, R. G. *Adv. Mag. Reson.* **1968**, *3*, 1−42.
(5) Oxtoby, D. W. *Adv. Chem. Phys.* **1979**, *40*, 1−48.
(6) Morresi, A.; Mariani, L.; Distefano, M. R.; Giorgini, M. G. Vibrational Relaxation Processes in Isotropic Molecular Liquids. A Critical Comparison. *J. Raman Spectrosc.* **1995**, *26*, 179−216.

S0001-4842(95)00172-5 CCC: $14.00

corresponding Raman line has a FWHM $\Gamma = (\pi T_2)^{-1}$. Although this classical description is sufficient for a qualitative understanding of dephasing, a quantum description is needed for a quantitative description of real systems. The reader is referred to standard references in spin and optical spectroscopy.[7−9]

Although valuable, measurements of the dephasing time by themselves have an inherent limitation; they cannot unambiguously determine the time scale of the solvent forces. The time domain interpretation of the problem is shown in Figure 1. If the solvent forces change slowly, each molecule retains its individual frequency shift for a long time. This leads to a dephasing time which depends only on the width of the frequency distribution (Figure 1a). On the other hand, if the forces change rapidly, the frequency of an individual molecule is a function of time (Figure 1b). In this case, the dephasing time depends on both the distribution of frequency shifts and the rate of frequency changes. In the frequency domain, the case with long-lived frequency shifts is called inhomogeneous broadening and the case with short-lived shifts is called homogeneous broadening.

The difficulty in interpreting dephasing times arises because either homogeneous or inhomogeneous processes can give rise to the same dephasing time. In Figure 1, both examples (a) and (b) have similar dephasing times, even though the frequency distribution in (b) is twice as large as in (a) and the time scale of the frequency shifts is quite different. Furthermore, homogenous and inhomogeneous broadening are only limiting cases where the frequency shifts are very fast or very slow.[1−3,9] In liquids, time scales intermediate between the homogeneous and inhomogeneous limits are also possible, making the situation even more complicated. With only the measurement of a dephasing time, it is difficult to disentangle the effects of the strength of the perturbing forces from the time scale of the forces.

The importance of knowing the time scale of solvent-induced forces is illustrated by an influential hypothesis of Schwiezer and Chandler.[10] They noted that a typical solvent−solute interaction potential consists of two distinct regions: a steep repulsive region where the interaction changes within a distance of ∼0.1 atomic diameter, and a shallower attractive region, where the interaction changes within a distance of ∼1 atomic diameter. They further argued that each region gives rise to forces acting on a different time scale. As a molecule bounces between its nearest neighbors, the repulsive forces change dramatically within a few hundred femtoseconds. However, the distance traveled in these motions is not large enough to affect the long-ranged forces. Movement of ∼1 atomic diameter is needed to change the attractive forces, and diffusion of the solvent molecules is required. It takes several picoseconds for a molecule to diffuse one molecular diameter, and this is the time scale expected for variation of attractive solvent−solute forces. Although this is a compelling picture, it remains for experimentalists to verify it and to determine the relative importance of attractive and repulsive forces in real systems.

Originally, dephasing times were measured from isotropic spontaneous Raman line shapes.[5,6] More recently, the development of picosecond and femtosecond lasers has allowed direct time-domain measurements of the vibrational coherence.[11−14] We will call these experiments Raman free-induction decays (FIDs), but they are also known as time-resolved coherent anti-Stokes Raman scattering experiments. As in NMR, the Raman FID is exactly the Fourier transform of the Raman line shape.[15] The Raman FID is a third-order nonlinear spectroscopy, because it involves three incoming electric fields. Almost all established nonlinear spectroscopies are third order, including CARS, two-photon absorption, saturation spectroscopy, Kerr-effect spectroscopy, etc.[8]

To go beyond the vibrational dephasing time and obtain information on the time scale of the solvent forces requires a seventh-order time-domain Raman spectroscopy, the Raman echo. Hartmann introduced the concept of the Raman echo in 1968[16] and later applied it to thallium vapor by using the relatively high cross section of a resonantly enhanced electronic Raman transition.[17,18] Buckner et al. performed a true vibrational Raman echo on nitrogen gas in 1984.[19] Loring and Mukamel clearly demonstrated theoretically that the Raman echo is directly sensitive to the time scale of solvent forces and that this sensitivity is a direct consequence of the high-order nonlinearity measured.[15] However, the very small cross section associated with such a high-order spectroscopy along with the high time resolution needed in liquids cast doubt on whether the Raman echo was a practical experiment for examining solvent−solute interactions.[20−22]

However, beginning in 1991, we have performed Raman echo experiments on a number of liquids.[23−26]

(7) Slichter, C. P. *Principles of Magnetic Resonance*; Springer-Verlag: New York, 1990.
(8) Levenson, M. *Introduction to Nonlinear Laser Spectroscopy*; Academic Press: New York, 1982.
(9) Mukamel, S. *Principles of Nonlinear Optical Spectroscopy*; Oxford University Press: Oxford, 1995.
(10) Schweizer, K. S.; Chandler, D. Vibrational Dephasing Frequency Shifts of Polyatomic Molecules in Solution. *J. Chem. Phys.* **1982**, *76*, 2296−2314.
(11) Zinth, W.; Leonhardt, R.; Holzapfel, W.; Kaiser, W. Fast Dephasing Processes Studied with a Femtosecond Coherent Raman System. *IEEE J. Quantum Electron.* **1988**, *QE-24*, 455−459.
(12) Inaba, R.; Okamoto, H.; Yoshihara, K.; Tasumi, M. Femtosecond Time-Resolved Coherent Anti-Stokes Raman Scattering of the CC Stretching in Liquid Alkynes. *J. Phys. Chem.* **1993**, *97*, 7815−7819.
(13) Joo, T.; Dugan, M. A.; Albrecht, A. C. Time-Resolved Coherent Stokes Raman Spectroscopy of Benzene. *Chem. Phys. Lett.* **1991**, *177*, 4−10.
(14) Purucker, H.-G.; Tunkin, V.; Laubereau, A. Femtosecond Three-Color CARS of Liquids with Magic Polarization Conditions. *J. Raman Spectrosc.* **1993**, *24*, 453−458.
(15) Loring, R. F.; Mukamel, S. *J. Chem. Phys.* **1985**, *83*, 2116−2128.
(16) Hartmann, S. R. Photon, Spin Raman Echoes. *IEEE J. Quantum Electron.* **1968**, *QE-4*, 802−807.
(17) Leung, K. P.; Mossberg, T. W.; Hartmann, S. R. Observation Density Dependence of the Raman Echo in an Atomic Thallium Vapor. *Opt. Commun.* **1982**, *43*, 145−150.
(18) Leung, K. P.; Mossberg, T. W.; Hartmann, S. R. Noble-Gas-Induced Collisional Broadening of the 6P1/2−6P3/2 Transition of Tl Measured by Raman Echoes. *Phys. Rev. A* **1982**, *25*, 3097−3101.
(19) Brückner, V.; Bente, E. A. J. M.; Langelaar, J.; Bebelaar, D.; Van Voorst, J. D. W. Raman Echo on a Picosecond Timescale in Nitrogen Gas. *Opt. Commun.* **1984**, *51*, 49−52.
(20) Müller, M.; Wynne, K.; Van Voorst, J. D. W. The Interpretation of Echo Experiments. *Chem. Phys.* **1988**, *125*, 225−230.
(21) Wynne, K.; Müller, M.; Brandt, D.; Van Voorst, J. D. W. Diagramatic Density Matrix Analysis of the Raman Photon Echo. *Chem. Phys.* **1988**, *125*, 211−223.
(22) Müller, M.; Wynne, K.; Van Voorst, J. D. W. No Raman Echo in Liquid Nitrogen. *Chem. Phys.* **1988**, *128*, 549−553.
(23) Vanden Bout, D.; Muller, L.; Berg, M. *Phys. Rev. Lett.* **1991**, *67*, 3700−3703.

Raman echo experiments have also been performed successfully by Tominaga and co-workers.[27−29] In addition to the Raman echo, several other high-order nonlinear vibrational spectroscopies have been developed more recently. In the last few years, closely related infrared echo experiments have been performed by Fayer and co-workers.[30] Several groups have also begun to explore fifth-order experiments to look at intermolecular, rather than intramolecular, vibrations[31−38] and overtone dephasing.[39] The introduction of these high-order spectroscopies promises to open a new chapter in the understanding of liquid dynamics.

In this Account, we will focus on a series of Raman echo experiments we have performed on the symmetric methyl stretch in several liquids.[23−25] Because the methyl stretch is a well-localized vibration, the vibrator in each system is essentially the same. However, the solvent environment changes, altering the dephasing dynamics. This series of experiments is a good illustration of how the introduction of a new spectroscopy can lead to a deeper understanding of molecular interactions in solution.

Principles of the Raman Echo

The Raman echo is best understood by first examining the simpler Raman free-induction-decay (FID) experiment in detail (Figure 1). In the Raman FID, the vibration is first excited at time $\tau = 0$ by simultaneously applying two pulses of visible light of differing frequency (E_1). The beat frequency corresponding to the difference of the two visible frequencies matches the vibrational frequency. By means of this stimulated Raman process, a low-frequency vibration is excited with high-frequency, visible light.

A crucial property of stimulated Raman is that the vibrational excitation is coherent; i.e., all the molecules in the sample initially vibrate with the same phase. During the excitation, each vibration matches its phase

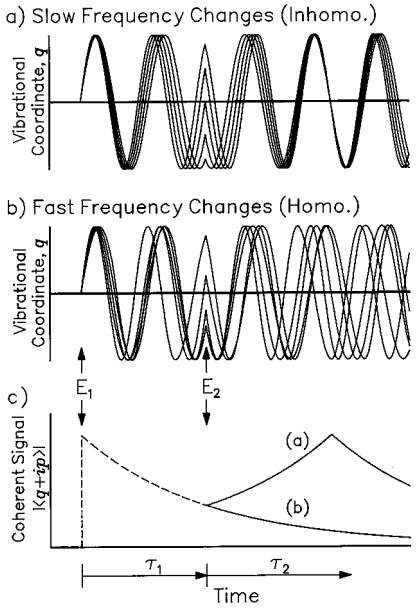

FIGURE 2. A schematic illustration of the Raman echo experiment. The initial excitation E_1 excites all the vibrators with the same phase. During the time τ_1, the vibrators begin losing their phase coherence. The second excitation E_2 reverses the momentum of the vibrators. If the vibrators continue at their original frequencies (a), the dephasing will be reversed, and the coherent signal will recur (c). If the vibrators change frequency during the experiment (b), the dephasing is unchanged relative to the FID (c). The Raman echo produces qualitatively different results depending on the lifetime of the solvent-induced frequency perturbations.

to the phase of the driving beat frequency of the light fields, and therefore all the vibrational phases match each other. As with incoherent excitation, the presence of vibrationally excited molecules can be detected by anti-Stokes Raman scattering of another pulse of light. However, with coherent vibrations, the anti-Stokes light fields emitted by each molecule have a definite phase relationship. Along one particular direction, all the fields add constructively, and there is a tremendous amplification of the anti-Stokes light. The coherent anti-Stokes light is emitted as a highly directional beam in a unique direction determined by the appropriate phase-matching equation.[9] The intensity of this beam is directly proportional to the square of the vibrational coherence, $|\langle q+ip\rangle|^2$. The dephasing time is measured by measuring the strength of this beam as a function of delay time between the excitation and scattering pulses.

In the Raman echo, a second excitation E_2 (again consisting of two visible light pulses) is applied between the first excitation and the detection pulse (Figure 2). Although the second excitation is physically identical to the first, its effect is quite different. The vibration is deexcited and then reexcited with exactly the same amplitude, but opposite momentum. During the period τ_1 between the two excitations, the vibrations start to dephase. If each molecule has a fixed frequency shift, the momentum reversal induced by E_2 sets up the vibrations to rephase during the time period τ_2 (Figure 2a). The coherent signal in the Raman echo (Figure 2c, solid curve a) shows an increase relative to the signal seen in the Raman FID. The effect is analogous to the one seen in

(24) Muller, L. J.; Vanden Bout, D.; Berg, M. *J. Chem. Phys.* **1993**, *99*, 810−819.
(25) Vanden Bout, D.; Freitas, J. E.; Berg, M. *Chem. Phys. Lett.* **1994**, *229*, 87−92.
(26) Vanden Bout, D.; Berg, M. Ultrafast Raman Echo Experiments in Liquids. *J. Raman Spectrosc.* **1995**, *26*, 503−511.
(27) Inaba, R.; Tominaga, K.; Tasumi, M.; Nelson, K. A.; Yoshihara, K. *Chem. Phys. Lett.* **1993**, *211*, 183−188.
(28) Tominaga, K.; Inaba, R.; Kang, T. J.; Naitoh, Y.; Nelson, K. A.; Tasumi, M.; Yoshihara, K. *Proceedings of the XIV International Conference on Raman Spectroscopy*; Wiley: New York, 1994.
(29) Yoshihara, K.; Inaba, R.; Okamoto, H.; Tasumi, M.; Tominaga, K.; Nelson, K. A. In *Femtosecond Reaction Dynamics*; Wiersma, D., Ed.; North-Holland: Amsterdam, 1994.
(30) Tokmakoff, A.; Fayer, M. D. *Acc. Chem. Res.* **1995**, *28*, 437−445.
(31) Tanimura, Y.; Mukamel, S. *J. Chem. Phys.* **1993**, *99*, 9496−9511.
(32) Khidekel, V.; Mukamel, S. *Chem. Phys. Lett.* **1995**, *240*, 304−314.
(33) Palese, S.; Buontempo, J. T.; Schilling, L.; Lotshaw, W. T.; Tanimura, Y.; Mukamel, S.; Miller, R. J. D. *J. Phys. Chem.* **1994**, *98*, 12466−12470.
(34) Tominaga, K.; Keogh, G. P., Naitoh, Y.; Yoshihara, K. *J. Raman Spectrosc.* **1995**, *26*, 495−501.
(35) Tominaga, K.; Yoshihara, K. Fifth-Order Optical Response of Liquid CS2 Observed by Ultrafast Nonresonant Six-Wave Mixing. *Phys. Rev. Lett.* **1995**, *74*, 3061−3064.
(36) Tominaga, K.; Yoshihara, K. Fifth-Order Nonlinear Spectroscopy on the Low-Frequency Modes of Liquid CS_2. *J. Chem. Phys.* **1996**, *104*, 4419−4426.
(37) Tominaga, K.; Yoshihara, K. Temporally Two-Dimensional Femtosecond Spectroscopy of Binary Mixtures of CS_2. *J. Chem. Phys.* **1996**, *104*, 1159−1162.
(38) Steffan, T.; Duppen, K. Femtosecond Two-Dimensional Spectroscopy of Molecular Motion in Liquids. *Phys. Rev. Lett.* **1996**, *76*, 1224−1227.
(39) Tominaga, K.; Yoshihara, K. Overtone Vibrational Dephasing in Liquids Studied by Femtosecond Fifth-Order Nonlinear Spectroscopy. *Phys. Rev. Lett.* **1996**, *76*, 987−990.

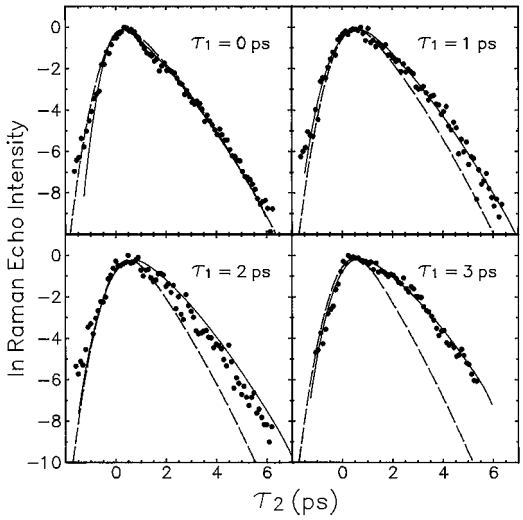

FIGURE 3. Raman echo data from a $CH_3I/CDCl_3$ mixture (●). As τ_1 increases, the echo data show an increasing deviation from the FID (dashed curve), indicating the presence of inhomogeneous broadening. The data are fit with a model which includes spectral diffusion within the inhomogeneous distribution (solid curve). The inhomogeneous broadening is attributed to concentration fluctuations (see Figure 4).

the spin echo on NMR transitions[7] or the photon echo on electronic transitions.[8,9,40]

On the other hand, if the solvent forces and resulting frequency perturbations change during the experiment, the second pulse cannot induce a recurrence of the coherence (Figure 2b). The hidden order which is apparent at long times in the inhomogeneous case (Figure 1a) is not present in the homogeneous case (Figure 1b), and the echo experiment cannot recover a well-ordered coherence. The dephasing is identical to the dephasing seen in the FID experiment (Figure 2c, solid curve b). By comparing the Raman echo and FID experiments, long-lived frequency perturbations can be distinguished from short-lived perturbations.

When the Raman echo is introduced, an inevitable question is, why does the second excitation have a different effect from the first excitation? Why does it create a deexcitation and reexcitation, rather than a single excitation as the first pulses did? If such double interactions are possible, why do they not occur during the first excitation? If both single and double interactions are allowed, why not triple, quadruple, and so on? In fact, all these other possibilities and their various combinations do occur. However, by correctly arranging the angles of the incident pulses, the constructive interference needed to generate coherent anti-Stokes scattering can be limited to only the combination responsible for the Raman echo.[9] The second excitation acts differently from the first, because we deliberately select out interaction sequences in which the two excitations have behaved differently.

Slow Frequency Shifts from Concentration Fluctuations

An example of rephasing is shown in Figure 3, which presents Raman echo and FID data on the symmetric methyl stretch of CH_3I in a 50:50 mixture with $CDCl_3$.[24] When the initial dephasing period τ_1 is short, the rephasing effect is weak, because there is little dephasing to undo. However, as τ_1 becomes longer, it becomes more apparent that the echo signal rises above the FID signal, indicating the presence of long-lived frequency shifts. However, the rephasing is not complete, i.e., the signal never returns to the initial level of $\tau_2 = 0$, indicating that there is also a source of homogeneous broadening present.

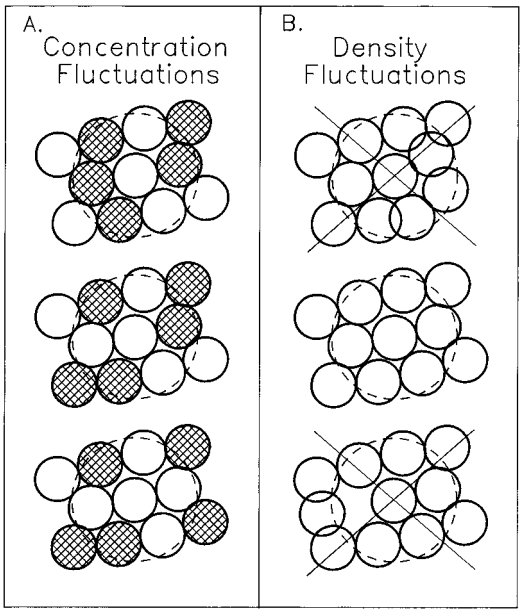

FIGURE 4. Schematic illustrations of concentration and density fluctuations. The vibrational frequency of the central molecule is affected by other molecules within ~1 molecular diameter (dashed circle). (A) The vibrational frequency is sensitive to the composition of neighboring molecules. If the average composition is 50:50 (center), it is easy to create fluctuations in the local concentration by exchanging molecules of different composition (top and bottom). (B) The vibrational frequency is sensitive to the number of neighboring molecules. Most attempts to insert (top) or remove (bottom) an extra molecule from the first solvation sphere will cause unacceptable overlap between molecular cores.

In this system, the long-lived frequency shifts are caused by concentration fluctuations (Figure 4a). The frequency of each methyl group is affected by only a few neighboring molecules. Although the average composition of the mixture is 50:50, an individual molecule will see significant statistical fluctuations in the number of each species in its local neighborhood. Changing the composition of the local neighborhood requires diffusion of molecules over long distances, which takes a relatively long time.

Qualitatively, this explanation is very satisfactory. However, when we applied a quantitative model, small discrepancies arose. The model must account for a large amount of data in addition to the Raman echo decays: the spontaneous Raman line shape, the changes in line width with changing concentration, and the shape of the Raman FID. Our initial models always predicted stronger echo signals at long times than were observed experimentally. Finally, we realized that although diffusion is slow, it may not be negligible over the entire time range of the experiments. When a slow diffusive interchange of the concentration fluctuations was included, the data fits became quantitative (Figure 3).

(40) Walsh, C. A.; Berg, M.; Narasimhan, L. R. Fayer, M. D. Probing Intermolecular Interacions with Picosecond Photon Echo Experiments. *Acc. Chem. Res.* **1987**, *20*, 120−126.

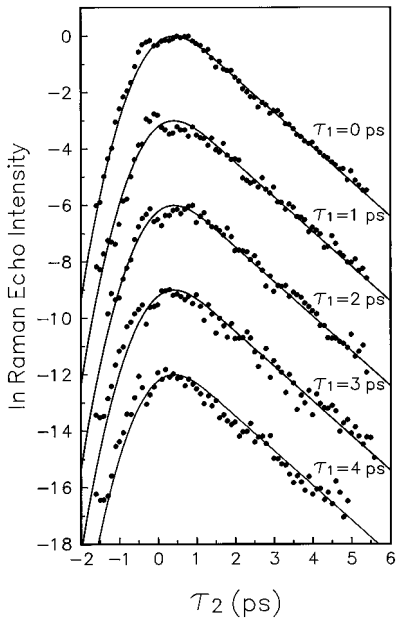

FIGURE 5. Raman echo data from neat CH_3CN at various values of τ_1 (●) compared to Raman FID decays (solid curves). The lack of any detectable rephasing indicates a homogeneously broadened line. Inhomogeneous broadening from density fluctuations (see Figure 4) is not significant.

The parameters derived from the model are illuminating. Each methyl group is affected by 5−6 solvent molecules. This number corresponds to the number of molecules in the first solvation sphere. The lifetime of concentration fluctuations is ∼6 ps, just the time expected for diffusion in and out of the first solvation sphere. Thus, this interaction corresponds to Schweizer and Chandler's prediction of a slow, attractive force with a range of ∼1 molecular diameter.

Role of Density Fluctuations

In the mixed solvent examined above, long-lived frequency changes were due to fluctuations in the number of each species in the first solvation shell of the vibrator. In a pure solvent, it is natural to ask if fluctuations in the number of solvent molecules in the first solvation shell can play the same role; i.e., can fluctuations in the local density create inhomogeneous broadening? Arguments over this issue have persisted in the literature for years. In the specific case of the symmetric methyl stretch of acetonitrile (CH_3CN), both theory and line shape experiments have come to varying conclusions regarding the existence of significant inhomogeneous broadening due to density fluctuations.[23]

The Raman echo experiment provides an unambiguous answer (Figure 5).[23] The Raman echo and Raman FID have the same decay, even as τ_1 becomes large. Inhomogeneous broadening due to density fluctuations is insignificant. Inaba et al. also found no inhomogeneous broadening for the CN vibration in pure benzonitrile.[27]

Given that the same methyl vibration is involved in both the $CH_3I/CDCl_3$ and CH_3CN systems, why are concentration fluctuations more effective than density fluctuations? To answer this question, we created a simple theoretical model for the inhomogeneous line width Δ of a mixture of A and B molecules in which both the concentration and density can fluctuate simultaneously, with the result[24]

$$\Delta^2 = \chi\frac{(x_A\delta\omega_A + x_B\delta\omega_B)^2}{N} + x_Ax_B\frac{(\delta\omega_A - \delta\omega_B)^2}{N} \quad (1)$$

In this expression, $\delta\omega_A$ and $\delta\omega_B$ are the gas-to-liquid frequency shifts for pure A and B, respectively. The mole fractions of A and B are x_A and x_B, and N is the number of solvent molecules interacting with the vibrator. The first term represents the effect of density fluctuations, the second term the effect of concentration fluctuations.

An examination of the terms in eq 1 shows no significant difference in the expected contributions of density and concentration fluctuations, except for χ, the ratio of the liquid compressibility to the compressibility of an ideal gas. For typical liquids, $\chi = 0.02-0.05$, causing a substantial suppression of the density fluctuations. Small values of χ result from correlations in the positions of solvent molecules.[41] Most attempts to move a solvent molecule either into or out of the first solvation shell creates a conflict with the positions of other molecules (Figure 4b). On the other hand, the compositions of nearby solvent molecules are uncorrelated in the ideal mixing approximation. The composition of a molecule in the first solvation sphere can be changed without regard to other solvent molecules (Figure 4a), so concentration fluctuations are more likely.

This example illustrates an important principle. In evaluating an interaction mechanism as a potential cause of inhomogeneous broadening, a strong interaction strength and slow dynamics are not sufficient. The correlations in the corresponding solvent coordinate must be sufficiently weak to allow substantial fluctuations.

Solvent-Assisted IVR

While the line width of the symmetric methyl stretch in both CH_3CN and $CH_3I/CDCl_3$ systems is around 7 cm^{-1}, the same vibration in ethanol is more than twice as broad at 15 cm^{-1}. Apparently, an additional source of broadening exists in ethanol. However, the broadening is not reduced at low temperatures. Just below the glass transition (80 K), where all diffusive motions have ceased, the line width is 19 cm^{-1}. At 12 K, the line width actually increases further to 23 cm^{-1}.[25]

These results clearly preclude homogeneous pure dephasing as the line broadening mechanism. As the temperature is lowered, the motions of the solvent must either slow or decrease in amplitude. Both effects reduce the rate of homogeneous pure dephasing and narrow the line width. Because no narrowing is seen over a 25-fold change in temperature, homogeneous pure dephasing cannot be important.

On the other hand, the highly structured nature of a hydrogen-bonded solvent like ethanol makes inhomogeneous broadening an attractive possibility. Inhomogeneous broadening is expected to be roughly temperature independent. However, Raman echo measurements show that this appealing hypothesis is wrong.[25] No rephasing

(41) McQuarrie, D. A. *Statistical Mechanics*; Harper Collins: New York, 1976; Section 13-5.

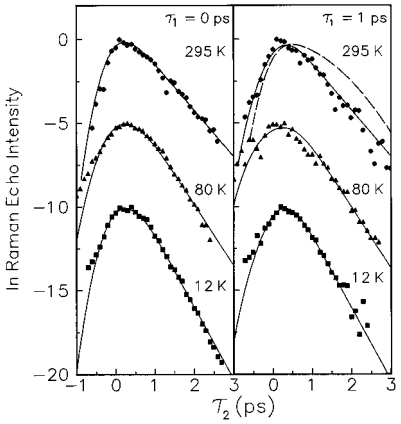

FIGURE 6. Raman echo data from ethanol-1,1-d_2 (●) compared to Raman FID decays (solid curves). Inhomogeneous broadening is not found at room temperature, nor just below the glass transition (80 K), nor in the low-temperature glass (12 K). If the additional line width in ethanol compared to CH_3CN were due to inhomogeneous broadening, significant rephasing in the echo would be expected (dashed curve).

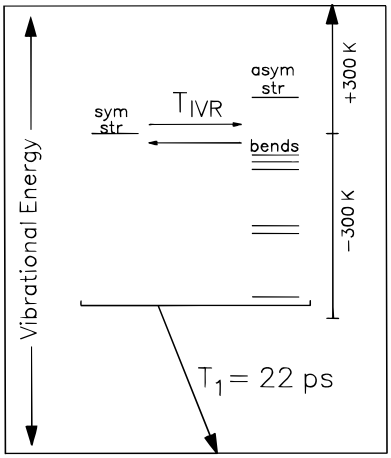

FIGURE 7. Dephasing due to intramolecular vibrational redistribution in ethanol is proposed. The symmetric methyl stretch is initially excited, but rapidly equilibrates with one or more modes within *kT* (the asym CH stretch and/or CH bend overtones). Dephasing occurs with this rapid equilibration time T_{IVR}. However, population remains in the symmetric methyl stretch after equilibration. Relaxation from this group of states to lower states causes the final relaxation of the population to zero, which is measured as T_1 in energy relaxation experiments.[42−44]

is seen at room temperature, just below the glass transition, or at 12 K (Figure 6).

Other mechanisms for dephasing can also be eliminated. Resonant energy transfer, in which the vibrational energy hops to the identical vibration of a nearby molecule, can cause dephasing.[5] However, isotopic dilution studies eliminate this possibility. A fast energy relaxation time (commonly denoted T_1) could also cause line broadening. However, several different measurements have found T_1 = 22 ps, much too long to affect the line width.[42−44]

At this point, all of the commonly discussed line broadening mechanisms have been eliminated. We suggest that a process which we call solvent-assisted intramolecular vibrational redistribution (IVR) is responsible. The methyl group is known to have several vibrational levels (the asymmetric stretch and overtones of CH bends) which are both close to the symmetric stretch in frequency and involve motions of the same atoms (Figure 7). It is believed that vibrational relaxation of the symmetric stretch involves initial equilibration between the asymmetric stretch and one or more of these other levels.[44,45] Because the levels are within *kT* of each other, this equilibration does not completely deplete the population of the asymmetric stretch, although it will cause complete dephasing. Unlike gas-phase IVR, the modes are far enough apart to be well-defined eigenstates in the isolated molecule. The relaxation is only possible because the solvent provides the coupling and the energy bath needed to make transitions.

The time for this process (T_{IVR}) is known to be faster than 10 ps, but has never been clearly resolved.[44,45] We suggest that T_{IVR} is fast enough to be the dominant source of line broadening. This model implies rates as fast as 360 fs.

This suggestion has serious implications for the interpretation of line widths. It is generally assumed that the homogeneous line width is caused by pure dephasing, i.e., frequency shifts without change of vibrational state, in large part because measurements of vibrational population relaxation give times too long to account for the observed widths. However, the final decay of the population to zero is governed by the irreversible relaxation out of the entire set of interacting modes to lower energy levels (T_1). A rapid and partial decay with time T_{IVR} should be present at early times, but current population decay experiments do not have the time resolution needed to observe this transient. Thus, existing population relaxation experiments do not guarantee that pure dephasing rather than solvent-assisted IVR is the dominant line broadening mechanism.

Concluding Remarks

We have discussed three different systems which consist of essentially the same vibrating methyl group immersed in different environments. Different behavior was found in each case. Looking at the IR echo studies of metal carbonyls by the Fayer group shows yet another pattern of behavior with strong inhomogeneous broadening at low temperature, and even at room temperature in one solvent.[30] Apparently, many types of solvent−solute interaction are possible, and different line broadening mechanisms dominate in different systems. Although it is too early to outline a complete picture of these interactions, it is already clear that echo experiments are raising basic questions and challenging accepted assumptions in what may have appeared to be a settled field.

Many important questions remain to be answered. Most obviously, a variety of modes must be examined to distinguish what is typical and what is anomalous behav-

(42) Laubereau, A.; von der Linde, D.; Kaiser, W. Direct Measurement of the Vibrational Lifetimes of Molecules in Liquids. *Phys. Rev. Lett.* **1972**, *28*, 1162−1165.
(43) Alfano, R. R.; Shapiro, S. L. Establishment of a Molcular-Vibration Decay Route in a Liquid. *Phys. Rev. Lett.* **1972**, *29*, 1655−1658.
(44) Laubereau, A.; Kehl, G.; Kaiser, W. Picosecond Spectroscopy of Molecular Vibrations in Liquids. A Vibrational Botteneck in Ethanol. *Opt. Commun.* **1974**, *11*, 74−77.
(45) Spanner, K.; Laubereau, A.; Kaiser, W. Vibrational Energy Redistribution of Polyatomic Molecules in Liquids after Ultrashort Infrared Excitation. *Chem. Phys. Lett.* **1976**, *44*, 88−92.

ior. Temperature-dependent studies in supercooled liquids and glasses will become increasingly important. Compared to existing studies over the equilibrium liquid range, these systems allow many orders of magnitude greater change in solvent properties. Existing theories of vibrational dephasing do not even predict physically reasonable results for supercooled systems. Electronic dephasing in liquids and glasses, which is also a very active area of current research, needs to be compared in detail to vibrational dephasing. Vibrational and electronic dephasing in the same solvent must arise from the same set of solvent dynamics, yet a serious effort to interrelate the two is lacking. Finally, a better understanding of vibrational energy relaxation and redistribution is linked to understanding vibrational dephasing. It is possible that in many systems the interaction of a vibration with the bath of intramolecular modes is just as important as the interaction with the bath of solvent molecules.

Fortunately, new tools are available to answer these questions. In addition to new information available from the Raman echo itself, the success of the Raman echo augurs well for other, as yet untried, high-order spectroscopies. The steady and rapid improvements in ultrafast lasers are making high-order experiments ever more practical. The experiments presented here are expected to be only the beginnings of an increasingly clear picture of molecular interaction dynamics in liquids which will develop in the near future.

We thank Dr. Laura J. Muller and Dr. John E. Freitas for their important contributions to this work. We also thank Professor Richard McPhail and Dr. Xun Pan of Duke University for providing us with Raman line shape data on the $CH_3I/CDCl_3$ *system. This work was supported by the National Science Foundation.*

AR950172E