

Temperature and density dependent solute vibrational relaxation in supercritical fluoroform

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Temperature- and density-dependent vibrational relaxation data for the ν_6 asymmetric stretch of $W(CO)_6$ in supercritical fluoroform (trifluoromethane, CHF_3) are presented and compared to a recent theory of solute vibrational relaxation. The theory, which uses thermodynamic and hydrodynamic conditions of the solvent as input parameters, shows very good agreement in reproducing the temperature- and density-dependent trends of the experimental data with a minimum of adjustable parameters. Once a small number of parameters are fixed by fitting the functional form of the density dependence, there are no adjustable parameters in the calculations of the temperature dependence. © 2001 American Institute of Physics. [DOI: 10.1063/1.1389853]

I. INTRODUCTION

Vibrational energy relaxation (VER) in dense media is dominated by nonradiative decay. The nonradiative relaxation can have a complicated and intertwined dependence on temperature and density. For this reason, supercritical fluids (SCFs) are useful solvents for the study of solute VER since the temperature and density can be controlled independently. In addition, the temperature and density dependence of solute VER can serve as a sensitive probe of solute-solvent interactions in supercritical fluids.

VER is caused by dynamic intermolecular interactions between the solvent and the solute. The dynamic interactions produce fluctuating forces that act on the solute mode of interest. The fluctuating forces are frequently described in terms of the force-force correlation function.¹⁻⁶ In polyatomic molecules, the pathway for VER can involve both intra- and intermolecular modes.⁷⁻⁹ For a polyatomic molecule in which there is a significant density of states of intramolecular modes at lower frequencies than the relaxing mode, the solvent ensures that energy is conserved by providing a continuum of very low-frequency modes^{7,8} that make up for intramolecular energy mismatches. In this context, the vibrational lifetime is related to the Fourier transform of the force-force correlation function at the frequency associated with the energy deposition into the bath.⁸

In this article, we report the temperature dependence of the vibrational relaxation of the ν_6 asymmetric CO stretching mode of $W(CO)_6$ (1985 cm^{-1}) in supercritical fluoroform (trifluoromethane, CHF_3) at the critical density, as well as improved density dependent data for the same system.^{10,11} The data are compared to a refined version of a recent theo-

retical treatment of VER in SCFs that utilizes thermodynamic and hydrodynamic properties of the solvent as input parameters.^{10,12-14} The theory has had considerable success in describing the density and temperature dependence of the asymmetric CO stretching mode of $W(CO)_6$ in, for example, supercritical ethane.^{10,14,15} In ethane, at the critical density, the temperature dependence displays an “inverted” region. As the temperature is increased above the critical temperature, the vibrational lifetime, T_1 , becomes longer, eventually turning over and becoming shorter as the temperature is increased sufficiently. The theory not only reproduces this behavior nearly quantitatively, but also describes the density dependence at fixed temperature in several solvents.^{10,14,15} The theory uses thermodynamic and hydrodynamic properties of the solvents obtained from their equations of state as input parameters. The principal adjustable parameters are the frequency associated with the deposition of energy into the solvent during VER and a scaling parameter that is used to match the theory to the data at one experimental point. The scaling does not influence the functional form of the calculated curves.

The theory employs realistic properties of the solvent through inclusion of parameters obtained from the equation of state. However, it uses a hard sphere solute-solvent direct correlation function to describe the solute-solvent spatial distribution and their interaction. While the theory has been quite successful, questions remain about the efficacy of employing a hard sphere model in part of the calculations. In this article, a more comprehensive version of the theory is compared to the fluoroform data, and, again, good agreement is found. A small number of parameters are adjusted to fit the density dependence at fixed temperature. With these parameters fixed, the temperature dependence is reproduced with no adjustable parameters. In addition, the relationships be-

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tween this theory and other theoretical approaches^{16,17} are explicated.

II. THEORY

Following an initial presentation of the basic theoretical approach,¹² the theory has gone through several versions that eliminated small wave vector approximations^{10,14,18} and added a quantum correction factor^{10,15} to enable quantitative comparisons between VER data in SCFs and theoretical calculations of the functional form of the density and temperature dependence of VER. The theoretical approach was developed to enable known macroscopic thermodynamic and hydrodynamic properties of the SCF solvent to be incorporated into the calculation of the vibrational relaxation. Here the full theory is presented with the inclusion of a temperature dependence of the direct correlation function.

The present approach, like many others, takes Fermi's Golden Rule as its starting point.¹⁹ If the coupling between the vibrating oscillator and the bath modes is weak, then, to lowest order, the transition rate from one vibrational level (m) to another (n) is given by Fermi's Golden Rule,

$$k_{mn}(\rho, T) = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle V_{mn}(t) V_{nm}(0) \rangle, \quad (1)$$

where k_{mn} is the transition rate, ρ is the density, T is the temperature, t is time, \hbar is Planck's constant divided by 2π , and $\langle V_{mn}(t) V_{nm}(0) \rangle$ is the solute-solvent potential autocorrelation function. This expression shows the relationship of the relaxation rate to the fluctuations in the oscillator-solvent coupling potential. For a diatomic, ω is the oscillator frequency. However, for a polyatomic, in which some fraction of the energy of the initially excited mode can be transferred to other intramolecular modes, ω is the frequency corresponding to the energy that is transferred to the bath (solvent).⁸ The perturbation V is assumed to be linear in the solute coordinate q , that is for a diatomic,

$$V = -qF, \quad (2)$$

so that F is the solvent force on the oscillator.⁷ If one makes the additional assumption that the oscillator is harmonic, q can be rewritten in terms of raising and lowering operators, and for a transition from the first vibrational excited state of the mode excited by the laser, 1, to the ground state of this mode, 0,

$$q_{10} = \sqrt{\frac{\hbar}{2\mu\omega_0}} \quad (3)$$

where μ is the oscillator reduced mass and ω_0 is the frequency of the oscillator excited by the laser. Equation (1) with Eqs. (2) and (3) can be reduced to⁷

$$k_{10} = T_1^{-1} = \frac{1}{2\mu\hbar\omega_0} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle F(t)F(0) \rangle_{qm}, \quad (4)$$

where T_1 is the vibrational lifetime. Note that ω_0 and ω are the same for a diatomic oscillator. However, as mentioned earlier, for a polyatomic molecule, ω is the Fourier component associated with the bath that participates in the relaxation process, that is, ω is the bath frequency responsible for

energy conservation.⁸ If the VER involves intramolecular modes, $\omega \neq \omega_0$, and the prefactor will change to reflect the participation of the intramolecular modes (see later in this work).^{8,20} The qm subscript in the rate expression indicates that the bracket is a quantum mechanical trace over the solvent modes. As several authors have pointed out,^{4,7,21-23} it is incorrect to directly replace the quantum mechanical correlation function with its classical analog. In terms of the classical force-force correlation function,

$$T_1^{-1} = \frac{Q}{2\mu\hbar\omega_0} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle F(t)F(0) \rangle_{cl}, \quad (5)$$

where Q is the "quantum correction factor" (not necessarily a simple multiplicative constant). The nature of the correction factor is a topic of considerable recent interest.^{4,22,23} Several forms of Q have been suggested, and they are generally functions of temperature and frequency. The form of the correction factor used in the calculations will be discussed in detail later.

The calculation of the lifetime is thus reduced to the problem of calculating the force-force correlation function, $\langle F(t)F(0) \rangle$. In previous presentations of the theory,^{10,12} density functional theory^{24,25} was employed to derive expressions for the correlation function that involve the thermodynamic parameters of the system.²⁵ In the treatment of vibrational relaxation in supercritical fluids, the density functional approach permits the use of known density- and temperature-dependent properties of the solvent in the calculation of T_1 . The final expression for the relaxation rate of the first excited state is

$$T_1^{-1} = \frac{2Q}{\mu\hbar\omega_0} \frac{2\pi}{3} k_B^2 T^2 \int_0^{\infty} dt \cos(\omega t) \times \int_0^{\infty} dk k^4 |C_{21}(k)|^2 \hat{S}_1(k, t), \quad (6)$$

where k_B is Boltzmann's constant, and k is the wave vector scalar. The functions in Eq. (6), as well as the integrals and functions given later, involve the scalar wave vector because the angular integrations have been performed. $C_{21}(k)$ is the solute-solvent direct correlation function, and $\hat{S}_1(k, t)$ is the dynamic structure factor of the solvent. Thus, the relaxation rate is related to the solute-solvent interactions through the direct correlation function and the time- and position-dependent evolution of the solvent through the dynamic structure factor. The prefactor, $1/\mu\hbar\omega_0$, is only appropriate for a diatomic in which intramolecular modes do not participate. For the experimental system discussed later, there is an unknown multiplicative factor that accounts for the particular intramolecular mode pathways that are involved in the relaxation.²⁰

The idea of evaluating the force-force correlation function through hydrodynamic/thermodynamic functions of the solvent is not entirely new.^{16,25} Hills was the first to describe the solute oscillator-solvent coupling potential as a function of the solvent's density fluctuations.^{16,26} He uses various superposition approximations to simplify the multi-particle density correlation functions⁷ and obtains the expression

$$T_1^{-1} \propto |D_{ij}|^2 \int dk k^2 V^2(k) S_1(k, \omega), \quad (7)$$

where V is the solute–solvent coupling potential and D_{ij} , which is temperature and density independent, is some function of the solute vibrational coordinates. Recently Nemtsov *et al.*¹⁷ have employed similar techniques, noting that they differ from Hills' work by calculating the force–force correlation function, rather than the potential–potential correlation function [which would be identical in the weak coupling limit of Eq. (1), i.e., Eq. (2)]. Their final result can be rearranged to be

$$T_1^{-1} \propto \frac{1}{T} \int dk k^4 V^2(k) S_1(k, \omega), \quad (8)$$

where V is again the solute oscillator–solvent interaction potential. The theory presented here can be compared to the other expressions by first taking the Fourier transform of the dynamic structure factor in Eq. (6) to obtain

$$T_1^{-1} \propto QT^2 \int dk k^4 C_{21}^2(k) S_1(k, \omega). \quad (9)$$

Next, for large distances (small k),^{24,27}

$$C_{21}(k) \rightarrow \frac{V(k)}{k_B T}. \quad (10)$$

Therefore, the current hydrodynamic/thermodynamic theory becomes

$$T_1^{-1} \propto Q \int dk k^4 V^2(k) S_1(k, \omega). \quad (11)$$

Neglecting constants, the only difference between Eqs. (8) and (11) is the $1/T$ versus Q . One commonly used quantum correction factor, derived by Bader and Berne⁴ for the case of single phonon processes of harmonic oscillators in harmonic baths, yields

$$Q \propto \frac{1}{T}. \quad (12)$$

Using this as the quantum correction factor, the temperature and density dependence of the theory of Nemtsov *et al.* [Eq. (8)] and the long wavelength limit of the current theory with the Bader–Berne form of Q [Eq. (11) with (12)] are identical.

To implement the theory as given in Eq. (6), explicit expressions are needed for the various factors. As shown earlier, the direct correlation function can be related to the solute–solvent potential, and thus to the nature of the k -dependent spatial distribution of the solvent around the solute. It is k dependent. $C_{21}(k)$ is calculated explicitly using the binary hard sphere expression²⁸

$$C_{21}^{\text{HS}}(k) = -2\pi(I_1 + I_2). \quad (13)$$

The variables I_1 and I_2 are functions of R_1 and R_2 , the solvent and solute hard sphere diameters, respectively, and ρ_1 and ρ_2 , the solvent and solute number densities, respectively. I_1 and I_2 were given previously.¹⁰ The hard sphere expression is temperature independent. However, it is known that direct correlation functions (and radial distribution func-

tions) of real fluids do change with temperature,^{24,27} due in part to the change in size of the solute and solvent molecules. At all but the shortest distances (largest k values), the temperature dependence of the direct correlation function is well approximated by^{24,27,29–31}

$$C_{21}(k) \propto \frac{1}{k_B T}. \quad (14)$$

The VER theory is dominated by contributions of the various components over a relatively narrow range of large k . From a reliable closure relationship, the mean spherical approximation, the direct correlation function in r -space goes as $1/k_B T$ for $r > \sigma$, where σ is the molecular diameter or, in the case of a mixture, the mean between the solvent and solute diameters.^{24,28} This behavior should be reasonably well satisfied at $r \sim \sigma$ as well.³¹ Though the Fourier transform is not a one-to-one mapping, the function's values at large r dominate the function's behavior at small k . As will be discussed in detail below, the most important k -range in the VER theory is between ~ 0.3 and 1.2 \AA^{-1} . The parameter σ for the experimental systems is roughly $5\text{--}5.5 \text{ \AA}$, depending on the solvent, which translates in k space ($k = 2\pi/r$) to a value k_{max} of $\sim 1.0\text{--}1.3 \text{ \AA}^{-1}$. Thus the theory involves a range with $k \leq k_{\text{max}}$, which indicates that the temperature dependence of the direct correlation function should be well approximated by $1/k_B T$. To incorporate this temperature dependence while still using the detailed expressions for hard spheres [i.e., $C_{21}^{\text{HS}}(k)$], the temperature-dependent direct correlation function is written as

$$C_{21}(k) = C_{21}^{\text{HS}}(k) \frac{k_B T_{\text{ref}}}{k_B T}. \quad (15)$$

T_{ref} is a reference temperature, which will be discussed more in Sec. III. Equation (15) is only used for a finite range of temperatures around T_{ref} , as it will clearly make the direct correlation function go to 0 in the limit of infinite T .

The dynamic structure factor, $\hat{S}_1(\mathbf{k}, t)$, plays an integral role in the theory. Physically, it describes the time-dependent solvent structure. Note that $\hat{S}_1(\mathbf{k}, t)$ is a function only of the solvent properties. $\hat{S}_1(\mathbf{k}, t)$ can be expressed in terms of hydrodynamic functions³² as

$$\hat{S}_1(\mathbf{k}, t) = \hat{S}_1(\mathbf{k}) \left[\left(1 - \frac{1}{\gamma} \right) e^{-D_T k^2 t} + \frac{1}{\gamma} \cos(c_s k t) e^{-\Gamma k^2 t} \right].$$

In using a hydrodynamic model for $\hat{S}_1(\mathbf{k}, t)$ in the VER theory, numerical analysis shows that contributions to the k integral in Eq. (6) from the combination of $|C_{21}(k)|^2$ and $\hat{S}_1(\mathbf{k}, t)$ are overwhelmingly dominated by the function at relatively large k , that is, $k \sim 1 \text{ \AA}^{-1}$. As discussed previously^{10,14} and demonstrated experimentally^{33–36} and theoretically,^{37–39} for the range of k of interest for the VER theory, the terms in $\hat{S}_1(\mathbf{k}, t)$ describing the acoustic modes (cos term) do not contribute significantly. The terms describing the diffusive modes, which account for the Rayleigh peak in light scattering, can be extended to large k using an expression developed by Kawasaki.⁴⁰ The end result is that $\hat{S}_1(\mathbf{k}, t)$ can be written as

$$\hat{S}_1(k, t) = \hat{S}_1(k) \left[\left(1 - \frac{1}{\gamma} \right) e^{-t/\tau_1(k)} \right], \quad (16)$$

where $\gamma \equiv C_p/C_v$ is the ratio of the constant pressure and constant volume heat capacities and

$$\frac{1}{\tau_1(k)} = \frac{k_B T}{8\pi\eta\xi^3} \left[1 + k^2\xi^2 + \left(k^3\xi^3 - \frac{1}{k\xi} \right) \tan^{-1}(k\xi) \right]. \quad (17)$$

η is the viscosity and ξ is the correlation length of density fluctuations. In Eq. (16), $\hat{S}_1(k)$ is the equilibrium structure factor of the solvent, which is approximated by the Ornstein–Zernike expression,³²

$$\hat{S}_1(k) = \frac{\rho_1 \kappa_T / \kappa_T^0}{1 + k^2 \xi^2}, \quad (18)$$

where ρ_1 is the number density of the solvent, κ_T is its isothermal compressibility, and κ_T^0 is the isothermal compressibility of the ideal gas.

As indicated before, Q in Eq. (6) is a quantum correction factor for which a number of expressions have been suggested in the past. Most involve a function of the temperature and the oscillator frequency and apply to simple model systems. One form that seems to have fairly wide applicability was developed by Egelstaff.⁴¹ In recent tests of several correction factors on exactly solvable systems²² and on vibrational relaxation in liquid oxygen,²³ Egorov and Skinner showed that the Egelstaff correction performed best overall. To apply this correction, the classical force correlation function is multiplied by

$$Q = e^{\hbar\omega/2k_B T}, \quad (19a)$$

and the time t in it is replaced by

$$t \rightarrow \sqrt{t^2 + (\hbar/2k_B T)^2}. \quad (19b)$$

In Eq. (6), only the dynamic structure factor component of the force–force correlation function, $\hat{S}_1(\mathbf{k}, t)$, contains t , and the substitution, (19b), is made in this term. Equation (6) is evaluated using Eqs. (15)–(19). The time integral in Eq. (6), including the Egelstaff correction factor, is related to a Bessel function and can be performed analytically. The result is

$$T_1^{-1} = \frac{e^{\hbar\omega/2k_B T}}{\mu\omega_0} \frac{2\pi}{3} k_B T \left(1 - \frac{1}{\gamma} \right) \int_0^\infty |C_{21}(k)|^2 \times \hat{S}_1(k) \frac{K_1((\hbar/2k_B T)[1/\tau_1^2(k) + \omega^2]^{1/2})}{\tau_1(k)[1/\tau_1^2(k) + \omega^2]^{1/2}} k^4 dk, \quad (20)$$

where K_1 is a modified Bessel function.⁴² $C_{21}(k)$ is given in Eq. (15), $\tau_1(k)$ is given in Eq. (17), and $\hat{S}_1(k)$ is given in Eq. (18). ω is the frequency associated with energy deposition into the bath, ω_0 is the frequency of the initially excited oscillator, and μ is the reduced mass of the initially excited oscillator. The k integral is performed numerically.

A wide variety of density and temperature-dependent input parameters are required to implement the theory. These include ρ_1 , the number density of the solvent; κ_T , the iso-

thermal compressibility; ξ , the correlation length of density fluctuations; $\gamma \equiv C_p/C_v$, the ratio of specific heats; and η , the viscosity. Accurate thermodynamic information is necessary to calculate the temperature and density dependence of VER data. Very accurate equations of state for ethane^{43,44} and CO₂ (Ref. 44) are available. These equations of state were employed in analyzing VER data previously.^{10,14,15} Fluoroform is not as well studied. However, it is possible to combine information from a number of reliable sources^{45–47} to obtain the required input information. The input parameters used below are significantly more accurate than those employed previously.¹¹

The thermodynamic and hydrodynamic parameters that enter the theory build in a detailed description of the SCF solvent. Most of these input parameters vary substantially with density and temperature. In the near critical region, the variations of the parameters are very large. In comparing the theory with experiment in the next section, the solvent thermodynamic/hydrodynamic parameters feed into the calculations. As discussed later, the zero density T_1 is removed from the data, and the resulting solvent-induced density- and temperature-dependent lifetimes, $T_1(\rho, T)$, are compared to the theory. Because the relaxation involves intramolecular vibrations as well as the bath, the form of the multiplicative prefactor [given in Eq. (20) for a diatomic] is unknown, the expression

$$T_1^{-1} \propto e^{\hbar\omega/2k_B T} \frac{1}{T} \left(1 - \frac{1}{\gamma} \right) \int_0^\infty |C_{21}^{\text{HS}}(k)|^2 \times \hat{S}_1(k) \frac{K_1((\hbar/2k_B T)[\tau_1^{-2}(k) + \omega^2]^{1/2})}{\tau_1(k)[\tau_1^{-2}(k) + \omega^2]^{1/2}} k^4 dk \quad (21)$$

is used for comparing theory and experiment where the interest is in the functional forms of the density and temperature dependences. The theoretical curves are scaled to match the data at one particular temperature and density point (a reference point). The solute and solvent hard sphere diameters are input parameters, which are based on molecular models, crystal structures, and other means. The results are not highly sensitive to the solute diameter, but are more sensitive to the solvent diameter. The parameter in Eq. (21) that has a substantial effect on the functional form of the density-dependent curve is the frequency, ω . Measurements of VER of the CO asymmetric stretch in the collisionless gas phase show that there is relatively rapid (~ 1.2 ns) VER in the absence of interactions with the solvent.⁴⁸ The solvent increases the VER rate by opening up additional pathways for VER. Thus, it is reasonable to assume that $\omega \neq \omega_0$. Since the details of the pathway or pathways for relaxation are not known, the frequency ω is taken to be unknown. It would be expected to fall within the continuum of the low-frequency states of the solvent.^{15,49,50} ω was determined to be 150 cm⁻¹ in ethane by fitting the VER density dependence.¹⁰

III. RESULTS AND DISCUSSION

Figure 1 shows $T_1(\rho)$ measured in fluoroform. The ν_6 mode of W(CO)₆ undergoes relatively rapid VER in the col-

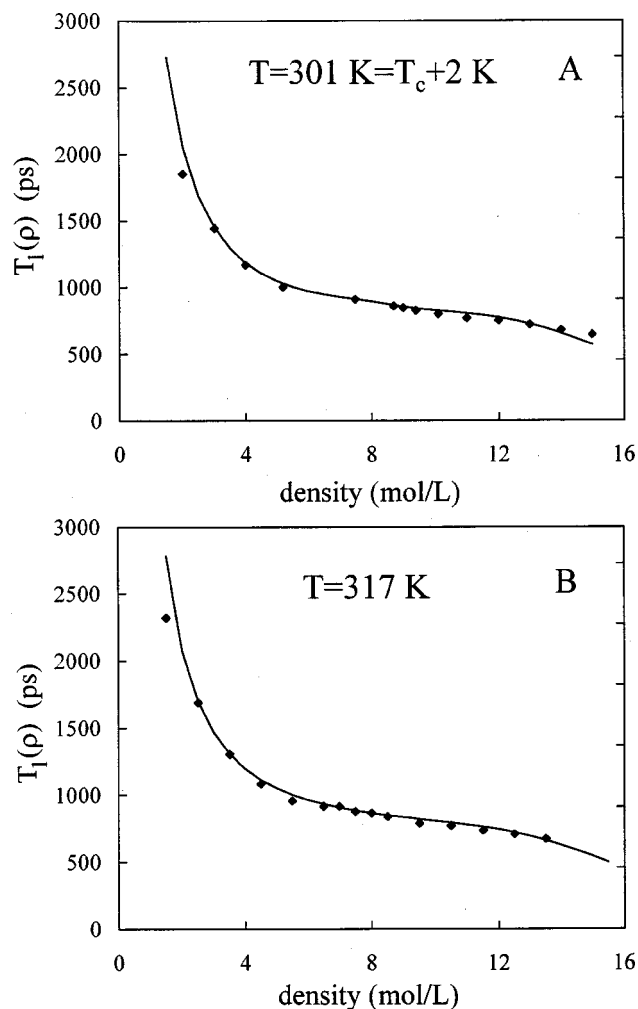


FIG. 1. (A) $T_1(\rho)$ data in supercritical fluoroform on the near critical isotherm (301 K), 2 K above T_c , and the calculated curve, which is scaled to match the data at the critical density, 7.6 mol/L. The theory does a very good job of reproducing the shape of the data with only a small adjustment in the solvent size from that obtained from a molecular model as a fitting parameter that affects the shape of the calculated curve. B) $T_1(\rho)$ data taken in fluoroform at 317 K. The theory curve is calculated with *no free parameters*; the theory does an excellent job of reproducing the higher temperature data.

tionless gas phase. Of interest here is the contribution to VER induced by interactions with the solvent. Therefore, the zero density T_1 (1.28 ± 0.10 ns) is removed from the data,^{14,48} and the resulting density-dependent lifetimes, $T_1(\rho)$, and temperature-dependent lifetimes, $T_1(T)$, are compared to the theory. Figure 1(a) is data on the near critical isotherm of 301 K, that is, 2 K above T_c . [In fluoroform, 2 mol/L is the lowest density for which $W(\text{CO})_6$ has sufficient solubility to perform the experiments at 301 K.] The calculated curve [Eq. (21)] is scaled to match the data at the critical density, 7.6 M. An accurate value of the hard sphere diameter is not available for fluoroform. A molecular space-filling model (Fisher–Hirschfelder–Taylor modeling kit) was used to estimate the fluoroform volume, from which a diameter of 3.64 Å was obtained. However, the best agreement with the $T_1(\rho, T)$ at 28 °C is obtained with a diameter of 3.28 Å (10% smaller than the model value). This value is used at all other temperatures. The temperature dependence of the direct correlation function is taken into account explicitly using Eq.

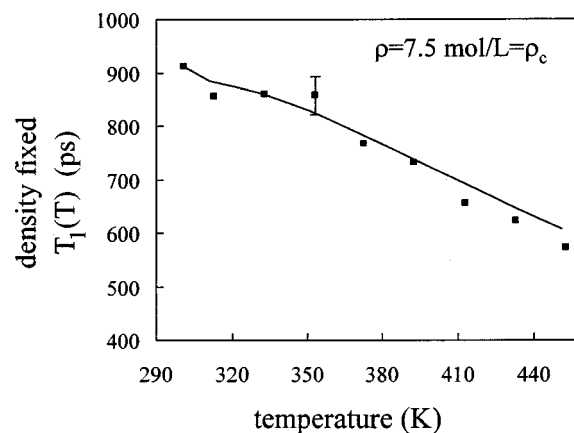


FIG. 2. Vibrational lifetime data and theoretical calculations for the CO asymmetric stretch of $W(\text{CO})_6$ in supercritical fluoroform at constant density (7.6 mol/L (ρ_c)). The error bar denotes \pm one standard deviation. The curve was calculated with *no adjustable parameters*; two parameters were determined from the fit to the data in figure 1A. All other parameters come from temperature dependent properties of the solvent obtained from the literature. The theory quantitatively fits the data over the entire experimental temperature range.

(15) with $T_{\text{ref}} = 301$ K (28 °C). In previous experiments on ethane,^{10,14,15} it was found that the optimal value for the bath frequency, ω , is 150 cm^{-1} . A distribution of frequencies centered at 150 cm^{-1} gives identical calculated results to those obtained using the single frequency.¹⁰ For example, if a Gaussian distribution centered at 150 cm^{-1} with a standard deviation of 20 cm^{-1} is employed, the calculated curve is the same as one calculated with the single 150 cm^{-1} frequency. Thus, the value of ω may represent the center of a distribution rather than a single frequency. Because of the high density of low-frequency intramolecular states,⁴⁸ it is unlikely that a single relaxation pathway with a single value of ω is appropriate. The distribution of relaxation pathways is reflected in the fact that a distribution of bath frequencies centered about 150 cm^{-1} is able to fit the data. In fitting the ethane data, ω was the principal adjustable parameter. It has a major influence on the shape of the calculated curves.¹⁰ In the fluoroform calculations presented here, ω is not adjusted, but is set to 150 cm^{-1} . Judging from the quality of the calculated curve in Fig. 1(a), the theory does a remarkably good job of reproducing the shape of the data with only a small adjustment in solvent size as a fitting parameter that affects the functional form of the density dependence.

Figure 1(b) shows data taken at 317 K, the higher temperature isotherm. The calculated curve (solid line) is obtained using the thermodynamic/hydrodynamic input parameters for the higher temperature and using the same scaling factor as at 301 K. $\omega = 150 \text{ cm}^{-1}$, and the fluoroform diameter is 3.28 Å. Therefore, there are *no free parameters in the calculation of the lifetimes along this isotherm*. As with the data taken in ethane, the theory does a very good job of reproducing the density-dependent data.

The variable temperature data along the critical isochore are displayed in Fig. 2, along with the theoretical calculations. The error bar represents \pm one standard deviation. The calculated curve uses the same scaling constant, hard sphere diameter, and bath frequency as the isothermal (Fig. 1) cal-

culations. Therefore, the theoretical calculations presented in Fig. 2 were performed *without recourse to adjustable parameters*. The theory does a quantitative job of predicting the experimental temperature dependence. The fluoroform critical isochoric data are more similar to those in carbon dioxide than ethane.¹⁵ In ethane, an inverted temperature dependence (lifetime becomes longer as the temperature increases above T_c) was observed, and an inverted region was predicted by the VER theory.¹⁵ It appears that there is no significant inverted region in the fluoroform data, and the theory is consistent with the data.

In the comparisons between the data and theoretical calculations previously presented, the calculations were scaled to match the data at one point in Fig. 1(a). The scaling factor determines the absolute magnitude of the solvent contribution to the relaxation rate. The intramolecular density of states for $W(CO)_6$ at the experimental temperatures and at an energy corresponding to the excited CO stretching mode is $\sim 10^8/\text{cm}^{-1}$.⁴⁸ Therefore, a vast number of relaxation pathways may be involved in determining the value of T_1 . In the gas phase (no solvent contribution) the decay time is 1.28 ns. Vibrational relaxation is relatively efficient even in the absence of the solvent. The role of the solvent is to open up additional paths that are not available in the gas phase.

IV. CONCLUDING REMARKS

In previous publications the density- and temperature-dependent T_1 for the ν_6 mode $W(CO)_6$ in supercritical ethane and CO_2 and preliminary density-dependent data on fluoroform were presented.^{10,14,15} The theory was able to reproduce the density- and temperature-dependent trends with considerable success. In this article, temperature-dependent and improved density-dependent T_1 data for the ν_6 mode $W(CO)_6$ in supercritical fluoroform were presented. The current detailed studies in supercritical fluoroform were made possible by better equations of state for fluoroform.^{46,47}

The relationships between the theory presented here and other theories were discussed. The theory in its general form contains the direct correlation function and the dynamic structure factor. As expected, numerical analysis of the resulting equations demonstrated that VER is dominated by large k (short distance) portions of the various factors. Therefore, a form of the dynamic structure factor appropriate for large k is employed.¹⁴ Calculation of the dynamic structure factor uses temperature- and density-dependent thermodynamic and hydrodynamic properties of fluoroform that are known with reasonable accuracy.^{45–47} The form of the potential that is employed determines a theoretical expression for C_{21} . To obtain an explicit expression for calculation of the observables, a hard sphere potential was utilized. For hard spheres, C_{21} has an analytical form, which was used in the calculations. An appropriate form of the temperature dependence of C_{21} was used. Excellent agreement was achieved between theory and experiment for the density dependence (Fig. 1) and temperature dependence (Fig. 2) of the solvent-induced vibrational relaxation using a detailed description of the solvent structural dynamics with known experimental properties of the solvent. The solvent properties (ρ_1 , the number density of the solvent, κ_T , the isothermal compress-

ibility, ξ , the correlation length of density fluctuations, $\gamma = C_p/C_V$, the ratio of specific heats, and η , the viscosity) are the inputs. A hard sphere description of the solute–solvent spatial distribution and interaction is employed. The experimental and theoretical results are in very good agreement. The broad agreement between theory and experiment that was achieved indicates that the hard sphere description of the solute–solvent interaction is adequate. Solvent density fluctuations, which become long range near the critical point, are incorporated through the detailed description of the solvent. Such density fluctuations can play a role in VER without enhanced solute–solvent interactions.^{51–53} The results show that it is possible to theoretically reproduce the data without using an attractive solute–solvent potential.⁵⁴

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