

Vibrational photon echoes in a liquid and glass: Room temperature to 10 K

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Picosecond infrared vibrational photon echo experiments were performed on the asymmetric CO stretching mode (1983 cm^{-1}) of tungsten hexacarbonyl in 2-methylpentane from room temperature to 10 K using a free electron laser. This is the first report of a room temperature infrared vibrational photon echo in a liquid.

Molecular vibrations are involved in a vast number of physical, chemical, and biological processes in condensed phases. The coupling between individual molecular vibrations and external degrees of freedom (heat bath) is responsible for fluctuations in the structure and energy levels of a molecule, the flow of energy into and out of molecules, and thermally activated processes. Vibrational dynamics are intimately related to the reactivity of chemical systems. In spite of the importance of the coupling of molecular vibrations to a heat bath, relatively little is known about the temperature-dependent dynamics of molecular vibrations in liquids and glasses.

A fundamental quantity that describes the dynamics of a molecular vibration in liquids or other condensed matter systems is the homogeneous dephasing time, T_2 . In principle, T_2 can be obtained from analysis of vibrational lineshapes. However, in liquids and glasses a vibrational absorption line can have a contribution from inhomogeneous broadening. The inhomogeneous line in a glass arises from the differing perturbations of the vibrational energy levels caused by the variety of local solvent structures that surround the molecule of interest. Inhomogeneous broadening masks the dynamic information contained in the homogeneous line. In low temperature glasses, inhomogeneous broadening overwhelms any contribution from the homogeneous line to the observed absorption spectrum. In a liquid, inhomogeneous broadening also comes about from a distribution of environments that result in a spread of vibrational transition energies. Unlike a glass, local structures in a liquid evolve rapidly and assume all possible configurations, so that a spectral line in a liquid will be dynamic on some time scale. However, if the time scale for structural evolution that randomizes the transition energy across the entire absorption line is long compared to other dephasing processes, the homogeneous line is masked. Infrared vibrational photon echo experiments can be used to remove the inhomogeneous contribution to an absorption line and reveal the true homogeneous line shape. As will be shown below, even in room temperature liquids a significant contribution to a vibrational spectral line may come from inhomogeneous broadening.

A description of dephasing dynamics in terms of homogeneous and inhomogeneous broadening implies a separation of time scales between fast fluctuations of the bath, slower dephasing dynamics, and essentially static structural contributions. This is the situation for electronic transitions in low temperature glasses and crystals, where the structure evolves

slowly and coupling to the bath is through thermally populated, low frequency modes of the glass.¹ However, in room temperature liquids, the dephasing of *electronic transitions* occurs on a time scale similar to that of the fastest dynamics of the bath.^{2,3} Coupling of the electronic states to ballistic motions of the bath results in non-Markovian dynamics.^{4,5} The dephasing can arise from dynamics of a liquid that are the same as those responsible for solvation of the electronic excited state.

In general, coupling of vibrations to a bath is substantially weaker than the coupling of electronic states. This is demonstrated by the fact that vibrational transition energies have much smaller percentage gas-to-“crystal” shifts than electronic transitions. The weaker coupling gives rise to longer dephasing times and little or no solvation dynamics. The weaker coupling makes it possible to study dephasing in liquids with relatively long pulses that have narrow enough bandwidths to coherently couple only a well-defined pair of states to the radiation field.

In this communication we report the results of ps infrared vibrational photon echo experiments on a sample that is taken from a room temperature liquid to a glass at 10 K. Measurements were made on the T_{1u} CO stretching mode of $\text{W}(\text{CO})_6$ in 2-methylpentane (2-MP), a glass forming liquid. These experiments are the first to follow the evolution of the homogeneous vibrational linewidth from a room temperature liquid to a low temperature glass. Further, it is demonstrated that vibrational transitions in room temperature liquids may be inhomogeneously broadened. This work extends recent observations of the homogeneous vibrational linewidth in a low temperature glass and supercooled liquid.⁶ The only other direct measurement of the dephasing times of vibrational transitions in room temperature liquids have been made with Raman echo experiments.⁷⁻⁹

The photon echo experiment is a line narrowing experiment that measures T_2 . In a vibrational photon echo experiment, two ps IR pulses tuned to a molecular vibrational transition are crossed in the sample. The first pulse induces a coherence that decays due to a combination of inhomogeneous and homogeneous dephasing. A second pulse, delayed by time τ , begins a rephasing of the *inhomogeneous* contribution to the spectral line and results in the emission of an echo pulse at time 2τ . The echo pulse is emitted in a unique direction determined by wave vector matching conditions. The intensity of the echo pulse is measured as a function of τ . The decay of the echo intensity measures the vibrational

homogeneous dephasing time. The decay of the photon echo is the Fourier transform of the homogeneous spectrum. For example, if the echo decay is an exponential, i.e.,

$$I(t) = I_0 \exp(-4\tau/T_2). \quad (1)$$

The Fourier transform is a Lorentzian homogeneous line having width, $1/\pi T_2$. The echo signal decays four times as fast as the dephasing time, due to the echo rephasing at 2τ , and intensity decaying twice as fast as the polarization.

The photon echo, through the time reversal of the rephasing process, eliminates inhomogeneous contributions to the vibrational transition and is thus the true measure of the homogeneous dephasing time.¹⁰ Although fs coherent anti-Stokes Raman scattering and Raman-induced birefringence measurements can measure dephasing times of low frequency vibrational modes, these experiments do not eliminate inhomogeneity, and thus observe the free induction decay for the transition (Fourier transform of the total inhomogeneously broadening line.^{10,11})

The photon echo experiments were performed with ~ 1.5 ps (~ 10 cm⁻¹ bandwidth) IR pulses at 5.04 μ m (1983 cm⁻¹) generated with the Stanford superconducting-accelerator-pumped free electron laser (FEL). The FEL emits a 2 ms macropulse at a 10 Hz repetition rate. Each macropulse consists of ~ 0.5 μ J micropulses at a repetition rate of 11.8 MHz. The micropulse repetition rate was reduced to 50 kHz by a germanium AOM single pulse selector, yielding an experimental repetition rate of 1 kHz. The two pulses for the echo pulse sequence were obtained with a ZnSe beam splitter. The data was taken with pulse energies of ~ 8 nJ for the first pulse and ~ 50 nJ for the second pulse. Power dependent effects were observed in the low temperature glass for higher energies. The more intense pulse was chopped at 25 kHz by a second AOM. The signal and a reference were measured with two HgCdTe detectors sampled by two gated integrators. The reference detector was used for shot intensity windowing.

Data was taken on 1×10^{-3} M solutions of W(CO)₆ in 2-MP (99.9%), corresponding to a mole fraction of $\sim 10^{-4}$. The sample was sealed with a 400 μ m Teflon gasket between two CaF₂ flats, and the temperature was controlled using a closed-cycled He refrigerator. The temperatures were measured to ± 0.2 K. The FEL wavelength was tuned at each temperature to follow the small temperature-dependent changes in the position of the absorption maxima of the solution.

Figure 1(a) displays photon echo data taken in the low temperature glass at 10 K. The inset shows a log plot of the data. The decay is exponential (except for a very fast initial transient that vanishes at sufficiently low power), indicating that the homogeneous line is a Lorentzian. At this temperature, the absorption linewidth is 10.5 cm⁻¹ (310 GHz). In contrast $T_2 = 240$ ps, yielding a homogeneous linewidth of 1.3 GHz. Thus the absorption line in massively inhomogeneously broadened. Figure 1(b) shows temperature dependent photon echo data for W(CO)₆ in 2-MP. The photon echo decays are exponential for all the temperatures, although convolutions are necessary to analyze the data above ~ 160 K. Below 160 K, where the echo decays yield a homoge-

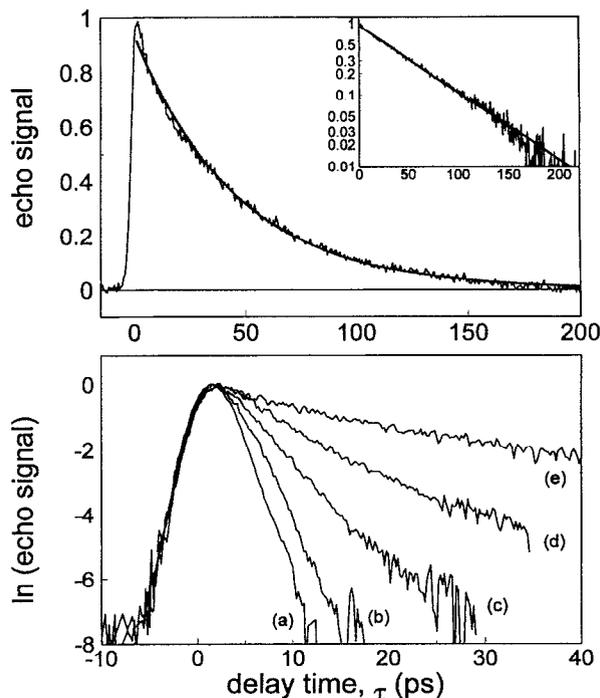


FIG. 1. (Top) Photon echo decay data for the CO asymmetric stretching mode (T_{1u}) of W(CO)₆ in 2-methylpentane glass at 10 K. The homogeneous linewidth determined by the echo decay is 1.3 GHz (0.04 cm⁻¹) in contrast to the absorption line which is inhomogeneously broadened to 310 GHz (10.5 cm⁻¹). (Bottom) Semilog plots of photon echo decays as a function of temperature. The decays correspond to (a) 300 K, (b) 125 K, (c) 110 K, (d) 95 K, and (e) 50 K. The glass transition temperature is 88 K. The decays in the liquid demonstrate that the vibrational line is inhomogeneously broadened in liquid solution.

neous linewidth that is much narrower than the width of the absorption spectrum, the results demonstrate conclusively that the vibrational lines of this system are inhomogeneously broadened.

Above 160 K, the dephasing times T_2 approach the pulse width. Under these conditions, the time scale for the rephasing of the echo pulse is shortened by the polarization decay due to homogeneous dephasing. This causes the echo to appear at times between τ and 2τ , and the echo signal at very short delay times decays at a slower rate than the $4/T_2$ given by Eq. (1). For this case, the correct dephasing time must be obtained by convolution of the pulses, with the homogeneous dephasing and the inhomogeneous rephasing, as given by the material response function.^{8,10} As the homogeneous dephasing time T_2 decreases, the rephasing of the echo is shifted to shorter times. In the limit that the absorption line is homogeneously broadened, a free induction decay (FID) will be observed along the echo phase matching direction. If the homogeneous line is a Lorentzian, then an exponential decay with a decay constant of $2/T_2$ will be observed.

Figure 2 shows a semi-log plot of the room temperature echo decay of W(CO)₆ in 2-MP. A fit of a single exponential with convolution is shown through the data, demonstrating that the echo decay is exponential over at least 5 factors of e . Also shown is the convolution with an instantaneous mate-

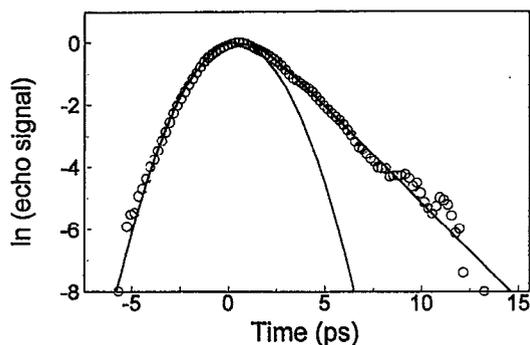


FIG. 2. Semilog plot of the room temperature echo decay, with a single exponential fit, and the instantaneous dephasing response function. The data decays in an exponential manner over >5 factors of e with a decay time of 1.6 ps, corresponding to a homogeneous linewidth of 49 GHz (1.6 cm^{-1}). The absorption linewidth at room temperature is 110 GHz (3.7 cm^{-1}).

rial response function. If the echo formation in the liquid is in the $4/T_2$ limit, and the absorption line is truly inhomogeneously broadened, then the echo decay of 1.6 ps corresponds to a homogeneous linewidth of 49 GHz. The $2/T_2$ limit, given by the FID, yields a linewidth of 98 GHz, which is similar to the absorption linewidth at room temperature of 110 GHz. From the data shown in Fig. 2 alone, it is not possible to distinguish between a true echo decay and the FID. At this point we assume that the observed data corresponds to a true echo decay described by Eq. (1). The possibility that the room temperature data are a FID is discussed below.

The temperature-dependent homogeneous linewidth for $\text{W}(\text{CO})_6$ in 2-MP is shown in Fig. 3. The inset is a log-log plot of the low temperature portion ($<100 \text{ K}$). The linewidths, $1/\pi T_2$, were calculated from photon echo data using Eq. (1). The linewidth increases gradually with temperature in the glass. The homogeneous linewidth is $<10 \text{ GHz}$ throughout the glassy region, compared to the inhomogeneous linewidth of $\sim 300 \text{ GHz}$. The rate of increase of the homogeneous width becomes much steeper after the glass transition, $T_g = 88 \text{ K}$. However, above 160 K, the temperature dependence of the linewidth appears to level off. Preliminary theoretical calculations indicate that the observed temperature dependence in the liquid could arise through a motional narrowing mechanism. At room temperature, the total linewidth is 3.7 cm^{-1} while the homogeneous linewidth is 1.6 cm^{-1} .

There are several features of the system that suggest that the data points between 160 and 300 K correspond to true echo decays, not FIDs. The absorption line is not Lorentzian. Thus the FID would not be observed as exponential. The data point at 160 K is certainly a true echo decay. The absorption linewidth is 5.5 cm^{-1} , which would give rise to a much faster FID than the observed decay. The decays between 160 and 300 K are very similar in character; a change from an echo decay to a FID would have to occur without a noticeable change in the nature of the data. In addition, using a conventional laser system with 10 ps time resolution, evidence of spectral diffusion has been observed in pump-probe experiments in the liquid up to 180 K. Above this

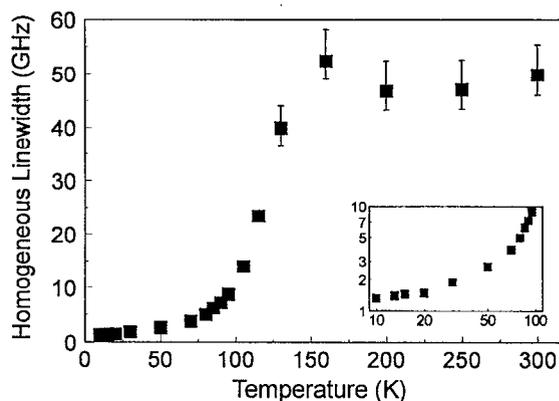


FIG. 3. Temperature-dependent vibrational homogeneous linewidths, $1/\pi T_2$ obtained from the photon echo data using Eq. (1). The inset shows a log-log plot of the data below 100 K. The glass transition temperature is 88 K.

temperature, the time resolution was inadequate to make further observations. The spectral diffusion, which is much slower than the echo decays, indicates inhomogeneity that exists on a time scale long compared to the homogeneous dephasing in the high temperature liquid.

While the information presented above is suggestive that the room temperature line is inhomogeneously broadened, it is not conclusive. If the room temperature line is in fact inhomogeneous, then spectral diffusion should occur to dynamically broaden the line. Spectral diffusion can be observed by comparing the results of the photon echo with stimulated echo decays.¹ Stimulated echoes will be employed to confirm the inhomogeneous broadening of the room temperature line.

Previously photon echo experiments were performed on the same mode of $\text{W}(\text{CO})_6$ in 2-methyltetrahydrofuran (2-MTHF) between 16 and 140 K.⁶ In this temperature range, the temperature dependence is qualitatively similar to that reported here for the 2-MP solvent. Below the 2-MTHF glass transition ($T_g = 86 \text{ K}$) the homogeneous linewidth increases gradually with increasing temperature, becoming much steeper above T_g . However, the homogeneous widths are consistently wider in 2-MTHF. For example, at 16 K in 2-MTHF, $1/\pi T_2 = 5.2 \text{ GHz}$, while at the same temperature in 2-MP, $1/\pi T_2 = 1.6 \text{ GHz}$. The wider homogeneous lines in 2-MTHF did not permit measurement of the echo decay above 140 K ($\sim 50 \text{ K}$ above T_g) because of inadequate time resolution. The line is almost certainly still inhomogeneously broadened above this temperature since $\text{W}(\text{CO})_6$ in 2-MTHF liquid has an absorption linewidth of 15 cm^{-1} , and the homogeneous width measured at 140 K is $\sim 3 \text{ cm}^{-1}$. The narrower homogeneous widths observed in 2-MP at all temperatures made it possible to perform the experiments up to room temperature.

The photon echo data presented above demonstrates that vibrational lines of solute molecules can be inhomogeneously broadened in liquid solutions as well as glassy solutions. The data suggest the existence of inhomogeneous broadening at room temperature. Raman echo experiments on room temperature neat acetonitrile⁷ and neat benzonitrile⁹

have determined that the vibrational bands studied are homogeneously broadened. However, Raman echo experiments on $\text{CH}_3\text{I}/\text{CDCl}_3$ in very concentrated solutions (50/50 mixtures) displayed inhomogeneous broadening at room temperature.⁸

The temperature dependence of the homogeneous linewidth reflects the wide variety of dynamic processes occurring in the liquid. The functional form of the increase in the homogeneous linewidth with temperature is due to the changes in the nature of the dynamical processes of the solvent that are coupled to the internal modes of $\text{W}(\text{CO})_6$. Continuing experimental work is aimed at elucidating the nature of the dynamic phenomena responsible for the vibrational dephasing.

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