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Vibrational echo studies of pure dephasing: Mechanisms in liquids and glasses

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Abstract

Temperature dependent vibrational dephasing experiments are presented on the asymmetric CO stretching mode (2010 cm^{-1}) of (acetylacetonato)bicarbonylrhodium(I) in the solvent dibutylphthalate in both the glass and liquid. The pure dephasing temperature dependence is linear (T^1) at very low temperature and an activated process ($\Delta E = 385 \pm 50$ cm^{-1}) above ≈ 20 K. Pure dephasing mechanisms are proposed. It is suggest that the T^1 dependence arises from dynamics of the glass' two level systems, while the activated process involves coupling of the CO stretch to a low frequency intramolecular mode. The experimental results are contrasted with vibrational dephasing experiments on $W(CO)_6$ also in dibutylphthalate. © 1997 Elsevier Science B.V.

1. Introduction

In this Letter, we present ps IR vibrational echo experiments on the asymmetric CO stretching mode of (acetylacetonato)bicarbonylrhodium(I) ($Rh(CO)_2acac$) in the organic glass-forming solvent dibutylphthalate (DBP) over the temperature range of 3.5–250 K. Vibrational echo measurements of pure dephasing provide an observable for the dynamic intermolecular interactions that influence a particular vibrational mode of a solute molecule [1,2]. By examining the temperature dependence of the vibrational pure dephasing, insights into the mechanisms responsible for energy level fluctuations can be obtained.

A great deal of experimental work has examined electronic excitation dephasing using non-linear four time correlation function experiments, e.g., photon echoes [3–6] and related experiments such as stimulated photon echoes [7,8] and hole burning [9–12]. Electronic dephasing experiments have been performed on many low temperature glass systems [3–6] and on a number of liquid systems [13,14].

The recent application of ps IR vibrational echoes to the study of liquids, glasses and proteins [1,2], extends the investigations of electronic transition pure dephasing to vibrational degrees of freedom. It is found that vibrational dephasing times, even in liquids, are relatively long. This makes it possible to use an IR pulse bandwidth that excites a single vibrational transition, removing some of the complexity associated with ultrafast electronic photon echoes in which a very large number of states are

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simultaneously excited by short, broad bandwidth pulses.

The pure dephasing of the asymmetric CO stretching mode of $Rh(CO)_2acac$ displays a linear dependence on temperature at low T ($\lesssim 20$ K) and an exponentially activated (Arrhenius) process at higher temperatures with an activation energy of ≈ 400 cm^{-1}. These results are different from previous vibrational echo studies of the pure dephasing of the asymmetric CO stretching mode of $W(CO)_6$ in organic solvents including DBP [1,2]. Dephasing mechanisms are proposed, and it is suggested that the triple degeneracy of the $W(CO)_6$ CO mode gives rise to distinct dephasing mechanisms.

2. The experimental method

The vibrational echo experimental method and procedures have been discussed in detail elsewhere [1,2]. The vibrational echo is a two pulse sequence that removes inhomogeneous broadening, and provides a direct measure of the vibrational homogeneous line shape. The homogeneous line shape is the ensemble averaged dynamic line shape obtained when inhomogeneous broadening is removed by the two pulse vibrational echo. The two pulse echo yields the narrowest line of the class four time correlation function experiments that examine ensemble averaged spectral shapes [1,2]. The integrated intensity of the echo pulse, which is emitted following the two excitation pulses, is measured as a function of the delay between the two input pulses. The Fourier transform of this echo decay curve is the homogeneous line shape [15]. For a Lorentzian homogeneous line with line width $\Gamma = 1/\pi T_2$, the echo decays as

$$I(\tau) = I_0 \exp(-4\gamma\tau), \tag{1}$$

where $\gamma = 1/T_2$ for the $v = 0{-}1$ transition and τ is the delay between the two input pulses. The homogeneous dephasing time has contributions from the pure dephasing time, T_2^*, and the vibrational lifetime, T_1,

$$\frac{1}{\pi T_2} = \frac{1}{\pi T_2^*} + \frac{1}{2\pi T_1}. \tag{2}$$

There can also be a contribution from orientational relaxation [16]. However, the experiments reported here were conducted in a high viscosity solvent. Polarization selective pump–probe experiments confirmed that there is no orientational relaxation on the time scale of the experiments over the entire temperature range. The pump–probe experiments were used to measure the lifetime as a function of temperature. When these measurements of T_1 are combined with the vibrational echo measurements of T_2, the temperature dependent pure dephasing contributions to the homogeneous line width are determined.

The vibrational echo experiments were performed using the Stanford Free Electron Laser (FEL). The details of the FEL parameters and the experimental setup are discussed elsewhere [1,2]. Considerable care was taken to make sure that the results are free of experimental artifacts [1,2].

3. Results and discussion

Fig. 1 shows temperature dependent data for the asymmetric CO stretching mode of $Rh(CO)_2acac$

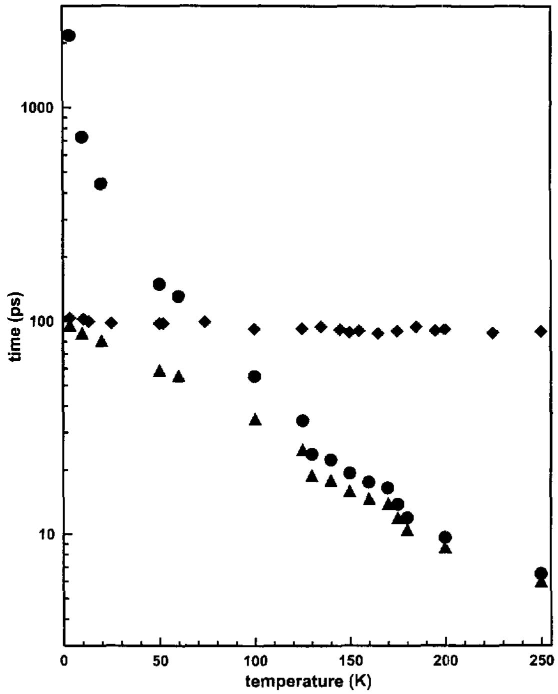

Fig. 1. Semi-log plot of the temperature dependent homogeneous dephasing times, T_2, measured with vibrational echo experiments (triangles), vibrational lifetimes, T_1, measured with pump–probe experiments (diamonds, plotted as $2T_1$), and homogeneous pure dephasing values obtained using Eq. (2) (dots).

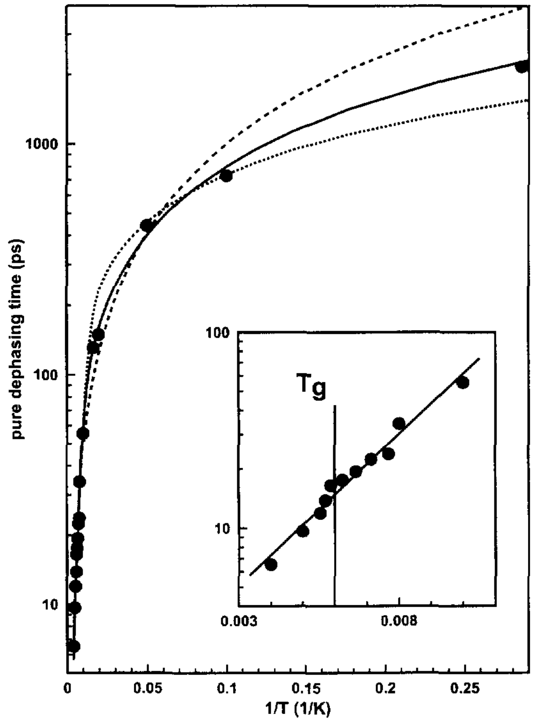

Fig. 2. Pure dephasing rate ($1/T_2*$) versus inverse temperature on a semi-log plot. An activated process appears as a straight line. The solid line is the best fit to Eq. (3) with $\alpha = 1.0$ and $\Delta E = 385$ cm^{-1}. The dotted and dashed lines are fits with $\alpha = 1.3$ and $\alpha = 0.7$, respectively and the other fitting parameters allowed to float. The inset shows the high temperature portion of the data demonstrating activated behavior in this temperature range.

displayed on a semi-log plot. The triangles are the measured values of T_2 obtained from the vibrational echo decays. The diamonds are $2T_1$, the relevant quantity (see Eq. 2). The circles are T_2^*, the pure dephasing times, obtained from T_2 and $2T_1$ using Eq. (2).

Fig. 2 shows the pure dephasing time versus inverse temperature on a semi-log plot. In this form, an Arrhenius temperature dependence appears as a straight line. The data were fit to Eq. (3) for reasons discussed below.

$$\frac{1}{\pi T_2^*} = a_1 T^\alpha + a_2 \exp(-\Delta E/kT) \qquad (3)$$

The solid line through the data is a fit with $\alpha = 1$ and $\Delta E = 385$ cm^{-1}. (The value of the a_2 parameter will be discussed below.) The dashed line and the dotted lines correspond to the best fits for $\alpha = 0.7$ and 1.3, respectively with the other three parameters allowed to float. From fits such as these, it is possible to establish error bars, which give $\alpha = 1.0 \pm 0.1$ and $\Delta E = 385 \pm 50$ cm^{-1}.

3.1. Low temperature power law dephasing

Pure dephasing of the form T^α where $\alpha \approx 1$ has been seen repeatedly for electronic transitions of molecules in low temperature glasses using photon echoes [3–5] and hole burning spectroscopy [9–12]. The electronic dephasing has been described using the two level system (TLS) model of low temperature glass dynamics that was originally developed in the early 70's to explain the approximately linear in T anomalous heat capacity of glasses at very low temperatures [17,18]. Even at low temperature, glasses are continuously undergoing structural changes. The complex potential surface on which local structural dynamics occur is modeled as a collection of double wells. These are referred to as TLS. At very low temperatures, where the Debye T^3 contribution to the heat capacity is small, the heat capacity is dominated by the uptake of energy in going from a lower energy structure to a higher energy structure. A glass is modeled as having an ensemble of TLS with a broad distribution of tunnel splittings, E. If the probability, $P(E)$, of having a splitting E is constant, $P(E) = C$, (all E's are equally probable), then the heat capacity is T^1.

The mechanism for electronic dephasing in low temperature glasses is based on the TLS dynamics [19,9,20,5]. We propose that identical considerations can apply to the vibrational dephasing of Rh(CO)$_2$acac at low temperature. A particular molecule is coupled to a number of TLS. For those TLS having tunnel splitting that are not too large ($E \lesssim 2kT$), the TLS are constantly making transition between local structures with rates determined by the E's and the tunneling parameters. The structural changes produce fluctuating strains. The fluctuating strains result in fluctuating forces on the CO oscillator. This is referred to as strain–dipole coupling. Thus the vibrational pure dephasing can be caused by TLS dynamics. It has been demonstrated theoretically that for $P(E) = CE^\mu$, the temperature dependence of the pure dephasing is $T^{1+\mu}$ [21]. Therefore, for the flat distribution, $\mu = 0$, the pure dephasing temperature dependence is T^1, as observed for CO vibrational dephasing of Rh(CO)$_2$acac in DBP. T^1 and somewhat steeper temperature dependences, e.g., $T^{1.3}$, have been observed in electronic dephasing experiments in low temperature glasses [3,12,22]. Recent theoretical work, which has examined the problem in more detail, suggests that even an apparent super linear temperature dependences may arise from an energy distribution $P(E) = C$ [23]. This theory predicts that the pure dephasing component of the echo decays will not be strictly exponential. Within the signal-to-noise ratio of the data at low temperatures, it is not possible to determine if the pure dephasing is totally exponential because the T_1 contribution to the data is substantial.

It is interesting to note that value of the pure dephasing times the lowest temperature is similar to those found for the dephasing of electronic transitions in different glasses [3–6]. It might be expected that a vibrational transition would couple more weakly to the solvent dynamics than an electronic transition. This has been found to be the case in liquids [1,2] and proteins [1,2]. It is possible that DBP has a far larger number of active and coupled TLS at low temperature than glasses that have been used in studies of electronic transitions.

Above ≈ 20 K, the T^1 dephasing is dominated by an exponentially activated process. Electronic dephasing experiments have also shown power law temperature dependences that go over to activated processes at higher temperatures [24]. However, in the electronic dephasing experiments, power law behavior is observed only to a few K after which the activated process dominates because the typical activation energies for electronic dephasing are 15–30 cm^{-1}. The low activation energy for electronic dephasing in glasses has been shown to arise from coupling of the electronic transition to low frequency modes of the glass [25,26]. In the vibrational dephasing experiments, the $\Delta E \cong 400$ cm^{-1}. Thus, the power law component of the temperature dependence is not masked until higher temperature.

3.2. High temperature activated dephasing

The temperature dependence of the vibrational pure dephasing changes rapidly above ≈ 20 K. By 100 K, the temperature dependence is well described by the activated process alone (see inset in Fig. 2). The glass transition temperature of DBP is 169 K. There is no obvious break in the pure dephasing data as the sample passes through T_g, and the activation energy, $\Delta E \cong 400$ cm^{-1}, is well above the typical cut-off for phonon modes of organic solids [27]. Furthermore, the far-IR spectra of neat DBP shows no significant absorption in the region around 400 cm^{-1}, indicating that there is no specific mode of the solvent that might couple strongly to the CO mode. These facts indicate that the high temperature activated dephasing process is not caused by a specific motion associated with the glass/liquid solvent, but rather that the dephasing arises from coupling of the CO mode to an internal low frequency mode of Rh(CO)$_2$acac.

We propose that the activated dephasing process is caused by the coupling of the CO asymmetric stretching mode to the Rh–C asymmetric stretch of Rh(CO)$_2$acac. The mechanism is illustrated in Fig. 3A. Thermal excitation of the low frequency mode causes the CO stretching mode transition frequency to shift an amount, $\Delta\omega$. The lifetime of the low frequency mode is $\tau = 1/R$. During the time period in which the low frequency mode is excited, the initially prepared CO superposition state processes at a higher (see below) frequency. Thus, a phase error develops. For a small $\Delta\omega$ and a short τ, the phase error is on the order of $\tau\Delta\omega$. Repeated excitation and relaxation of the low frequency mode will produce homogeneous dephasing [28,29]. The rate of excitation of the low frequency mode increases exponentially with temperature as long as $\Delta E \gtrsim kT$.

For the proposed mechanism to account for the observed high temperature pure dephasing, a mode of ≈ 400 cm^{-1} must couple non-negligibly to the asymmetric CO stretch so that $\Delta\omega$ is significant. The Rh–C asymmetric stretching mode has an energy of 405 cm^{-1} [30]. The closest other modes of Rh(CO)$_2$acac are outside of the error bars on the activation energy [30]. There is a reasonable explanation why the Rh–C stretch couples significantly to the CO mode, but modes of lower frequency, which would become populated at lower temperature, do not. Rh(CO)$_2$acac has significant back donation of electron density from the Rh d_π to the CO $p_{\pi*}$ antibonding orbital (back bonding) that weakens the

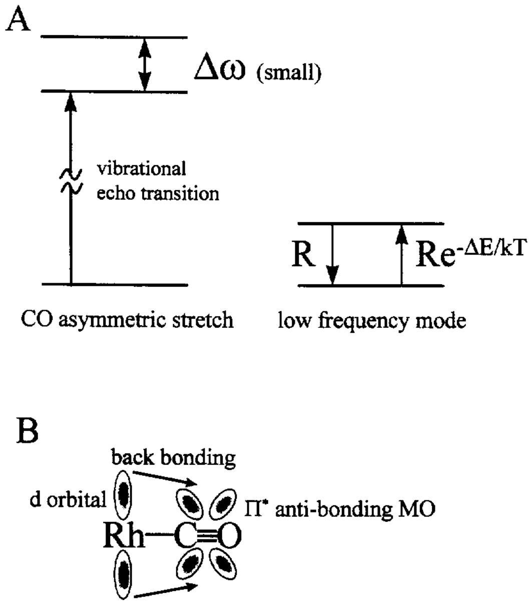

Fig. 3. (A) Schematic of the proposed high temperature dephasing mechanism. Coupling of the CO asymmetric stretching mode to the internal low frequency Rh–C stretching mode of $Rh(CO)_2acac$ can induce pure dephasing. Thermal excitation of the Rh–C mode causes the CO stretching mode transition frequency to shift an amount, $\Delta\omega$. The lifetime of the low frequency mode is $\tau = 1/R$. (B) Schematic of the $Rh(CO)_2acac$ back donation of electron density from the Rh d_π to the CO $p_{\pi*}$ antibonding orbital (back bonding).

CO bond and red shifts the transition energy about 100 cm^{-1} to ≈ 2045 cm^{-1} (see Fig. 3B). (The splitting of the symmetric and asymmetric linear combination of the 2 CO stretches further shifts the asymmetric mode to the observed value of 2010 cm^{-1}.) Thus, back bonding plays a significant role in determining the transition frequency. It is well known that in metal-carbonyl compounds, the CO frequency is very sensitive to changes in back bonding [31]. Also, a combination of isotope substitution spectroscopic experiments and calculations show that for metal-carbonyls, there is substantial coupling between the M–C stretch and the C–O stretch [32]. When the Rh–C mode is thermally excited from the $v = 0$ state to the $v = 1$ state, the average bond length will increase. The increase in the sigma bond length will increase the d_π–$p_{\pi*}$ separation, and, therefore, decrease the magnitude of the back bonding. Thus, excitation of the Rh–C mode will blue shift the CO stretching frequency by decreasing the back bonding. Although data is not available for $Rh(CO)_2acac$, experiments on $Mo(CO)_6$ and similar molecules support this mechanism [1,2]. For the equivalent modes of $Mo(CO)_6$, the combination absorption band of the Mo–C stretch and the Mo–CO asymmetric stretch is ≈ 20 cm^{-1} higher in energy than the sum of the two fundamental energies [1,2]. Thus, $\Delta\omega \cong 20$ cm^{-1}. The change in back bonding upon excitation of the Rh–C mode provides a direct mechanism for coupling excitation of the Rh–C stretch to the CO stretch transition frequency. Other low frequency modes, such as a methyl rocking mode of the acac ligand, will not have this type of direct coupling, and, therefore, will not cause dephasing even though they may be thermally populated.

Perturbation theory for the case of weak coupling has been used to theoretically analyze dephasing mechanisms analogous to the one proposed above [28,29]. Perturbation theory predicts an exponentially activated temperature dependence with the value of the a_2 coefficient in Eq. (3) determined the values of τ and $\Delta\omega$. Using $\Delta\omega \cong 20$ cm^{-1}, a value of lifetime of the Rh–C stretch, $\tau \cong 0.5$ ps yields the experimental value of a_2.

3.3. Comparison to dephasing of $W(CO)_6$

Vibrational pure dephasing has been directly measured using vibrational echoes and pump–probe experiments over a wide range of temperatures for the asymmetric CO stretching mode of $W(CO)_6$ (≈ 1980 cm^{-1}) [1,16]. Experiments were conducted in three glassy solvents, DBP, 2-methylpentane (2MP) and 2-methyltetrahydrofuran (2MTHF). The pure dephasing was also measured in liquid 2MP. The pure dephasing of $W(CO)_6$ is fundamentally different at all temperatures than that reported above for $Rh(CO)_2acac$ even though an asymmetric CO stretch at ≈ 2000 cm^{-1} was studied in both molecules.

The asymmetric CO stretch of $W(CO)_6$ pure dephasing is rigorously T^2 in DBP from 10 K to slightly about T_g (≈ 190 K) [16]. There is no break in the temperature dependence below T_g like there is for $Rh(CO)_2acac$. Furthermore, the $W(CO)_6$ pure dephasing is also T^2 in 2MP and 2MTHF up to these solvents' T_gs [1]. Thus, $W(CO)_6$ pure dephasing displays a T^2 dependence in the glassy state independent of the solvent. In all three solvents there is a break in the temperature dependence of the pure dephasing at $\approx T_g$. The pure dephasing of $W(CO)_6$ in the liquid state has only been studied in detail in 2MP [16]. The pure dephasing above T_g can be described by a Vogel–Tammann–Fulcher (VTF) type of equation [33,34].

The distinct pure dephasing mechanisms in $W(CO)_6$ and $Rh(CO)_2acac$ will be discussed in some detailed in a subsequent publication. It is proposed that the $W(CO)_6$ pure dephasing is different because of the high symmetry of the T_{1u} asymmetric CO stretching mode, which makes it triply degenerate in the gas phase [32], while the $Rh(CO)_2acac$ is not degenerate. The $W(CO)_6$ T_{1u} mode consists of all six CO's moving in concert, one pair along the molecular x-axis, one pair along y, and one pair along z. In a liquid or glass, the local solvent structure is anisotropic. In general, there will be different solute/solvent interactions (forces exerted on the oscillator) along x, y and z. These interactions will break the triple degeneracy, yielding three modes with some energy splittings. There will be a range of such splittings reflecting the range of local solvent structures.

The three closely space levels could enable $W(CO)_6$ to dephase through mechanisms that are not available to $Rh(CO)_2acac$. In the glass, the local solvent structure about a $W(CO)_6$ is essentially fixed on the time scale of the pure dephasing. Two phonon elastic scattering that causes fluctuations in the anisotropic solvent structure will induce fluctuations of the level splittings causing pure dephasing. The T^2 temperature dependence indicates that the scattering is a two phonon process in the high temperature limit, i.e. $kT > \hbar\omega_p$ where ω_p is a typical phonon frequency involved in the scattering. This mechanism is independent of the nature of the solvent and is, therefore, consistent with the observation of the T^2 dependence in three solvents.

The pure dephasing of $W(CO)_6$ above T_g in 2MP has the very steep VTF temperature dependence. Above T_g, the local solvent structure surrounding $W(CO)_6$ is no longer fixed. Translational and rotational motions of the solvent will produce fluctuating forces that do not occur below T_g. The evolution of the local solvent structure will cause the splittings of the three closely spaced modes to evolve in time inducing pure dephasing. The pure dephasing is caused by the very high frequency solvent motions that are ultimately responsible for longer time scale processes such as translational and rotational diffusion and dielectric relaxation. The observed VTF temperature dependence would seem to be consistent with this dephasing mechanism.

4. Concluding remarks

In this Letter, we have examined the homogeneous pure dephasing of the CO asymmetric stretching mode of $Rh(CO)_2acac$ in liquid and glassy dibutylphthalate. The temperature dependence follows a power law, T^{α}, at very low temperatures plus an exponentially activated process at higher temperatures, with $\alpha = 1.0 \pm 0.1$ and $\Delta E = 385 \pm 50$ cm^{-1}. There is no apparent change in the temperature dependence at the glass transition (169 K). The T^1 may reflect the glassy solvent's two level system dynamics while it has been suggested that the activated process involves coupling to the low frequency Rh–C stretching mode.

Picosecond infrared vibrational echo experiments make it possible to examine vibrational homogeneous dephasing in condensed matter systems. By combining vibrational echoes with IR pump–probe experiments, the contributions to the homogeneous line can be separated, thus providing detailed insights into the dynamical coupling of a medium and molecular vibrational degrees of freedom.

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