Temperature-dependent vibrational relaxation in polyatomic liquids: Picosecond infrared pump–probe experiments

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Vibrational lifetimes of metal carbonyl solutes in two liquids were studied as a function of temperature from the melting points to the boiling points. Picosecond infrared pump–probe experiments were performed at the absorption maxima of the T_{1u} CO stretching vibration (~1980 cm^{-1}) of $Cr(CO)_6$ and $W(CO)_6$ dissolved in carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$). The temperature dependencies of the lifetimes in CCl_4 are dramatically different from those in $CHCl_3$. A decrease in the vibrational lifetime with temperature is seen for both metal carbonyls in CCl_4. However, the vibrational lifetime of $W(CO)_6$ in $CHCl_3$ becomes longer as the temperature is increased, while the lifetime of $Cr(CO)_6$ decreases only slightly. To understand the vibrational dynamics in these systems it is necessary to consider the temperature dependencies of the thermal populations of low frequency phonons (instantaneous normal modes) of the liquids, the phonon density of states, and the anharmonic coupling matrix elements.

I. INTRODUCTION

Understanding the temperature-dependent dynamics of vibrations of molecules in liquid solutions is fundamentally important. The vibrational degrees of freedom of a molecule are coupled to its environment through intermolecular interactions. For a molecule to rid itself of excess vibrational energy, that energy must ultimately be transferred into the surrounding heat bath. Vibrational relaxation depends on anharmonic couplings among different vibrations and the phonon states (instantaneous normal modes) of the liquid bath. When the temperature of a liquid is changed, the density of the liquid changes and the populations of vibrations and phonons change. These changes affect the anharmonic interactions and other factors that result in vibrational relaxation. Thus, the temperature-dependent changes in vibrational relaxation is sensitive to the interactions and dynamics that influence the mechanical degrees of freedom of a molecule. Thermal excitation of chemical processes in solution involves the transfer of energy from the heat bath (solvent) into the vibrational degrees of freedom of the solutes. The flow of thermal energy into and out of molecules are closely related;[1,2] the flow in is the inverse of the radiationless processes that are responsible for relaxation of vibrations. In addition, processes such as photoinduced electron transfer and thermally or optically activated chemical reactions often depend on vibrational relaxation to trap the reacting system in the product state.[3,4]

In spite of the importance of vibrational dynamics to processes in chemistry, biology, and physics, little is known about the temperature dependence of vibrational relaxation of polyatomic molecules in liquid solutions. In this paper we present a detailed study of the temperature-dependent relaxation of a vibrational mode of two molecules, tungsten hexacarbonyl [$W(CO)_6$] and chromium hexacarbonyl [$Cr(CO)_6$] in two solvents, carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$). The temperature is varied from the melting points to the boiling points of the solvents. The T_{1u} CO stretching modes of the two metal carbonyls at ~5.05

μm (~1980 cm^{-1}) are studied using ps pump–probe experiments. These systems were first studied by Heilweil and co-workers[5] at room temperature. The relative simplicity of the solutes and the solvents makes these systems well suited for a study of the influence of temperature on the vibrational relaxation dynamics.

Developments in picosecond and subpicosecond mid-infrared (mid-IR) sources have produced major advances in the understanding of vibrational dynamics in the ground electronic state of molecules in liquids. Mid-IR sources with pulses faster than the time scales of relevant processes, as well as time-resolved coherent Raman scattering, have generated a substantial amount of room temperature data on vibrational relaxation.[6] Particular interest has been in the relaxation of high frequency vibrations, such as OH (OD),[7–10] CH (CD),[6,11–14] NH (ND),[15] and CO.[5,16–20] These investigations have studied vibrational relaxation through the effects of isotopic substitution, excitation frequency, concentration, and the complexity of the liquid. More recently, experimental information has begun to appear on homogeneous vibrational dephasing in liquids.[20–23] To this point, a careful study of the temperature dependence of vibrational lifetimes of a polyatomic solvent in a polyatomic liquid has not been made, although it is essential for understanding vibrational relaxation.

Metal carbonyls offer many characteristics desirable for such a study. A large transition dipole moment and narrow absorption lines allow data to be taken on dilute solutions with low pulse energies. Dilute solutions are necessary to avoid dipole–dipole (Förster) energy transfer.[5] With low pulse energies, thermal effects can be eliminated. Initial measurements of the lifetimes of metal carbonyl vibrations at room temperature by Heilweil and co-workers[5] demonstrated that their lifetimes are sufficiently long to study even small lifetime changes with picosecond pulses provided high quality data can be obtained. The long lifetime is likely due to the relative isolation of the high frequency (~1980 cm^{-1}) CO vibrations from the remaining lower frequency modes (<700 cm^{-1}) of the metal carbonyls. As discussed later, this fre-

quency disparity necessitates a high order anharmonic process for relaxation to occur. Previously, it was observed that increased vibrational complexity of the solvent at higher frequency decreased the lifetime.[5] Therefore, it is clear that both the intramolecular and intermolecular processes are essential to the relaxation of the vibration.

The vibrational lifetimes of the four systems studied are in the range of 300–800 ps. Both $Cr(CO)_6$ and $W(CO)_6$ dissolved in CCl_4 display a decrease in the CO vibrational lifetime with increasing temperature. For the ~1980 cm^{-1} CO mode to relax it is necessary to transfer the vibrational energy to other vibrational and phonon modes. Since the vibrational modes are discrete, it requires a coincidence for the initially populated mode to relax without the participation of a phonon. The phonon modes of the liquid provide a continuum of low frequency modes. The dominant relaxation pathways will involve the excitation of one or more vibrational modes of the solute and/or solvent and the excitation of at least one phonon to make conservation of energy possible. In the temperature range covered in the study, kT corresponds to ~200 cm^{-1} of thermal energy. Therefore, the phonon modes, which typically lie below 150 cm^{-1},[24,25] will be populated. Since the probability of phonon creation depends on the phonon population (occupation number), the change in the phonon occupation number with temperature is one factor that contributes to the temperature dependence of the vibrational relaxation. However, the vibrational lifetime of $W(CO)_6$ in $CHCl_3$ actually shows a pronounced increase in lifetime with increasing temperature. This is opposite of the behavior that results from changing phonon occupation numbers. Two other factors must be considered to understand the temperature dependence. These are the change in the phonon density of states as the liquid density changes with temperature, and the change in the anharmonic coupling constants. Analysis of the data indicates that changes in the anharmonic vibrational potentials with temperature may be an important factor in the overall temperature dependence of the vibrational lifetime.

The theoretical approach used to understand the temperature-dependent vibrational lifetimes in the liquid solutions is based on the approach used to describe vibrational relaxation in crystals.[26,27] This is made possible by the recent advances in understanding and calculating low frequency instantaneous normal mode (phonon) spectra of liquids.[24,28,29] The more traditional theoretical approach describing vibrational relaxation in liquids is the force correlation function method in which solvent forces are projected along the vibrational coordinate.[30–33] This method has been applied to diatomic molecules and diatomics in monatomic solvents.[30,33] A brief discussion of the relationship between these approaches is presented.

In the following sections, the experimental methods are described first in Sec. II. The data is presented and discussed qualitatively in Sec. III. In Sec. IV, the results are considered in a more quantitative fashion, and the importance of changes with temperature in the density of states and the anharmonic vibrational potential is demonstrated.

II. EXPERIMENT

Two sources of mid-IR ps pulses were used for the experiments: a system based on conventional lasers and the Stanford Free Electron Laser. The conventional laser system generated picosecond mid-IR pulses with a $LiIO_3$ optical parametric amplifier (OPA). The laser system is a modified version of a system that has been described in detail previously.[34] Briefly, the pulse train of a Q-switched, mode-locked, cavity-dumped Nd:YAG with a 10% output coupler is doubled and synchronously pumps a Rhodamine B dye laser. The dye laser and the Nd:YAG laser are cavity-dumped simultaneously to form the idler and pump pulses for the OPA. The cavity-dumped pulse of the Nd:YAG is frequency doubled (532 nm, 80 ps, 700 μJ), and the remaining fundamental is frequency doubled again to amplify the dye pulse in a single-stage double-pass amplifier yielding tunable dye pulses of 40 ps, 50 μJ at ~595 nm. The cavity-dumped pulse and the amplified dye pulse are made time coincident and are mixed in a 30 mm $LiIO_3$ crystal generating 3 μJ, 40 ps pulses at $\lambda \approx 5.05$ μm with a 900 Hz repetition rate. The mid-IR is separated from the visible with a CaF_2 Brewster prism. The bandwidth of the dye pulse was measured to be 1.3 cm^{-1}. The bandwidth of the mid-IR was not measured, but is approximately the same, based on the bandwidth of the dye pulse following its amplification by the OPA. The 5.05 μm beam is collimated and split into the pump and probe pulses. The probe beam is sent through an optical delay line allowing up to 5 ns of delay behind the pump pulse. Before the sample, 50% of the probe beam is split off and directed into a PbSe reference detector. Both beams are focused to 200 μm in the sample with a 114 mm off-axis parabolic reflector. The intensity changes in the probe pulse with probe delay are detected with another PbSe signal detector.

Pump–probe (transient absorption) data is collected by measuring a shot-normalized absorption change in the probe pulse with and without the pump beam. The 900 Hz reference and signal intensities are each sampled with a gated integrator, and the pump beam is chopped at 450 Hz. An analog divide signal processor normalizes the signal intensity to the reference intensity and takes the logarithm of the result. This result is fed into a lock-in amplifier, which detects the absorption change in the probe at 450 Hz by subtracting the chopped and unchopped result. When the gated integrators are properly zeroed, this technique measures the absorbance change, effectively eliminating detector proportionality constants, while still allowing for shot normalization. The linearity of the detection electronics was carefully tested. The system was found to be linear over more than three decades. The fits for data sets taken at all temperatures have error bars of ±1%. However, the reproducibility for identical data points taken days apart is ±3%. This does not influence the trends with temperature since all data for a temperature-dependent study of a given sample were taken on a single day.

The mid-IR was tuned by tuning the dye laser with a 100 μm etalon. The mid-IR wavelength was determined by measuring the dye wavelength to ±0.5 Å in a 0.5 m monochrometer, corresponding to approximately ±1.4 cm^{-1} in the mid-IR. Although the error in measuring the mid-IR frequency is

not negligible, tuning the laser to the peak of the CO absorption could be done accurately by observing the magnitude of the pump–probe signal.

The second mid-IR source is the Stanford superconducting linear-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 μJ micropulses at a repetition rate of 11.8 MHz. The micropulses were measured to be Gaussian ~2 ps transform limited pulses by performing autocorrelations in $AgGaSe_2$. The macropulse was intensity stabilized by a germanium acousto-optic modulator (AOM) feedback system. The micropulse repetition rate of 11.8 MHz was reduced to 50 kHz by a germanium AOM single pulse selector which provides 90% pulse selection efficiency. The effective experimental repetition rate is 1 kHz. Because of the macropulse structure of the FEL, use of a lock-in amplifier is not practical. The signal and a reference were measured with two HgCdTe detectors sampled by a pair of gated integrators. The gated integrators were read out by a computer with a 16 bit A/D board. The computer also controlled a stepper motor delay line with a total travel corresponding to 330 ps. The FEL was used to examine the short time behavior of the pump–probe signal while the conventional system was used for the bulk of the measurements which could be performed with longer pulses (40 ps) and required the long delay line (5 ns).

Both CCl_4 and $CHCl_3$ were purchased as >99.9% pure and used without further purification. Data was taken on 2×10^{-3} M solutions of each metal carbonyl in each liquid, corresponding to a mole fraction of ~10^{-4}. With this concentration, the samples had an optical density of 0.7–0.8 using a 100 μm path length. The concentration is sufficiently low that Förster excitation transfer does not occur.[5] In a previous set of experiments, a concentration study was performed to assure that excitation transfer did not occur and that there were no other concentration dependent effects at the concentration employed in the experiments.[20] The sample was sealed with a 100 μm Teflon gasket between two CaF_2 flats, and the temperature was controlled using a regulated liquid nitrogen cooled cryostat. The temperatures were measured to ±0.5 K with a type T thermocouple mounted with silicone heat sink compound directly into a hole drilled in one of the CaF_2 flats. Pump–probe data was taken with increasing temperature from the melting point to the boiling point of the liquid. This range corresponds to 250–350 K in CCl_4 and 210–334 K in $CHCl_3$. Temperature-dependent pump–probe measurements were made with varying frequency. The laser was tuned to follow the small temperature-dependent changes in the position of the absorption maxima of the solutions.

Using the conventional laser, it is possible to employ pulse energies that are large enough to produce significantly non-exponential decays of the long time signal. Detailed power studies were performed. Data was collected with pump and probe energies of 200 nJ and 15 nJ, respectively. At these energies all of the long time decays are perfect single exponentials. At higher pulse energies, there is a pronounced slowing of the decays at relatively short time (<1 ns). In a previous study of $W(CO)_6$ in CCl_4 at room tempera-
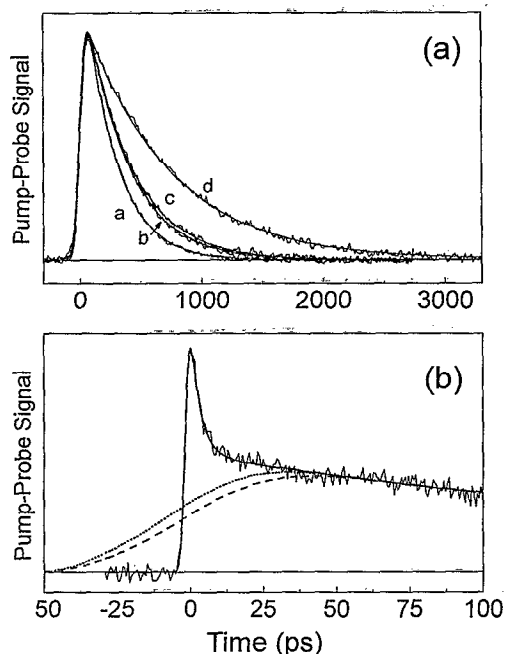

FIG. 1. (a) Room temperature pump–probe decays and convoluted single exponential fits for all four solutions taken at the absorption maxima. The decays correspond to (a) $Cr(CO)_6/CHCl_3$; (b) $W(CO)_6/CHCl_3$; (c) $Cr(CO)_6/CCl_4$; (d) $W(CO)_6/CCl_4$. (b) Pump–probe decay and biexponential fit for $W(CO)_6/CHCl_3$ taken with the Stanford free electron laser. The decay times for the fit are 3.3 and 260 ps. The figure shows the first 100 ps in order to emphasize the fast decay, but the fit was made to 290 ps. The dotted line shows the biexponential response convolved with a 40 ps pulse, while the dashed line shows a single exponential response with the long component convolved with a 40 ps pulse.

ture which examined the decays over a small time range, it was reported that reducing the power resulted in faster decays.[5] This is consistent with our results if the data are restricted to <1 ns. Based on our power dependence study and examining the decays out to long time showed that the conditions used in the previous study did not reach the low power exponential limit. The nonexponential decays at high power are a result of multiphoton pumping of higher vibrational levels of the T_{1u} mode. This will be discussed in detail elsewhere.[35,36]

Temperature-dependent IR absorption spectra of the metal carbonyl solutions were taken with a Bruker 113 FTIR Spectrometer equipped with the same temperature regulated dewar used for the pump-probe experiments. The spectra were taken with 0.2 cm^{-1} resolution.

III. RESULTS

Figure 1 displays pump–probe data taken on two time scales at 295 K. Figure 1(a) shows the data of all four solutions taken with the conventional laser system with 40 ps pulses. The data are for (a) $Cr(CO)_6/CCl_4$; (b) $Cr(CO)_6/CHCl_3$; (c) $W(CO)_6/CHCl_3$; (d) $W(CO)_6/CCl_4$. The calculated lines through the data are single exponential fits that include convolution with the pulse shape. The decays can be followed for greater than 4 factors of e. As can be seen from Fig. 1, the data are very high quality, and the fits are excel-

lent. The vibrational lifetimes for these room temperature samples are 260, 340, 370, and 700 ps, respectively. These values are within the larger error bars of previously reported lifetimes for these solutions.

In Fig. 1(b), room temperature data from $W(CO)_6/CHCl_3$ taken using the ~2 ps pulses from the FEL are displayed. Similar biexponential decays were observed for all of the solutions studied here. The calculated curve through the data is a biexponential fit and yields a decay time for the fast component of 3.3 ps. This first component is not observable with the 40 ps pulses used for the measurements shown in Fig. 1(a) and below. In Fig. 1(b), two calculated curves are shown to illustrate the influence of the fast decay component on the data taken with the 40 ps pulses. The dotted curve is the same biexponential used to fit the data, but it is convolved with the 40 ps pulse. The dashed curve is the slow exponential component only convolved with the 40 ps pulse. Except for the small displacement at $t=0$, these curves are indistinguishable, showing that with 40 ps pulses, the 3.3 ps component has no influence on the observable and that it is sufficient to use a single exponential to fit the temperature-dependent data presented later.

The fast decay component displayed in Fig. 1(b) is caused by orientational relaxation. This was confirmed using magic angle probing in experiments conducted with the FEL. However, even at the magic angle, there is a very fast residual decay that is not resolvable with the ~2 ps pulses used in the experiments. This very fast component, estimated to be ~1 ps, is most likely caused by phonon scattering of population from the initially populated IR active T_{1u} mode into nearby Raman active modes. The six carbonyl stretches yield a triply degenerate IR active T_{1u} mode, a double degenerate Raman active E_g mode, and a single Raman active A_{1g} mode. The two Raman active modes lie 32 and 136 cm^{-1}, respectively, to higher energy than the T_{1u} mode. The Raman mode positions were measured by Stokes Raman scattering from the solutions studied here. This explanation of the fast component is supported by IR pump/anti-Stokes probe experiments. Following excitation of the IR active T_{1u} mode, the anti-Stokes spectrum was recorded with a delayed dye laser probe pulse. The E_g mode 32 cm^{-1} to higher energy was observed to be populated and to decay in the same manner as the T_{1u} mode. This shows that the IR and Raman modes are in equilibrium, established by rapid phonon scattering between them. With the 40 ps pulses used in the IR/Raman experiments, it was not possible to observe the rise in population in the E_g mode. Therefore, the transfer of population to the E_g mode must be fast compared to 40 psec. Since no fast transients were observed in the FEL 2 ps pump–probe experiments other than the ~1 ps transient, it is reasonable to assign this transient to population transfer from the T_{1u} mode to the E_g mode. However, the A_{1g} mode, 136 cm^{-1} to higher energy, was not observed in the anti-Stokes spectrum. Given the relative strengths of the two Raman modes and the signal-to-noise ratio, this indicates that phonon scattering does not occur to the A_{1g} mode. A complete description of these experiments will be given elsewhere.[35,36] Similar phonon scattering processes between infrared active metal carbonyl modes has been observed before.[16,18,19]
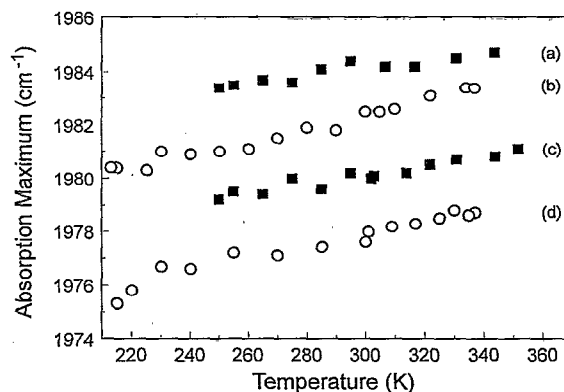

FIG. 2. Absorption maxima of the metal carbonyl solutions as a function of temperature. The limits of the data correspond to the melting and boiling points. (a) $Cr(CO)_6/CCl_4$; $Cr(CO)_6/CHCl_3$; (c) $W(CO)_6/CCl_4$; (d) $W(CO)_6/CHCl_3$.

Since the rate of scattering between the IR and Raman active modes is very fast compared to the hundreds of ps decays seen for the four solutions, equilibrium is maintained during the population relaxation from the T_{1u} mode. The pump–probe decay at long times measures the population relaxation out of the T_{1u} mode. This decay rate actually reflects the combined decay kinetics of the T_{1u} mode and the E_g mode as long as the scattering rate between them is fast compared to the overall rate of population relaxation. That the pump–probe experiment actually measures the rate of population flow out of the T_{1u} mode has been established for $W(CO)_6/CCl_4$ at room temperature by pumping the $\nu=0\rightarrow1$ transition and probing at the $\nu=1\rightarrow2$ frequency.[37] This method, which directly measures the relaxation rate out of $\nu=1$ without a contribution to the signal from ground state recovery, gave a decay time identical to the slow component measured in these experiments at room temperature with the single wavelength pump–probe experiment.

Infrared absorption spectra of all four solutions were taken as a function of temperature. As shown in Fig. 2, there is a small shift of the peak position with temperature. Over the entire temperature range, the T_{1u} mode shifts to the blue in going from the melting point to the boiling point: ~2 cm^{-1} in CCl_4 and ~3 cm^{-1} in $CHCl_3$. The room temperature absorption linewidth, $\Delta\nu$, in each solvent is similar for both metal carbonyls. For $W(CO)_6$, $\Delta\nu=10$ cm^{-1} (FWHM) in CCl_4, and $\Delta\nu=19$ cm^{-1} in $CHCl_3$. The linewidth of all solutions narrows with increasing temperature over the range studied: from 11.6 to 8.5 cm^{-1} for $W(CO)_6/CCl_4$ and from 20.5 to 18.6 cm^{-1} for $W(CO)_6/CHCl_3$. There is also an approximately linear decrease in the integrated intensity of the lines with increasing temperature in both liquids. This is due to the linear decrease in density[38] of the liquids with increasing temperature. For $Cr(CO)_6/CCl_4$ the integrated intensity decreases ~15% from 250 to 350 K, which corresponds approximately to the 12% decrease in the density over this range. Similar results were obtained for the other solutions. Although the change in the line position with temperature is small relative to the linewidth, the IR wavelength used in the
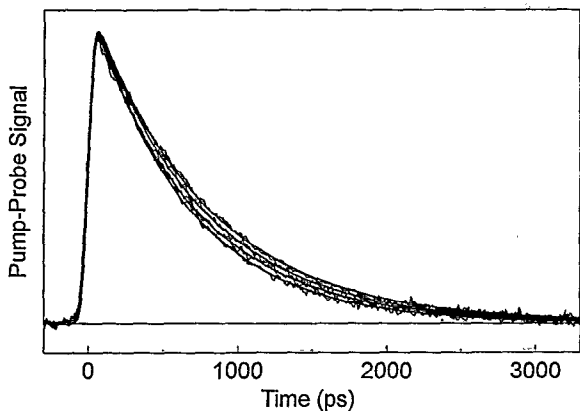
FIG. 3. Pump–probe decays and fits for $W(CO)_6/CCl_4$ as a function of temperature. Data sets from top to bottom are for temperatures of 255, 281, 308, and 338 K.

experiments was changed to match the peak absorption frequency at each temperature.

In Fig. 3, pump–probe data taken on $W(CO)_6$ in CCl_4 at four temperatures (255, 281, 308, and 338 K) are shown. The solid lines through the data are the single exponential fits with convolution. Although the change in the decay with temperature is not large, given the excellent signal-to-noise ratio of the data, the differences are readily discernible. The vibrational relaxation times as a function of temperature for $W(CO)_6$ and $Cr(CO)_6$ in CCl_4 are shown in Fig. 4. From the melting point to the boiling point, the pump–probe decays decrease monotonically by 17% and 14% for $W(CO)_6$ and $Cr(CO)_6$, respectively. For $W(CO)_6$, the values range from 775 ps at the melting point (250 K) to 650 ps at the boiling point (350 K). For $Cr(CO)_6$, the values range from 400 ps at
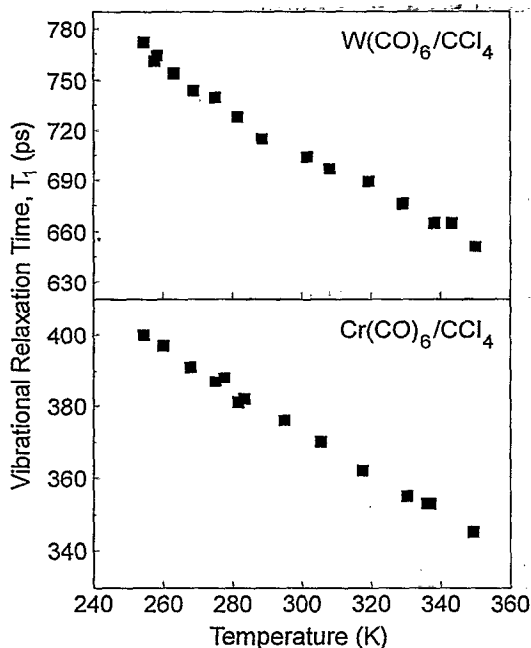

FIG. 4. Temperature-dependent vibrational relaxation times, T_1, of $Cr(CO)_6$ and $W(CO)_6$ dissolved in CCl_4.
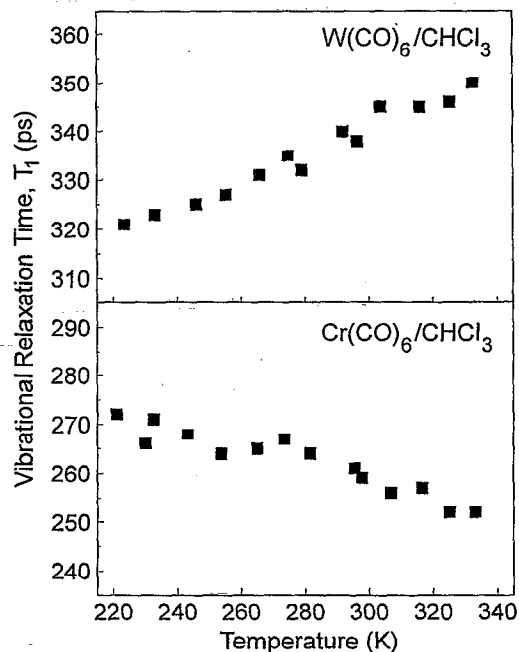

FIG. 5. Temperature-dependent vibrational relaxation times, T_1, of $Cr(CO)_6$ and $W(CO)_6$ dissolved in $CHCl_3$.

the melting point to 345 ps at the boiling point. Although the $Cr(CO)_6$ and $W(CO)_6$ T_{1u} carbonyl stretching frequencies vary by only 4 cm^{-1}, the decay constants differ by nearly a factor of 2.

The results of the pump–probe lifetime measurements of $Cr(CO)_6$ and $W(CO)_6$ in $CHCl_3$ are shown in Fig. 5. The decay times are substantially different from those in CCl_4 although the solvents differ only by substitution of a hydrogen for a chlorine. Even more significant is that the basic nature of the temperature dependence is different. Vibrational relaxation times for $W(CO)_6/CHCl_3$ actually become *slower as the temperature is increased*, changing by 9% from 322 ps at the melting point (210 K) to 350 ps at the boiling point (334 K). The lifetimes for $Cr(CO)_6/CHCl_3$ become faster over the same temperature range by only 7%, varying from 271 to 253 ps.

IV. DISCUSSION

For vibrational relaxation to occur, energy must be conserved. The initially excited vibration will pass its energy to a combination of several lower frequency modes of the solute-solvent system. The combination can involve lower frequency modes of the solute, lower frequency internal vibrational modes of the solvent, and solvent phonons. Barring exceptional circumstances in which there is a coincidence between the initial vibrational energy and the sum of the energies of several lower frequency vibrations, the continuum of low energy phonon modes will be required to conserve energy. Figure 6 shows a schematic illustration of a vibrational relaxation pathway. The solutes, $W(CO)_6$ and $Cr(CO)_6$ have a number of internal modes that are lower in frequency than the initially excited T_{1u} CO stretching frequency.[39-41] Both CCl_4 and $CHCl_3$ have a variety of lower
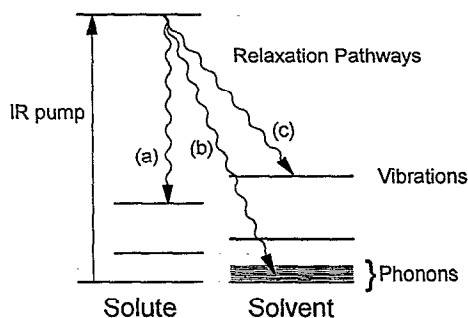
FIG. 6. Diagram of processes in relaxation of an optically excited, high frequency vibrational mode. The solid line represents the optical excitation of the vibrational mode. Radiationless relaxation pathways, given with wavy lines, that contribute to relaxation of the mode are coupling to (a) intramolecular solute vibrations, (b) solvent phonon modes, and (c) intermolecular solvent vibrations.

energy vibrational modes than the initially excited mode at ~ 1980 cm^{-1}.[42,43] CHCl$_3$ also has a CH stretching mode at higher energy, ~ 3000 cm^{-1}, which is too high in energy to participate in the vibrational dynamics.

In the vibrational relaxation of diatomic molecules in pure liquids or in atomic solvents, vibrational relaxation can only occur by coupling to rotations and translations.[30] For polyatomic molecules in polyatomic solvents, relaxation can occur through much lower order anharmonic processes involving high frequency vibrations of the solute and solvent. We assume that in the relaxation process, the lowest order process possible will always dominate. Thus, given that both components of a relaxation pathway are available, it will be preferable to excite one 1000 cm^{-1} vibration rather than five 200 cm^{-1} phonons. The simplest relaxation pathway would involve the deposition of the initial vibrational energy into a single vibration and one phonon. However, as discussed later, neither CCl$_4$ nor CHCl$_3$ are expected to have phonon bandwidths that extend much beyond 150 cm^{-1}. Therefore, in CHCl$_3$ it is necessary for the initial vibration to relax into at least two vibrations and a phonon, and in CCl$_4$ to relax into at least three vibrations and a phonon. This difference may be responsible for the generally longer relaxation times observed in CCl$_4$. It is possible that it is necessary to excite more than one phonon to conserve energy. For simplicity, the following discussion assumes that only one phonon is involved, although this will not influence the conclusions that are reached.

The rate constant for vibrational relaxation, K, can be written as

$$K = \frac{2\pi}{\hbar} \rho |\langle n,m,...,0| V^{(i)} |s,t,...,1\rangle|^2, \qquad (1)$$

where ρ is the density of states. The ket $|s,t,...,1\rangle$ is the initial state, represented by occupation numbers of the various modes of the system, including solute vibrations, solvent vibrations and phonons. The 1 in this ket is for the state initially excited by the IR pump. Before the pump it is unoccupied, since it is at ~ 2000 cm^{-1}, and following IR excitation, it has an occupation number of 1. The other states of

the solute/solvent system, $s,t,...$, are also described by thermal occupation numbers. The bra $\langle n,m,...,0|$ is the final state with the initially populated state having occupation number 0 after relaxation and some of the other states having increased occupation numbers.

In Eq. (1), $V^{(i)}$ is the anharmonic coupling matrix element responsible for vibrational relaxation that couples the initial and final states through an ith order process.[26,27] The potential energy surface for the system V, when expanded about the potential minima of the various instantaneous normal mode coordinates ψ_i, gives

$$V = \sum_{\psi_i} V^{(2)} \cdot \psi^2 + \sum_{\psi_i} V^{(3)} \cdot \psi_1 \psi_2 \psi_3 + \cdots, \qquad (2)$$

where

$$V^{(i)} = \frac{\partial^i V}{\partial \psi_1 \cdots \partial \psi_i}\bigg|_{\{\psi_0\}}. \qquad (3)$$

Here, $V^{(i)}$ is the matrix element that describes the interactions which couple i modes, and $\{\psi_0\}$ denotes the expansion about the potential minimum. The anharmonic terms, $i \geq 3$, govern relaxation processes involving the coupling of multiple vibrational modes.

As discussed previously, given the vibrational energies of the solutes and the solvents, the relaxation of the initially excited mode results in the excitation of at least two other vibrations and a phonon. For such a process, the anharmonic coupling matrix element is at least fourth order, or quartic. In Eq. (1), $V^{(4)}$ contains the magnitude of the quartic anharmonic coupling term, $V^{(4)'}$, and combinations of four raising and lowering operators that annihilate the initial mode and create the lower frequency vibrations and phonon. A raising operator brings out a factor of $\sqrt{n+1}$ and a lowering operator brings out a factor of $\sqrt{n}$, where n is the occupation number of the particular mode involved in the fourth order process. Since the vibrations are high frequency modes, the initially excited mode has an occupation number of one and the other high frequency vibrations have occupation numbers $n \approx 0$. However, the phonon mode, which is necessary to conserve energy, is part of the continuum of low frequency states and has a nonzero occupation number, since its energy is typically ≤ 150 cm^{-1}. The result is[26,32]

$$K = \frac{2\pi}{\hbar} \rho |\langle V^{(4)'}\rangle|^2 (n_p+1), \qquad (4)$$

where n_p, the phonon occupation number, is temperature dependent through

$$n_p = [\exp(E_p/kT) - 1]^{-1}, \qquad (5)$$

where E_p is the phonon energy. Considering only this factor, K should become larger and the observed decay times should become faster as the temperature is increased. If more than one thermally occupied phonon were involved in the relaxation pathway, the temperature dependence would be even steeper. If the phonon occupation number were the only factor responsible for the temperature dependence, then for E large compared to kT, K follows an exponentially activated process. For E small compared to kT, K would increase

linearly with temperature. This is inconsistent with the experimental data for $W(CO)_6$ in $CHCl_3$ shown in Fig. 5(a). The factors that cause the $W(CO)_6/CHCl_3$ vibrational lifetimes to become longer as the temperature is increased are almost certainly operative in the other samples even though they do display vibrational lifetimes that decrease with increasing temperature.

In examining Eq. (4), there are two other factors that can contribute to the temperature dependence of the decay constant. They are the density of states, ρ, and the magnitude of the anharmonic coupling matrix element, $\langle V^{(i)\prime} \rangle$. First, consider the density of states. The vibrational density of states is unlikely to change with temperature. However, the phonon density of states will be temperature dependent. The nature of the low frequency states of liquids (instantaneous normal modes) is a subject of substantial current theoretical interest.[24,28,29] We use the term phonons in analogy to the collective states of crystals, although liquid phonons have characteristics which are very different from those of crystals. In crystals, the structure is fixed and phonons arise from periodic potentials that involve only bound surfaces. In a crystal, the density of states, at some energy not close to the Debye cut off, increases as the temperature is increased.[44] There are two factors that contribute to this. As the temperature is increased, the material density of the crystal decreases, causing a reduction in the density of phonons. However, as the material density is decreased, the intermolecular interactions become weaker, reducing the Debye frequency of the solid. The reduction of the Debye frequency dominates the decrease in the number of particles per unit volume. The net result is that the density of states for phonon frequencies away from the Debye frequency increases with temperature. With such behavior, the density of states contribution to the decay constant would cause the lifetime to become faster as the temperature increases.[2]

The nature of the low frequency modes of liquids is fundamentally different from those of crystals. Since the liquid structure is not fixed, not all of the degrees of freedom involve bound states. Calculations of the low frequency states display both real and imaginary frequencies.[24,28,29] The real frequencies are true oscillations. The imaginary frequencies are related to potential barriers involved in structural evolution of the liquid. While it is still an open question, it is expected that the real frequency part of the spectrum will be predominantly involved with the take up of energy in the vibrational relaxation. This is because the system spends most of its time near a potential minimum with infrequent excursions into the region of the potential associated with structural change. Thus, the real frequency modes are available for excitation during vibrational relaxation the majority of the time.[45] In addition, the density of states of the imaginary part of the spectrum are peaked at significantly lower frequency than the real part. Therefore, if a moderately high frequency mode (~ 100 cm^{-1}) is required for vibrational energy conservation, the density of states will be much greater for the real part of the spectrum.

Recently, Moore and Keyes calculated the temperature-dependent density of states of liquids CS_2.[25] For the real frequency part of the spectrum, they found that above ~ 25

cm^{-1}, the density of states actually decreased as the temperature increased. At 50 cm^{-1}, the decrease is $\sim 20\%$ between 150 (approximately the melting point) and 250 K. At 100 cm^{-1}, over the same temperature range, the density of states decreased $\sim 10\%$. At very low frequency the density of states increased a few percent. The decrease in the density of states of the real frequencies over most of the spectrum is accompanied by an increase in the overall area of the imaginary part of the spectrum.

The results on CS_2 suggest that the density of phonon states in CCl_4 and $CHCl_3$ may also decrease with increasing temperature. The material densities for CCl_4 and $CHCl_3$ at room temperature are 1.592 and 1.480 g/cm^3. While the densities are different, the temperature dependencies are virtually identical, with a slope of -0.002 g/cm^3 K.[38] Therefore, any differences in the temperature-dependent density of states cannot arise simply from a difference in the change in the number densities of particles in the two liquids. As the temperature increases, the phonon occupation number n [Eq. (5)] increases. For $W(CO)_6/CHCl_3$ to show a decrease in K with increasing temperature, the reduction of the density of states would have to more than offset the increase in n [see Eq. (4)]. In comparing the temperature dependencies of K for $W(CO)_6$ in CCl_4 and in $CHCl_3$, it is important to recognize that the vibrational relaxation pathways will not be the same. The highest frequency fundamental mode in CCl_4 is 790 cm^{-1} while $CHCl_3$ has a mode at 1250 cm^{-1}. It is very likely that this higher frequency mode will come into play. If in CCl_4 a fairly high frequency phonon is necessary to conserve energy, while in $CHCl_3$ a much lower frequency phonon is involved, the result could be a change in the sign of the slope of the temperature dependence. In CCl_4, a decrease in the density of states might not be sufficient to overcome a steep increase in n with temperature, while in $CHCl_3$ a decrease in the density of states might overcome a mild increase in n even if the changes in the densities of states in the two liquids are approximately the same.

Calculations for molecular crystals have shown that anharmonic coupling matrix elements are density dependent.[2] Therefore, the magnitude of the anharmonic coupling matrix element, $\langle V^{(i)\prime} \rangle$, should also be temperature dependent, due to material density changes. As the density decreases with increasing temperature, the intermolecular separation are increased on average. This will change the intermolecular potential, and therefore, the anharmonic coupling matrix elements will change. If the change in potential causes the matrix elements to become smaller with increasing temperature, then the vibrational relaxation rate constant, K, will decrease with increasing temperature. When combined with a decrease in density of states, if this effect is sufficiently large to overcome the increase in n with increasing temperature, the vibrational lifetime will increase, as observed for $W(CO)_6/CHCl_3$.

The theory employed here to qualitatively describe vibrational relaxation of a polyatomic molecule in a polyatomic liquid solvent is based on the approach used in molecular crystals. In crystals, the low frequency continuum is provided by the lattice phonons. Here, we have replaced the lattice phonons with the instantaneous normal modes of the

liquid. In the lattice problem, the potential is expanded about the potential minimum of the fixed lattice structure, as in Eq. (2). The expansion provides the time independent anharmonic coupling constants. In the liquid problem, the potential is expanded about the potential minimum of the instantaneous liquid structure. Since the structure is evolving in time, the magnitudes of the coupling matrix elements are time dependent. In the experiments previously discussed, the vibrational relaxation times are long compared to time scales for structural relaxation. Therefore, the time dependent magnitudes of the anharmonic matrix elements become the time averaged matrix elements, which are equal to the ensemble average. This would not be the case for liquids where the vibrational relaxation time is fast compared to the structural evolution, such as supercooled liquids. In such a system, the vibrational relaxation rate could be spatially inhomogeneous. The instantaneous normal modes will vary from one point in the sample to another on a time scale long compared to the vibrational relaxation. The net result will be that a distribution of rates will exist, and the vibrational relaxation will be nonexponential. If the local rate is not highly sensitive to the details of the local structure, then the decay may still appear to be exponential. However, if the rate is highly sensitive to structure, the nonexponential decays observed in an experiment will be related to the distribution of local rate constants.

Another approach that is often used to obtain expressions for Golden Rule vibrational relaxation rate constant is the force correlation function (FCF) method.[30-33] The FCF description of vibrational relaxation is analogous to a common method used to describe spin-lattice relaxation in magnetic resonance. In a magnetic system, a spin experiences a fluctuating magnetic field produced by the other spins in the system. The Fourier component of the fluctuating magnetic dipolar field at the spin transition frequency induces transitions in a manner analogous to the application of a resonant RF field. In the FCF treatment of vibrational relaxation, thermal motions of the bath are coupled to the vibration of interest through anharmonic terms in the potential. Thus the vibration experiences a spectrum of fluctuating forces. The Fourier component of the FCF at the vibrational transition frequency induces transitions and is responsible for vibrational relaxation.

In most incarnations of the FCF method, at some point in the theoretical development, the quantum mechanical FCF is replaced with a classical correlation function,[30-32] although there are fully quantum mechanical treatments of some simple model systems.[31,46-48] An example of the classical correlation function approximation is found in the work of Oxtoby.[30] After developing a fully quantum mechanical expression for the vibrational relaxation rate constant, the quantum correlation function, expressed in symmetrized form to ensure detailed balance, is replaced by a classical correlation function. In spite of the multiplicative detailed balance factor, the classical correlation function results in zero relaxation at the absolute zero of temperature. An analogy can be made to the quantum theory of radiation. An excited system can be relaxed radiatively by stimulated emission if there is a radiation field present. The field is described by the photon occupation number n. Since the

photon creation operator brings out a $\sqrt{n+1}$, and this is squared in the expression for the transition probability, even when $n=0$, a transition can still take place. This is spontaneous emission of photons. In the classical FCF treatment, there is only the equivalent of stimulated emission; the equivalent of spontaneous emission is not included.

In vibrational relaxation, the classical FCF treatment will only be useful when the phonon and vibrational occupation numbers of all modes, n_i, involved in the relaxation are large compared to 1. If $n_i < 1$ for any of the modes, then the classical treatment will leave out the "spontaneous" relaxation pathway. To date, a fully quantum mechanical treatment does not exist for relaxation of high frequency modes ($h\nu > kT$) of polyatomic systems. The approach presented here, which is based on solid state theory, allows a number of qualitative issues to be clarified. The expression is fully quantum mechanical, including high frequency relaxation pathways. The density of states factors and the coupling matrix elements are shown explicitly which permits a direct comparison of competing influences and the use of instantaneous normal modes. A comparison of the method embodied in Eqs. (1)–(5) and the subsequent discussions to the FCF, both quantum mechanical and classical, and the development of the quantum mechanical FCF for polyatomic systems will be presented in a future publication.[49]

V. CONCLUDING REMARKS

Examination of the temperature dependences of the T_{1u} CO stretching modes of $W(CO)_6$ and $Cr(CO)_6$ in CCl_4 and $CHCl_3$ from the melting points to the boiling points of the solvents yields detailed insights into the nature of vibrational dynamics in liquids. The observation that the vibrational lifetime of $W(CO)_6$ in $CHCl_3$ actually becomes longer as the temperature increases demonstrates that lifetimes are not simply controlled by an activation energy. Even in a system that shows a decrease in vibrational lifetime with increasing temperature, it is unrealistic to assign an activation energy based solely on the data.

Three factors were discussed that will influence the vibrational lifetime of the metal carbonyls studied and, presumably other systems as well. They are (1) the temperature-dependent occupation number of the phonon excited in the relaxation of the initially pumped vibration; (2) the temperature dependence of the liquid's density of phonon states; and (3) the temperature dependence of the magnitude of the anharmonic coupling matrix element responsible for vibrational relaxation. Since the phonon occupation number always increases with increasing temperature, it is necessary for the other two factors to offset the increasing occupation number to yield the observed increase in the lifetime with increasing temperature that is observed in $W(CO)_6$ in $CHCl_3$. CCl_4 and $CHCl_3$ are simple enough liquids that it is within current theoretical ability to calculate the temperature-dependent density of states in these two liquids.[25] These calculations will be of fundamental importance in understanding vibrational relaxation. If the temperature dependencies of the density of low frequency states in the liquids are essentially constant or possibly increase with temperature then

such calculations will show that the key factor is the temperature dependence of the anharmonic coupling matrix elements.

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