Temperature dependence of vibrational lifetimes at the critical density in supercritical mixtures

D. J. Myers, R. S. Urdahl,[a] Binny J. Cherayil,[b] and M. D. Fayer
Department of Chemistry, Stanford University, Stanford, California 94305

Experimental measurements are reported for the temperature dependence of the vibrational lifetime, T_1, of the asymmetric CO stretching mode of tungsten hexacarbonyl in supercritical ethane at constant density from just above the critical temperature to substantially higher temperatures. T_1 is found initially to increase with temperature along an isochore (reaching a maximum at about 70° above the critical point of ethane), and then subsequently to decrease. Using a recent classical theory of vibrational relaxation, we attempt to rationalize the T_1 data. This behavior can be semiquantitatively reproduced by the theory if quantum corrections to the classical rate expressions are assumed to be temperature independent in the limit when the transition energy is much greater than thermal energy. In this case, the theory indicates that the initial increase in T_1 with temperature arises because of a competition between properties of the solvent which are changing rapidly as the temperature is raised above the critical temperature. At sufficiently high temperature, properties of the solvent vary slowly with temperature, and the explicit temperature dependence of the vibrational relaxation dominates, producing a decrease in T_1 with increasing temperature. The predictions of the theory are also examined when other postulated forms of the quantum correction factors are used, and the implications of these results for theoretical approaches to vibrational relaxation are discussed. © *1997 American Institute of Physics.* [S0021-9606(97)50447-8]

I. INTRODUCTION

Although studied extensively over the years,[1] the subject of vibrational relaxation in condensed phases continues to raise interesting and unanswered questions. Experiments from this laboratory[2] have demonstrated that the vibrational relaxation of polyatomic solutes in supercritical solvents near the critical point is affected by critical fluctuations in the medium in ways that involve consideration of a complex interplay of critical anomalies. For instance, the vibrational lifetimes of the asymmetric CO stretching mode of $W(CO)_6$ along an isotherm of ethane in the vicinity of its critical point show no significant dependence on density.[2] Vibrational lifetimes generally decrease with density [as indeed they do in the experiments on $W(CO)_6$ *away* from the critical point], so this result is somewhat counterintuitive. Even more so are results presented below, which show that above the critical temperature and along a critical isochore the vibrational lifetime of the asymmetric CO stretching mode of $W(CO)_6$ *increases* with temperature, and then eventually decreases.

In general, an increase in temperature (at constant density) should *decrease* lifetimes. Vibrational relaxation is caused by fluctuating forces in the bath acting on the vibrational oscillator. To be precise, it is caused by the Fourier component of the force–force correlation function at the oscillator frequency. Since the bath is incoherent, there are no well defined phase relationships between modes that could lead to destructive interference at some frequencies. Thus, when the temperature is increased, all Fourier components of the force–force correlation function increase in amplitude because all modes increase in population. The Fourier component of the force at the oscillator frequency will therefore increase with temperature, and vibrational relaxation, at constant density, should become faster. In the experiments presented below, however, the relaxation becomes faster only after the temperature is raised to about 70° above the critical point of ethane, which is well away from what would normally be considered the region of influence of critical fluctuations. Note that vibrational lifetimes can increase with temperature in normal liquids, since the increase in temperature is accompanied by a decrease in density.[3,4] No similar tradeoff between temperature and density occurs in the present experiments, which are carried out at constant density.

Several developments in the theoretical study of vibrational dynamics have also taken place recently.[5–7] For instance, work by Berne and his collaborators suggests that the quantum mechanical correlation functions that define vibrational lifetimes and other, related quantities cannot simply be replaced by classical analogs (as they have tended to be in the past) without introducing some error.[6,7] If this is indeed the case, quantum corrections to classical expressions may actually contribute significantly to the calculated temperature dependence of dynamical processes in liquids. The present paper is an attempt to understand the observed behavior in the context of a recent theory of vibrational relaxation[8] (also developed in this laboratory) that has been applied to the study of critical anomalies in dilute supercritical mixtures. We shall look specifically at the theory's predictions for the temperature dependence of the lifetimes in the $W(CO)_6/C_2H_6$ system.

[a]Permanent address: Applied Materials, Santa Clara, CA.
[b]On leave from the Inorganic and Physical Chemistry Dept., Indian Institute of Science, Bangalore, India.

II. EXPERIMENTAL PROCEDURES

The apparatus used to perform vibrational relaxation experiments in supercritical fluids consists of a picosecond mid-infrared laser system and a variable-temperature, high-pressure optical cell. The apparatus has been described previously and will only be briefly discussed here.[3] An output-coupled, acousto-optically Q-switched and mode-locked Nd:YAG laser is used to synchronously pump a Rh610 dye laser. A cavity-dumped 1.06 μm pulse is doubled to give $\sim$600 μJ of light at 532 nm with a pulse width of $\sim$70 ps. The output pulse from the amplified dye laser ($\sim$30–40 μJ@595 nm, 40 ps) and the cavity-dumped, frequency-doubled pulse at 532 nm serve as the signal and pump inputs, respectively, in a $LiIO_3$ optical parametric amplifier (OPA) used to generate the idler output near 5 μm. The infrared IR wavelength is determined to within $\pm$0.25 cm^{-1} using a FTIR spectrometer. The IR pulse ($\sim$2 μJ) is split into a weak probe beam, which passes down a computer controlled variable delay line with up to 5 ns of delay, and a strong pump beam. Vibrational lifetimes were obtained by fitting the data to a convolution of the instrument response and an exponential using a grid-search fit method.

The high-pressure optical cell is comprised of a Monel 400 body, gold O-rings, and sapphire windows. Stable temperatures are produced using coaxial heating cable (Philips Thermocoax) together with a fuzzy-logic controller/power supply (Solitech). Two 100 Ω platinum resistance temperature detectors (RTD's) are inserted in the body of the cell to permit careful measurement and control of the temperature to within $\pm$0.2 °C. A syringe pump (Isco 100-DX) was used to generate the variable pressures required to compress the fluid to the desired density. The pressure was accurately monitored to less than $\pm$1 psia with a precision strain-gauge transducer (Sensotech).

The experiments were conducted on the asymmetric CO stretching mode of $W(CO)_6$ near 1990 cm^{-1} (5.03 μm). The concentrations were $\sim$$10^{-5}$ mol/L. A typical sample was prepared by placing a few micrograms of solid $W(CO)_6$ (Aldrich, 99%) on the tip of a syringe needle, inserting the powder into the center of the supercritical fluid (SCF) cell through a sideport, and then compressing the system to the final operating pressure with high-purity ethane (Byrne Specialty Gases, 99.99%; T_c=305.4 K, P_c=706 psia, ρ_c=6.87 mol/L). The SCF cell was flushed repeatedly with gas before final pressurization to eliminate any air introduced into the system during insertion of the solid solute.

The optical density of the sample was varied by repeatedly diluting the mixture with fresh gas until a value of roughly 0.8–1.2 was obtained. Absorbance measurements were made directly in the cell using a Mattson Research Series FTIR spectrometer (0.25 cm^{-1} resolution) configured for external beam operation.

III. EXPERIMENTAL RESULTS

Figure 1 shows pump–probe data taken on the asymmetric CO stretching mode of $W(CO)_6$ in supercritical ethane at the critical density, 6.87 mol/L, and at the temperature 423
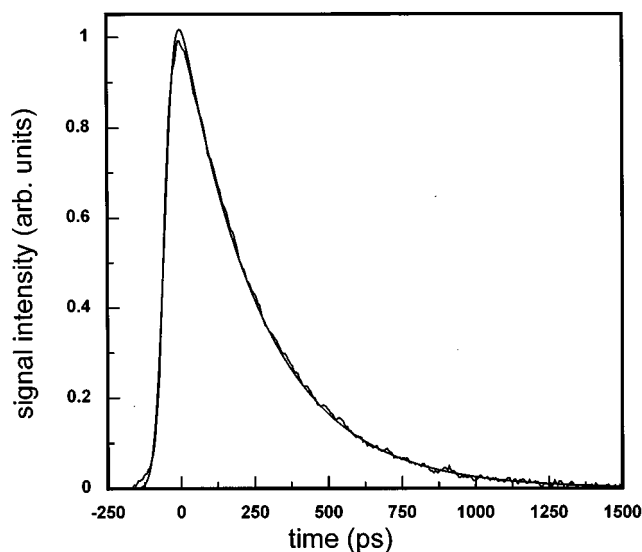

FIG. 1. Pump–probe data for the asymmetric CO stretching mode of $W(CO)_6$ in supercritical ethane (1990 cm^1) at a density of 6.87 mol/L (the critical density) and a temperature of 423 K. The fit is obtained using a convolution of the Gaussian instrument response with a single exponential decay. Similar quality data were obtained at all temperatures.

K. The critical temperature is 305.4 K. The solid curve through the data is a fit to a single exponential decay. The vibrational lifetime is 268 ps. All of the decay curves measured were single exponentials within the signal-to-noise ratio of the data. Similar data were collected over a range of temperatures. In order to check reproducibility, a number of decay curves were recorded at each temperature, the temperatures ranging from about 2 to 200 K above the critical temperature. In addition, the entire temperature dependence was repeated several times. During the course of the data collection, many fresh samples of $W(CO)_6$ and ethane were used. It was found that the data were very reproducible at a given temperature and that the entire trend with temperature was completely reproducible. A typical error bar is shown in Fig. 2.

Figure 2 is a plot of the vibrational lifetimes versus temperature for temperatures between about 2 and 200 K above the critical temperature and for a fixed density of 6.87 mol/L. The left-hand ordinate is the lifetime in ps, while the right-hand ordinate is a dimensionless lifetime, i.e., the lifetime at each temperature normalized to the lifetime at 323 K (50 °C). The dimensionless lifetimes facilitate comparison to the theoretical calculations discussed below.

As the temperature is increased, the lifetime first becomes longer (see Fig. 2). It reaches a maximum at $\sim$373 K, and then begins to decrease. At $\sim$443 K, the lifetime is the same as it is at $\sim$307 K. As the temperature is increased further, the lifetime continues to shorten. The lifetime decreases monotonically from $\sim$373 K to the highest temperature studied, $\sim$503 K. A temperature dependence of this kind has not been observed previously, although there was a hint of it in the data presented in Ref. 2, where the lifetimes were reported for a broad range of densities at two tempera-
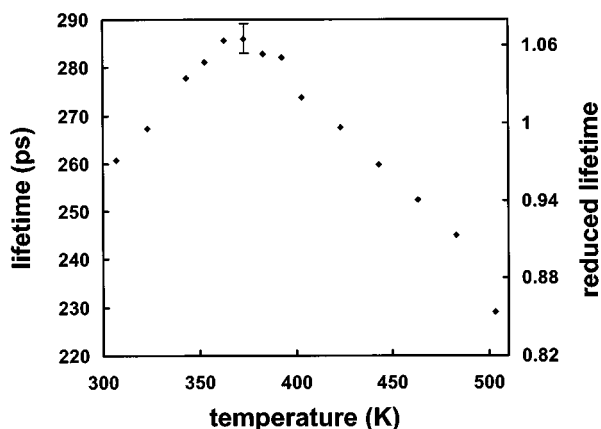
FIG. 2. Experimental vibrational lifetime data as a function of temperature for the asymmetric CO stretching mode of $W(CO)_6$ in supercritical ethane at constant density (6.87 mol/L). The lowest temperature, 307 K, is 2 K above the critical point, and the highest temperature is 503 K. The left-hand ordinate is the lifetime in ps, and the right-hand ordinate is the reduced lifetime, i.e., lifetimes normalized to the lifetime at 323 K (267 ps). A representative error bar is shown.

tures, 307 and 323 K. For a substantial range of densities around the critical density, the 323 K lifetimes are longer than the 307 K lifetimes. This indicates that the type of behavior shown in Fig. 2 will also be observed at other densities.

It must be emphasized again that the data displayed in Fig. 2 are at fixed density. At each temperature, the pressure was adjusted to bring the density back to 6.87 mol/L, the required pressure being determined from an accurate equation of state for ethane.[9] Had the density not been held constant, the increase of the lifetime with temperature would not have been as remarkable. For instance, the lifetime of the CO asymmetric stretching mode of $W(CO)_6$ in liquid $CHCl_3$ has been observed to lengthen as the temperature is increased from the melting point to the boiling point of the liquid.[3] But in this system, as the temperature increases, the liquid density decreases significantly. For the experiments in $CHCl_3$ liquid, as indicated earlier, the increase in lifetime with temperature can be ascribed to effects arising from the decrease in density.[3,4,10] For the present data, however, another explanation is required.

IV. THEORETICAL BACKGROUND

The lifetime T_1 of a vibrationally excited state of a molecule is generally defined in terms of the rates of transition $k_{m,n}$ between states m and n of the molecule.[10,11] If the dynamics of the vibrational mode of interest is modeled as a harmonic oscillator weakly coupled to a thermal reservoir, first order time-dependent perturbation theory can be used to show that the transition rate between adjacent vibrational levels is given by[5]

$$k_{n,n-1} = \frac{n}{2m\hbar\omega} \int_{-\infty}^{\infty} dt \, e^{i\omega t} \langle F(t)F(0)\rangle_{qm}, \quad (1)$$

where $\hbar$ is Planck's constant divided by 2π, m is the reduced mass of the oscillator, ω is its frequency, and $F(t)$ is the fluctuating force acting on it at time t. The angular brackets denote a quantum mechanical average over the solvent degrees of freedom.

In general, the calculation of the time correlation function in this expression is difficult. Because the corresponding *classical* time correlation function is far simpler to handle, however, efforts to determine T_1 theoretically frequently replace the quantum correlation function by the classical correlation function, with varying degrees of rigor. Until recently, this was often done by first symmetrizing Eq. (1) (to obtain a correlation function even in the time), and then replacing the symmetrized quantum correlation function by the corresponding classical correlation function.[5,11] Within this scheme, Eq. (1) is transformed to

$$k_{n,n-1} \approx \frac{2n}{m\hbar\omega(1+e^{-\beta\hbar\omega})} \int_0^{\infty} dt \, \cos\omega t \, \langle F(t)F(0)\rangle, \quad (2)$$

where $\beta = 1/k_B T$, with k_B Boltzmann's constant and T the absolute temperature. The angular brackets now denote a classical average over the solvent degrees of freedom. If the oscillator of interest (the solute vibration) is modeled as a harmonic oscillator, the relaxation to thermal equilibrium for any number of populated levels can be derived. The relevant transition in the experiments described earlier is the $1 \rightarrow 0$ transition. Since this is a high frequency transition with $\hbar\omega \gg kT$, the only vibrationally excited population resides in the $v=1$ level. The population in $v=1$ is created by the pump pulse. Therefore, relaxation to thermal equilibrium corresponds to the experimentally measured $v=1 \rightarrow 0$ rate, and the appropriate expression for the lifetime is[11]

$$T_1^{-1} = \frac{2}{m\hbar\omega} \tanh(\beta\hbar\omega/2) \int_0^{\infty} dt \, \cos\omega t \, \langle F(t)F(0)\rangle. \quad (3)$$

Bader and Berne later showed that for the case of a harmonic solute coupled linearly to a harmonic bath, the passage from quantum to classical rate expressions produces[6]

$$T_1^{-1} = \frac{\beta}{m} \int_0^{\infty} dt \, \cos\omega t \, \langle F(t)F(0)\rangle. \quad (4)$$

In their treatment, a factor of $(\beta\hbar\omega/2)\coth(\beta\hbar\omega/2)$ appears as a coefficient in Eq. (3), and is the quantum correction to the classical result. Equations (3) and (4) both refer to single phonon processes in the bath, but as is evident, their temperature dependences are quite different.

More recently, Egorov and Berne have shown that for a multiphonon process involving a harmonic solute coupled by a Lennard-Jones interaction to a Lennard-Jones solvent in which the translational and rotational degrees of freedom have been mapped onto an effective harmonic Hamiltonian, the lifetime can be calculated from[7]

$$T_1^{-1} \approx \frac{2}{m\hbar\omega} \sinh(\beta\hbar\omega/2) \int_0^{\infty} dt \, \cos\omega t \, \langle F(t)F(0)\rangle. \quad (5)$$

The hyperbolic sine term in this expression (and other factors that have been omitted for the sake of clarity and that Egorov and Berne argue are of order unity) is the quantum correction to the classical result. In the limit where $\beta\hbar\omega\gg1$ (the limit most relevant to the data involving tungsten hexacarbonyl in ethane), the differences between Eqs. (3) and (5) are even more pronounced (in respect to their temperature dependences) than those between Eqs. (3) and (4).

These differences have important implications for the temperature dependence required of $\langle F(t)F(0)\rangle$ in order that calculated values of the lifetime be in reasonable accord with the experimental trends observed in the $W(CO)_6$/ethane system. This means, in particular, that along the critical isochore and over the temperature range 307 to 503 K, calculated T_1s must first increase and then decrease. If the asymmetric CO stretching mode of $W(CO)_6$ (which absorbs at ~2000 cm^{-1}) is represented by an oscillator of frequency $\omega\approx4\times10^{14}$ Hz, the lifetimes calculated from, say, Eq. (5), can be expected to reproduce this behavior only if the force correlation function decreases steeply enough with temperature (perhaps exponentially) that it counteracts the effects of the hyperbolic sine term. On the other hand, if either Eqs. (3) or (4) are used to calculate lifetimes, the force correlation function will only need to decrease algebraically to exhibit the same behavior.

Against this background we now ask whether the hydrodynamic model of the force correlation function that was used to rationalize constant temperature lifetime data near the critical point[8] can be applied equally well to constant density data away from the critical point. As shown in Ref. 8, this correlation function is given by

$$\langle\mathbf{F}(t)\cdot\mathbf{F}(0)\rangle=\frac{1}{3V}\int d\mathbf{k}\ k^2|\hat{C}_{12}(\mathbf{k})|^2\hat{S}_1(\mathbf{k},t), \qquad (6)$$

where V is the volume of the system, $\hat{C}_{12}(\mathbf{k})$ is the two-particle direct correlation function between solvent (subscript 1) and solute (subscript 2), and $\hat{S}_1(\mathbf{k},t)$ is the dynamic structure factor of the solvent, defined as

$$\hat{S}_1(\mathbf{k},t)=\langle\delta\hat{\rho}_1(\mathbf{k},t)\delta\hat{\rho}_1(-\mathbf{k},0)\rangle. \qquad (7)$$

Here $\delta\hat{\rho}_1(\mathbf{k},t)$ is the Fourier transform of the local solvent density fluctuation at time t. A hydrodynamic approach was employed to be able to describe vibrational relaxation in supercritical fluids both close to and away from the critical point. Full details are given in Ref. 8, along with a consideration of the use of hydrodynamics in the calculation of the force correlation function.

Equation (6), along with Eq. (4), was found to describe, qualitatively, the density dependence of the lifetime of $W(CO)_6$/C_2H_6 away from the critical point when $\hat{C}_{12}(\mathbf{k})$ was approximated by the $\mathbf{k}=\mathbf{0}$ value of the binary hard sphere direct correlation function and $\hat{S}_1(\mathbf{k},t)$ was obtained from the linearized equations of hydrodynamics. These approximations led to the following analytic expression for the force correlation function:

$$\int_0^\infty dt\ \cos\ \omega t\ \langle\mathbf{F}(t)\cdot\mathbf{F}(0)\rangle$$

$$\propto T^2\rho_1\frac{\kappa_T}{\kappa_T^0}\hat{C}_{12}(0)^2\Lambda^3\left(Q_A-\frac{1}{\gamma}Q_A+\frac{1}{\gamma}Q_B\right), \qquad (8)$$

where ρ_1 is the number density of the solvent, κ_T is its isothermal compressibility, κ_T^0 is the isothermal compressibility of the ideal gas, Λ is a cutoff on high momenta, and $\gamma\equiv C_p/C_V$ is the ratio of specific heats. Q_A is a function of the correlation length of density fluctuations ξ and of the thermal diffusivity D_T; it is defined as

$$Q_A=\frac{\bar{\Lambda}^2}{D_T(1+\omega_1^2)}[R_1+R_2-R_3], \qquad (9a)$$

where $\bar{\Lambda}=\Lambda\xi$, $\omega_1=\omega\xi^2/D_T$, and

$$R_1=1-\frac{5}{3\bar{\Lambda}^2}\left[1+\frac{3}{\bar{\Lambda}^2}\left\{\frac{\tan^{-1}\bar{\Lambda}}{\bar{\Lambda}}-1\right\}\right], \qquad (9b)$$

$$R_2=\frac{5}{3\bar{\Lambda}^2}\left[1+\frac{3}{4\sqrt{2}}\omega_2^{3/2}\{\ln\ S_1-2\tan^{-1}\ S_2\}\right], \qquad (9c)$$

$$R_3=1-5\omega_2^2+\frac{5}{4\sqrt{2}}\omega_2^{5/2}[\ln\ S_1+2\tan^{-1}\ S_2], \qquad (9d)$$

with $\omega_2=\omega/\Lambda^2D_T$. The functions S_1 and S_2 are defined by $S_1=(1+\sqrt{2\omega_2}+\omega_2)/(1-\sqrt{2\omega_2}+\omega_2)$, and $S_2=\sqrt{2\omega_2}/(\omega_2-1)$. Q_B is identical to Q_A except that D_T is replaced everywhere by the sound attenuation constant Γ, which is given by $\Gamma=D_T(\gamma-1)+(4\eta_s/3+\eta_b)/\rho_m$, where η_s is the shear viscosity, η_b is the bulk viscosity, and ρ_m is the mass density. In deriving Eqs. (9a)–(9d), the limit $c_sk\ll\omega$ was assumed to hold, c_s being the adiabatic sound velocity. The thermodynamic quantities in these relations are obtained from the equations of state for ethane derived by Younglove *et al.*[9]

In anticipation of the results of the calculations presented below, it is informative to consider an alternative form of the force correlation function. In particular, the long wavelength limit used to calculate the correlation function above may be too restrictive. To test this possibility, consider an extreme short distance approximation, where, for instance,[12,13]

$$\langle\delta\hat{\rho}_1(\mathbf{k},t)\delta\hat{\rho}_1(-\mathbf{k},0)\rangle=n_s\ \exp[-k_BTk^2t^2/2m_s]. \qquad (10)$$

Here m_s is the reduced mass of a solvent molecular "oscillator," and n_s is the number of such molecules [which becomes a number density when Eq. (10) is substituted into Eq. (7) and then Eq. (6), where the expression is divided by the volume]. At very short distances, the two-particle direct correlation function for the binary hard sphere model is small, so as a further approximation let $\hat{C}_{12}(\mathbf{k})$ equal $\hat{C}_{12}(\mathbf{k}_c)$, where $\mathbf{k}_c$ is the wave vector at which the direct correlation function has its maximum. Then one can show that
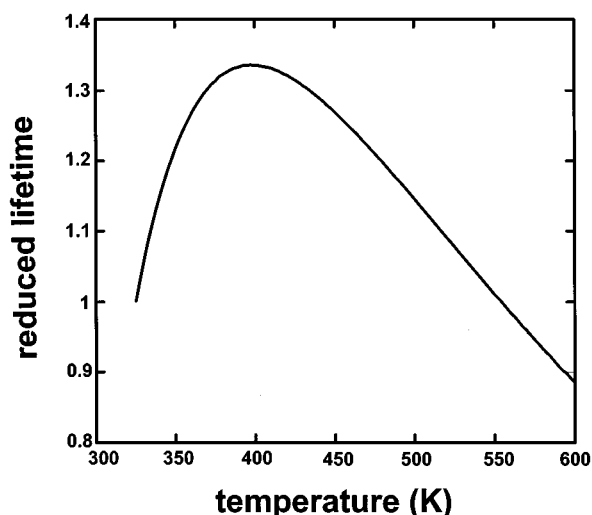
FIG. 3. Theoretically calculated reduced vibrational lifetimes versus temperature for the asymmetric CO stretching mode of $W(CO)_6$ in supercritical ethane at a fixed density of 6.87 mol/L without adjustable parameters. The calculations were performed using Eqs. (3) and (6)–(9). The curve peaks at a temperature $\sim 6\%$ higher than the data in Fig. 2, and the maximum lifetime is $\sim 23\%$ greater than the corresponding experimental value. After the peak, the decrease in lifetime with increasing temperature is similar to the data.

$$\int_0^\infty dt \cos \omega t \, \langle \mathbf{F}(t) \cdot \mathbf{F}(0) \rangle$$

$$\propto (k_B T)^{5/2} \exp[-\omega^2 m_s / 2\Lambda^2 k_B T], \qquad (11)$$

provided $\omega^2 m_s / 2\Lambda^2 k_B T$ is large.

V. COMPARISON OF THEORY AND EXPERIMENT

Figure 3 displays T_1 (expressed as a reduced lifetime) calculated as a function of T from Eq. (3) using Eqs. (8)–(9d). The calculated lifetimes are normalized to unity at 323 K, i.e., ~ 20 K above the critical temperature because the form of the force correlation function used was derived for the noncritical regime (see Ref. 8). However, it was found that the calculation could be performed to temperatures within a few degrees of the critical temperature without apparent discrepancies. The theoretical curve is found to be in reasonably good agreement with the experimental curve. (See Fig. 2.) The peak of the calculated curve occurs at ~ 395 K, about 6% higher than the data curve. The value of the reduced lifetime at the peak, 1.33, is $\sim 23\%$ greater than observed experimentally. Following the peak, the calculated T_1s decrease steadily. However, at 503 K, the highest temperature at which data were taken, the experimental value is 0.86, while the calculated value is 1.14. This is mainly a manifestation of the fact that the theoretical curve peaks at too high a temperature with too large a reduced lifetime. From the peak to the highest temperature, the data have dropped 20%, while the calculated reduced lifetime has dropped 14%.

It is important to point out that aside from the normalization of the theoretical and data curves at one temperature,

323 K, there are essentially no adjustable parameters in the calculations. (The cutoff is an adjustable parameter, but it is constrained by the requirement that $k\xi \ll 1$ away from the critical point, and it was not varied to produce agreement with the data.) The calculations include many detailed temperature dependent properties of ethane, including the isothermal compressibility, the correlation length of density fluctuations, the thermal diffusivity, the ratio of specific heats, and the sound attenuation constant, which in turn is determined by the viscosity. All of these properties are highly temperature dependent in the range from the critical temperature to ~ 70 K above T_c. For instance, in this range both the correlation length and the isothermal compressibility decrease rapidly, while the thermal diffusivity increases rapidly. It is the complex interplay of these effects, which are determined by the equation of state of ethane, that is responsible for the initial increase of T_1 with temperature. By ~ 70 K above the critical point, however, the various physical properties of ethane are no long changing as rapidly. It is at this point that the explicit T^2 temperature dependence in Eq. (8) dominates, and, therefore, the lifetime decreases with increasing temperature. Once the last vestiges of the influence of the critical point are gone, the expected constant density temperature dependence is manifested, i.e., the lifetime decreases with increasing temperature. From a microscopic perspective, as argued earlier, when the temperature is increased, the occupation numbers of all modes of the solvent increase. The amplitude of every Fourier component of the force correlation function therefore also increases, including the Fourier component at ω, the solute oscillator frequency. This leads to a decrease in the vibrational lifetime. Only in the vicinity of the critical point does the interplay of fluid physical properties overcome the normal temperature dependence.

Figure 4 shows T_1 (reduced lifetime) calculated from Eq. (4) using Eqs. (8) and (9). The resulting curve also shows an initial increase in T_1 followed by a decrease, but now the maximum of the curve occurs at ~ 475 K compared to the experimental result of 373 K. In addition, the maximum value is 64% too large, and the decrease following the peak is very gradual compared to the experimental data. Equation (4) uses the one phonon, harmonic bath quantum correction. It differs from the form of Eq. (3) [with Eqs. (8) and (9)] in the explicit temperature dependence. Equation 4 [with Eqs. (8) and (9)] is linear in T, while Eq. (3) [with Eqs. (8) and (9)] goes as $T^2 \tanh(\beta\hbar\omega/2)$. However, over the temperature range of interest, with the solute oscillator energy equal to ~ 2000 cm^{-1}, the $\tanh(\beta\hbar\omega/2)$ is essentially unity. Therefore, the difference between Fig. 4 and Fig. 3 is the factor of T vs. T^2. The explicit temperature dependence of T in the expression for T_1^{-1} is not sufficiently steep to compete with the temperature dependences of the physical properties of ethane contained in the theory of the force correlation function embodied in Eqs. (8) and (9).

Figure 5 shows T_1 (reduced lifetime) calculated from Eq. (5) using Eqs. (8) and (9). The lifetimes rise monotonically over the entire temperature range that is of any relevance to the $W(CO)_6/C_2H_6$ data. The $\sinh(\beta\hbar\omega/2)$ totally
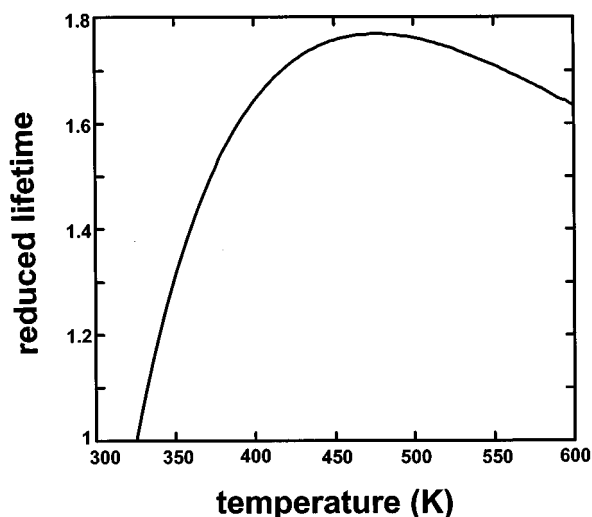
FIG. 4. Theoretically calculated reduced lifetime versus temperature for the asymmetric CO stretching mode of $W(CO)_6$ in supercritical ethane at a fixed density of 6.87 mol/L. The calculations were performed using Eqs. (4) and (6)–(9). Note that the y-axis scale is different from that in Fig. 3. The curve peaks at a temperature $\sim 25\%$ higher than the data in Fig. 2, and the maximum lifetime is $\sim 64\%$ greater than the corresponding experimental value. After the peak, the decrease in lifetime with increasing temperature is much more gradual than the data.
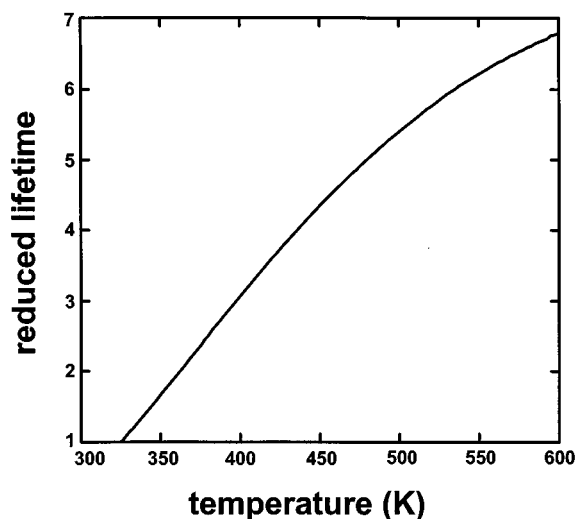

FIG. 5. Theoretically calculated reduced lifetime versus temperature for the asymmetric CO stretching mode of $W(CO)_6$ in supercritical ethane at a fixed density of 6.87 mol/L. The calculations were performed using Eqs. (5) and (6)–(9). Note that the y-axis scale is different from that in Fig. 3. The lifetimes rise monotonically over the entire temperature range that is of experimental relevance. After ~ 1500 K the curve begins to flatten.
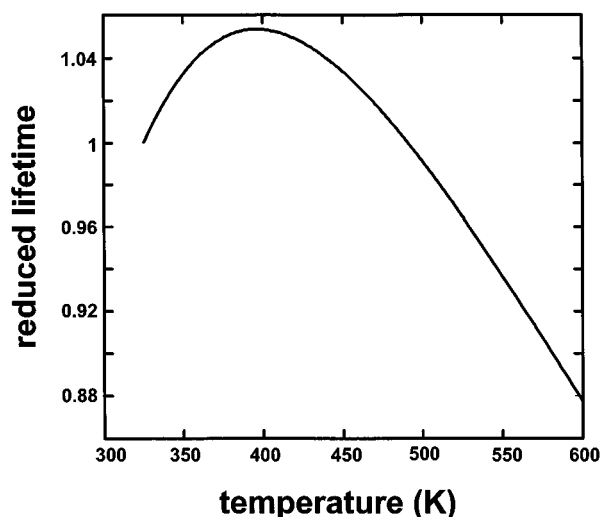

FIG. 6. Theoretically calculated reduced lifetime versus temperature performed using Eqs. (5) and (11) with the best set of adjustable parameters. The curve peaks at a temperature $\sim 6\%$ higher than the data in Fig. 2, and the maximum lifetime is $\sim 3\%$ less than the corresponding experimental value. The temperature dependence after the peak is much more gradual than the experimental data.

dominates the temperature dependence. Because the oscillator energy (2000 cm^{-1}) is large compared to $k_B T$, the positive exponential in the sinh is very large and the negative exponential is negligible. The temperature dependence contained in the force correlation function is too mild to compete with the exponential temperature dependence that arises from the multiphonon Lennard-Jones effective harmonic Hamiltonian quantum correction to the classical force correlation function. The result is that the lifetime increases approximately exponentially with temperature until very high temperature, ~ 1500 K, where the negative exponential term of the sinh becomes important.

Figure 6 shows the results of Eq. (11) in combination with Eq. (5). Equation (11) embodies a short distance (large k) approximate form of the force correlation function. This form of the force correlation function, combined with the multiphonon Lennard-Jones effective harmonic Hamiltonian quantum correction, can qualitatively reproduce the experimental temperature dependence of T_1 if m_s and Λ are chosen appropriately. It is found that the value $m_s = 1.2 \times 10^{-26}$ kg, along with $\Lambda = 3.7 \times 10^{11} \text{ m}^{-1}$, best matches the experimental data. As in Fig. 3, the peak of the curve is at 395 K. The value of the reduced lifetime is $\sim 3\%$ low at the peak. As the temperature is increased further to 503 K, the temperature of the highest temperature experimental point, the lifetime only drops 5% compared to the experimental drop of 20% and the drop of 14% calculated with Eq. (3) using Eqs. (8) and (9). The above ''best-fit'' value of m_s corresponds to the reduced mass of a diatomic whose atoms have atomic masses of 15, roughly the mass of the CH_3 fragment in ethane. This is almost certainly a coincidence, since the force correlation function does not in any manner account for internal vibrational modes of the solvent. The wave vector cutoff corresponds to about 0.2 Å in real space.

Although this alternative description of the force correlation function [in combination with Eq. (5) for the quantum correction, but not with Eq. (4)] is consistent with the experimental data on tungsten hexacarbonyl in ethane, the absence of any parameters that distinguish one solvent from another (apart from an adjustable reduced mass) suggests that calculated lifetime data for $W(CO)_6$ in other solvents are likely to

be similar to the results presented in Fig. 6. However, that is not likely to be true for real data. Recent preliminary experiments on $W(CO)_6$ in supercritical carbon dioxide indicate that at constant density the lifetime of the asymmetric CO stretching mode is essentially temperature independent up to ~ 20 K above T_c, and is then a slowly decreasing function of temperature thereafter. In addition, the calculated turnover in the temperature dependence is not affected by proximity to the critical point, so there is no physical explanation for the initial increase, turnover, and subsequent decrease of the lifetime. What the force correlation function of Eq. (11) does show is the form that is necessary to overcome the very steep temperature dependence of the quantum correction in Eq. (5).

The failure of the force correlation function of Eqs. (8) and (9) to qualitatively reproduce the experimental data when combined with quantum corrections, particularly Eq. (5), could be a failure either of the force correlation function itself or of the quantum corrections. As a test of the first possibility, we have also looked at the predictions of a much simpler force correlation function description of liquid phase vibrational relaxation, developed by Zwanzig and also based on hydrodynamics.[14] In this theory, Zwanzig relates the force correlation function to the self-diffusion coefficient of the solvent, D. Using the Stokes–Einstein equation, D can be related to the solvent viscosity. From the ethane equation of state, the viscosity is obtained as a function of temperature at the experimental density. Combining the Zwanzig force correlation function with the quantum correction of Eq. (5), a result similar to that displayed in Fig. 5 is obtained. Over the range of temperatures of experimental interest, the lifetime increases rapidly with increasing temperature. A turnover does not occur until ~ 1150 K, when the reduced lifetime is 3.9. At higher temperatures, the calculated lifetime falls off very gradually. It still has a value of 3.6 at 1800 K.

VI. DISCUSSION

The theoretical results presented above reflect the different ways in which the temperature dependence of the force correlation function plays off against the temperature dependence of the quantum correction. Both factors are obviously potential sources of error, but it appears to be the latter that most sensitively depends on details of the solute–solvent model. For instance, in going from a representation where the solute and solvent are characterized by one phonon harmonic interactions, to one where they are characterized by multiphonon Lennard-Jones effective harmonic interactions, the temperature dependent quantum correction contribution to T_1^{-1} goes from $1/T$ to $\sinh(\beta\hbar\omega/2)$. These striking differences in the calculated temperature dependence illustrate the need for caution when using classical approximation schemes in the absence of information on quantum mechanical pathways of relaxation.

The work of Bader and Berne,[6] and Egorov and Berne,[7] and the comparisons to the experimental data, have highlighted the nature of the problem. For both one phonon and multiphonon bath relaxation, Berne and co-workers[6,7] have

obtained specific quantum corrections to the classical ensemble average of the force correlation function. But these results apply only to a limited class of models. For more complex systems it is clearly desirable to have a theory that permits details of the solvent to be included in the force correlation function, as in Eq. (6).[8] The theory of Ref. 8 has been shown to be reasonably successful both near and far from the critical point, but because it is thermodynamic, it does not have associated with it a simple Hamiltonian that would permit the determination of the quantum correction. Figures 3 through 5 demonstrate the major differences that arise when the different quantum corrections for the classical ensemble average of the force correlation function are used [Eqs. (3)–(5) with Eqs. (6)–(9)]. Other methods of determining the force correlation function are also not readily amenable to the determination of the quantum correction.[5,14] The problem is that a general prescription for a quantum correction to the classical ensemble average of a particular form of the force correlation function does not exist, nor is it clear under what circumstances a quantum correction will make a substantial difference to the theoretical results.

The lack of success in combining the quantum corrections developed by Berne and co-workers with the thermodynamic force correlation function of Eqs. (6)–(9) to describe the experimental data should not be too surprising. The quantum corrections were developed in the context of a diatomic molecule in an atomic liquid. Thus, the solvent has only translational degrees of freedom. The experiments are conducted on a high frequency mode (2000 cm^{-1}) of a polyatomic solute in a polyatomic solvent. The solvent degrees of freedom consist of translational and rotational modes as well as a distribution of high frequency vibrational modes. The thermodynamic theory does not explicitly take these into account, but they are present, inasmuch as they influence the thermodynamic properties of the solvent that enter into the theoretical calculations. In addition, the solute itself has other vibrational modes, and these along with the vibrational modes of the solvent may participate in the vibrational relaxation. There are many modes, e.g., C–H bends and the C–C stretch, that could take up a significant amount of the energy in the vibrational relaxation of the initially excited CO mode. In applying the quantum corrections, the oscillator energy of 2000 cm^{-1} is an input. This would be appropriate for a diatomic in an atomic liquid. It is unclear how the problem should be handled if most of the energy is transferred to high frequency modes of the solvent and solute.

As an exercise with no formal theoretical justification, it is interesting to consider the possibility that the frequency used in the sinh term of Eq. (5) should not be the frequency of the initially excited solute oscillator. In the relaxation of a high frequency mode of a polyatomic molecule in a polyatomic solvent, a significant fraction of the initially excited oscillator's energy may be transferred to other high frequency vibrational modes of the solute or the solvent. Assume that the fraction of the initial oscillator energy that is transferred to high frequency vibrational modes either does not contribute to the quantum correction or is described by a factor with a very weak temperature dependence. Further, the

energy, $\hbar\omega$, which is the portion of the initial oscillator energy that actually relaxes by multiphonon emission, is the energy that is used in the $\sinh(\beta\hbar\omega/2)$ term in Eq. (5). In this case, using Eq. (5) for energies $\hbar\omega$ of a few hundred cm^{-1} with Eqs. (6)–(9) (with the full oscillator energy used in the calculation of the force correlation function) produces a temperature dependence that is identical to that displayed in Fig. 4. This occurs because expanding the $\sinh(\beta\hbar\omega/2)$ for small argument in Eq. (5) yields Eq. (4). [Note that in the full treatment by Egorov and Berne[7] of the quantum correction that leads to Eq. (5), there are additional small terms on the order of unity. The full expression does not reduce identically to Eq. (4) for small argument.) Since Eq. (5) reduces approximately to Eq. (4) the agreement with experiment is better. The lifetime initially increases, peaks, and then decreases as the temperature is raised. However, even for these low energies, the peak is too large in magnitude and occurs at too high a temperature. This exercise may indicate that the correct treatment of high frequency vibrational modes in the description of the relaxation of polyatomic molecules in polyatomic solvents is important.

The data presented in Fig. 2 demonstrate that vibrational relaxation of a polyatomic solute in a polyatomic supercritical solvent can have a complex temperature dependence even when the experiments are conducted at constant density. The reduced lifetime calculations without adjustable parameters using Eqs. (3) and (6)–(9) give a reasonable reproduction of the experimental results without a quantum correction. The results were explained qualitatively in terms of the mutual tradeoffs among physical parameters that are rapidly changing as the temperature moves above the region influenced by the presence of the critical point. Whether the agreement between theory and experiment is fortuitous will be tested by subsequent experiments. The results of measurements at different densities in ethane and in other solvents, such as CO_2, can be readily compared to theory. The changes in density and solvent enter into the calculations through different thermodynamic parameters that can be obtained from the equations of state of the solvents. The calculations displayed in Fig. 6, which are based on using the large k approximation for the force correlation function with the sinh quantum correction [Eq. (5) with Eqs. (6), (7), (10), and (11)] also give reasonable agreement with the data when appropriate values of the adjustable parameters are selected. This relationship did not involve physical properties of the solvent or the proximity of the critical point. The density dependence of this expression only enters through the density dependence of the hard sphere direct correlation function in Eq. (6) and the number density, n_s/V. Comparison to experiment can test the validity of this model as well.

An improved theoretical understanding of vibrational relaxation in condensed phases is clearly needed to provide a full explication of the intriguing experimental results on supercritical mixtures presented in this paper and to increase our comprehension of a wide variety of other problems. The present analysis underscores the need for refinements both to the description of fluctuating forces in the solvent medium and to the quantum corrections to classical approximations of the force–force correlation function.

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