# Vibrational relaxation of a polyatomic solute in a polyatomic supercritical fluid near the critical point

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Vibrational lifetimes and absorption spectra of the asymmetric CO stretching mode ($\sim$1990 $cm^{-1}$) of $W(CO)_6$ in supercritical $CO_2$ are reported as functions of solvent density and temperature. Close to the critical temperature, the observables are density independent over a twofold range of density. Possible explanations are discussed for this unique behavior. © *1996 American Institute of Physics.* [S0021-9606(96)51543-6]

## I. INTRODUCTION

In this Communication, we present the first vibrational relaxation measurements of a polyatomic solute in a polyatomic supercritical fluid (SCF). Infrared ps pump–probe experiments are used to measure the vibrational lifetime of the asymmetric CO stretching mode of $W(CO)_6$ ($\sim$1990 $cm^{-1}$) in supercritical $CO_2$ at $T=33$ °C and $T=50$ °C over a wide range of densities. The absorption line frequencies acquired at the same temperatures over the same range of densities show trends remarkably similar to those of the lifetime data. At 33 °C, two degrees above the critical temperature, $T_c$, the vibrational lifetime and line frequency remain essentially unchanged over nearly a twofold range in density around the critical density ($\rho_c$). The data also show that this intriguing behavior vanishes by 50 °C, where the lifetime and line frequency change continuously with density. If interpreted in terms of a clustering model, the data indicate the formation of solvation structures which have static and dynamic intermolecular interactions that are constant against changes in the bulk density.

It has been known for many years that low volatility solids can dissolve in gases at temperatures above $T_c$, and that the ability of a gas to act as a solvent depends on its density.[1] Recent interest in the solvating properties of SCF's was initiated by the experimental measurements of Eckert and co-workers[2] in which they observed large, negative solute partial molar volumes (PMV's) when organic molecules, e.g., naphthalene and camphor, at infinite dilution were dissolved in supercritical $CO_2$ and $C_2H_4$. They interpreted their data as suggestive of some type of clustering process of the solvent about the solute. Debenedetti[3] and Cochran, Lee, and Pfund[4] pursued the idea of clustering on a molecular level using fluctuation analysis and integral equations coupled with the solution theory of Kirkwood and Buff.[5] Their treatments predict an increase in the correlation length of solute–solvent density fluctuations near the critical point. The magnitude of these fluctuations at infinite dilution is then taken as a statistical measure of the extent of clustering. Molecular dynamics simulations of Lennard-Jones fluids give further evidence for the clustering model in solute–solvent systems.[6]

Numerous experimental studies have been performed to elucidate the nature of the solute–solvent interactions near the critical point. The bulk of this work involves comparing the local dielectric constant in the vicinity of a dilute solute to that predicted by continuum models of dipole solvation,[7,8] which are commonly based on the Onsager reaction field theory.[9] The experimental observable is some property of the system, e.g., peak in absorption or fluorescence spectrum, referenced to its value in the gas phase. A wide variety of solute–solvent systems have been studied using infrared[10,11] and UV-visible[12] absorption techniques as well as fluorescence spectroscopy.[13,14] Although compelling evidence exists in support of a local density enhancement about an infinitely dilute solute near the critical point, results based on variations in macroscopic quantities, e.g., dielectric constants, PMV's, cannot be readily used to give a description of microscopic solute–solvent interactions. Hochstrasser and co-workers studied *trans*-stilbene isomerization in supercritical ethane in order to investigate the influence of clustering on dynamics induced by optical excitation.[15] The fluorescence lifetime of *t*-stilbene was found to be essentially constant over roughly a factor of two change in pressure. This result was taken to imply the presence of clusters sufficiently large as to be insensitive to bulk density changes.

Recent experiments on vibrational dynamics in polyatomic liquids have shown that density variations can play an important role in determining vibrational lifetimes.[16–18] The results on SCF systems presented below will be discussed in terms of relationships between the vibrational experimental observables and the local solvent density about a solute when the system is near the critical point. The use of transient vibrational spectroscopy, which interrogates the dynamics of a system on the ground state potential surface, avoids possible complications associated with changes in intermolecular interactions that occur upon excitation to excited electronic states.

## II. EXPERIMENTAL PROCEDURES

The apparatus for performing vibrational relaxation experiments in supercritical fluids consists of a picosecond mid-infrared laser system and a variable temperature, high pressure optical cell. The laser system used to generate tunable light near 5 $\mu$m is a slightly modified version of a design previously described in detail.[19] Its use to perform IR pump–probe experiments has also been thoroughly discussed.[16]

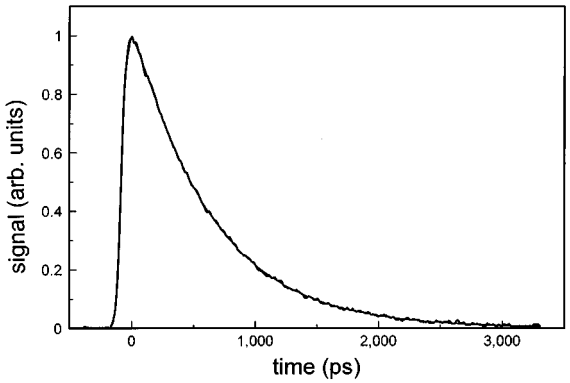


FIG. 1. Typical infrared pump–probe decay and fit for the $T_{1u}$ asymmetric CO stretch of $W(CO)_6$ in $CO_2$ at 33 °C and a density of 17 mol/L. The quality of the data is sufficiently high that it is difficult to discern the fit, which gives a vibrational lifetime of 623 ps. The critical temperature is 31 °C, and the critical density is 10.6 mol/L.

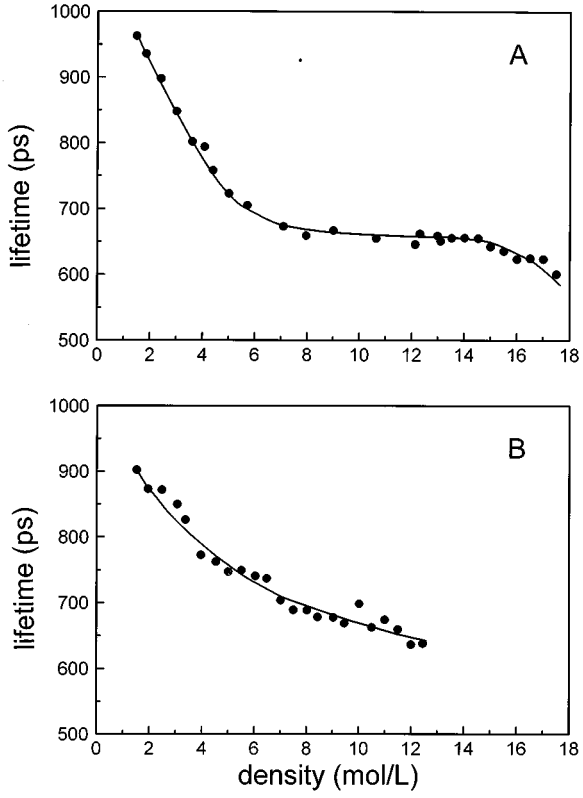


FIG. 2. (A) Vibrational lifetimes of the $T_{1u}$ asymmetric CO stretch of $W(CO)_6$ versus density of $CO_2$ at 33 °C. The line through the data is a visual aid. For a range of densities near $\rho_c$, the vibrational lifetime is density independent. (B) Lifetime data at 50 °C. The line through the data is a visual aid. Note that the lifetime changes continuously with density.

The high pressure optical cell was designed specifically for IR spectroscopic studies and has $CaF_2$ windows and teflon seals. Stable temperatures are produced using coaxial heating cable together with a fuzzy-logic controller/power supply. Two separate platinum RTD's, one for feedback stabilization and the other as a reference (calibrated at 31 °C), are inserted in the cell body to allow for careful monitoring and control of the temperature to within ±0.2 °C. Variable pressures are generated with a syringe pump, and are accurately monitored to within ±1.0 psia by a precision strain-gauge transducer. The maximum pressure in these experiments did not exceed ~1500 psia.

The experiments were conducted on the asymmetric CO stretching mode of $W(CO)_6$ at ~1990 $cm^{-1}$ (5.03 $\mu$m). The vibrational frequency varies slightly with density and solvent, and the laser was tuned to the absorption maximum at each density. Samples were prepared by inserting a few milligrams of solid $W(CO)_6$ (Aldrich, 99%) into the center of the SCF cell through a sideport, and then compressing the system to the desired pressure with high purity $CO_2$ (Middleton Bay Airgas, 99.9995%). The entire system was flushed thoroughly with $CO_2$ before final pressurization to eliminate any air introduced into the lines during insertion of the $W(CO)_6$. The optical density of the sample was adjusted by repeated dilution with fresh $CO_2$ to give a value typically within the range of 0.8–1.2. Absorbance measurements are made directly in the cell using a Fourier transform infrared spectrometer.

## III. RESULTS AND DISCUSSION

Figure 1 shows a pump–probe decay measurement of the lifetime of the $T_{1u}$ asymmetric CO stretching mode of $W(CO)_6$ in supercritical $CO_2$ at 33 °C, i.e., two degrees above $T_c$. The density is 17 mol/L, which is about 85% of the room temperature liquid density (23 °C, 2000 psia, 20 mol/L).[20] Superimposed on the data is a fit including convolution with the instrument response. The quality of the data is excellent and the fit is so close that it is difficult to distinguish it from the data, which yields a lifetime ($T_1$) of 623 ps. The lifetime of this mode has been measured previously in a number of liquids over a wide range of temperatures.[16] For comparison, the lifetimes in room temperature $CCl_4$ and $CHCl_3$ are 700 ps and 350 ps, respectively.

Figure 2(A) shows data taken at 33 °C over a factor of ~17 change in density, which spans a range of densities from well below the critical density ($\rho_c$=10.6 mol/L) to densities nearing that of the liquid. The densities were calculated using a modified 32-term Benedict–Webb–Rubin equation of state.[20] At the lowest densities, the vibrational lifetime becomes shorter as the density increases. However, as the density approaches $\rho_c$, the data displays a remarkable feature; the lifetime becomes essentially *independent of density* over a wide range. Unpublished data at 40 °C shows a similar behavior, but the flat region is narrower, appearing more as an inflection point. Figure 2(B) presents lifetime data taken at 50 °C, only 19° above $T_c$. At this temperature, there is no indication of a flat region near $\rho_c$.

Figure 3 displays the absorption line frequencies of the $T_{1u}$ mode as a function of density, also at 33 °C and 50 °C. As the density is increased, the absorption line shifts to the red. There is a striking similarity between the line center data and the vibrational lifetimes. At 33 °C, both types of data display a constant response near $\rho_c$ which is absent at 50 °C. In addition, the slope of the curve prior to the flat region is

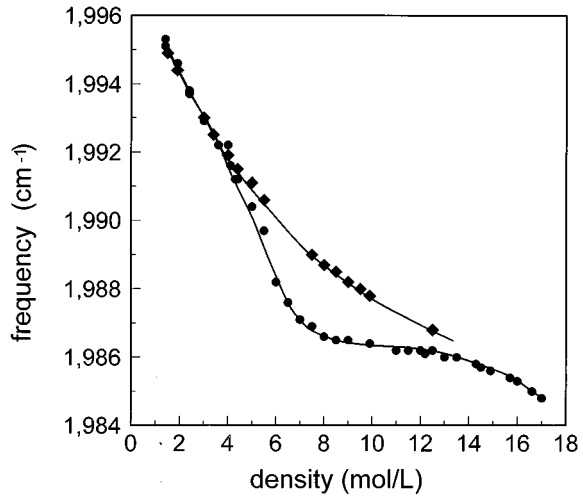


FIG. 3. Absorption line centers of the $T_{1u}$ asymmetric CO stretch of $W(CO)_6$ versus density of $CO_2$ at 33 °C (circles) and 50 °C (squares). The lines through the data are a visual aid. The line frequency vs density data shows a remarkable similarity to the lifetime vs density plots given in Fig. 2. At 33 °C, the line frequency is density independent near $\rho_c$, whereas at 50 °C, it varies continuously with density.

greater at 33 °C than at 50 °C for both types of data. Being near the critical temperature and density has a profound influence on both experimental observables.

The dependence of vibrational lifetimes on intermolecular interactions with the solvent has been discussed theoretically in considerable detail, both in general[18,21] and specifically for $W(CO)_6$.[16–18] Analysis of experiments in liquids has shown that an increase in density causes the vibrational lifetime to become shorter.[17] High pressure experiments in liquids and solids have shown that vibrational line frequencies are also density dependent.[22] A red shift results from an increase in the attractive part of the intermolecular potential. Therefore, as the density is increased at 50 °C and at the lower densities at 33 °C, the decrease in the lifetime and the red shift of the spectrum reflect increased strength of the solute–solvent intermolecular interactions. However, the lack of a density dependence of either the lifetime or the line frequency at 33 °C near $\rho_c$ does not have a straightforward explanation.

The range in density near the critical point over which the anomalous behavior occurs coincides almost exactly with the region of the phase diagram characterized by large variations in solvent compressibility.[23] At 33 °C this region is broad, but by 40 °C it has become quite narrow, just like the 40 °C vibrational data.[24] By 50 °C, the compressibility, lifetime, and line frequency data vary continuously with density. Like the compressibility, the vibrational data display anomalous behavior near $T_c$ over the range of densities where there is critical behavior. This region is characterized by density fluctuations with large correlation lengths. As $\rho_c$ is approached, the correlation length grows, reaching the macroscopic distance scales which give rise to critical opalescence. Vibrational relaxation of a solute is intimately related to fluctuations in the solvent, as is made clear in the force correlation function formulation of vibrational relaxation.[18,21] Therefore, it is possible that the existence of critical fluctuations plays a role in the vibrational relaxation. However, it is not obvious how critical fluctuations would be involved in the anomalous density dependence of the line frequency or the vibrational lifetime.

The vibrational lifetime is determined by dynamic intermolecular interactions. The CO quantum oscillators experience fluctuating forces generated by nuclear motions of the solvent, as described in the force correlation function formulation of the dynamics.[18,21] Vibrational relaxation is induced by the Fourier component of the force correlation function at the oscillator frequency. For the vibrational lifetime to be density independent, the magnitude of the Fourier component of the force correlation function at the oscillator frequency must not change with density. It is reasonable to assume that this one Fourier component remains unchanged because the entire spectrum of fluctuating forces remains constant as the bulk density is varied near the critical density. The vibrational line frequency depends on the average interaction of the oscillator with its environment. In a crystal, even at 0 K, the application of pressure, which changes the density, will cause shifts in vibrational line frequencies. When the density is changed, the potential experienced by the oscillator changes, and the frequency shifts.[22] For the frequency to remain constant as the bulk SCF density is increased, the oscillator potential must remain unchanged. Therefore, the observations of constant lifetime and line frequency for a range of densities near the critical point imply that both the oscillator potential and the fluctuations in this potential are density independent.

A lack of density dependent behavior for both the vibrational lifetime and the line frequency will occur if the local density experienced by the $W(CO)_6$ solute is independent of the bulk SCF density. However, the vibrational data cannot be explained by a simple postulate of clustering as has been done to describe macroscopic observable, such as PMV's. The dynamic and static properties of the solute–solvent cluster must not change with density. The proposal by Lee, Holtom, and Hochstrasser[15] of a cluster so large that the properties do not change also cannot explain the data. First, the onset of the density independent region is abrupt, which does not suggest the presence of a cluster that has finally grown so large that its properties stop changing. More significant is the fact that both the lifetime and the line position data start changing again when the density increases well past its critical value. If a cluster sufficiently large to possess static properties were responsible for the density independent region near the critical point, then the lifetime and line position would not be expected to change as the density is increased further.

A cluster model can explain the data if small fixed size solute–solvent clusters are formed in the range of densities around the critical density. If the size, and therefore the properties, e.g., local density, spectrum of fluctuations, are density independent then the observables will be as well. Such a structure may form if there is a liquidlike condensation about the solute. Although the bulk system is slightly above the

critical temperature, an attractive solute–solvent interaction greater than that between solvent molecules changes the local properties of the system. A ''localized phase transition'' could occur forming a nanodroplet composed of only two or three solvent shells. The nanodroplet would have a small fixed size because the range of the solute/solvent attractive interaction will fall off relatively rapidly, e.g., as $1/r^6$, so beyond a few solvent shells, condensation is no longer favorable. The result could be the formation of a stable structure that does not change over a range of densities. When a sufficiently high pressure is applied, there is an overall favorable change in the local free energy, the structure grows, and the vibrational observables again become density dependent. At higher temperature (50 °C) the increased solute–solvent interaction is insufficient to form the stable nanodroplet structure. Clustering may still occur, but the cluster properties change continuously with density.

Data taken on the vibrational lifetimes and line frequencies of $W(CO)_6$ in supercritical ethane at 34 °C, again two degrees above $T_c$, show that they are also independent of density near $\rho_c$.[24] These observables change both above and below the range of densities around $\rho_c$, which is consistent with the idea of a small fixed size structure for densities near $\rho_c$. Further experiments and theoretical investigations into the fixed size cluster model and the possible role of critical fluctuations are aimed at elucidating the mechanism responsible for these anomalous vibrational observables near the critical point, as well as providing insights into the nature of the local intermolecular interactions and dynamics in SCFs.

## ACKNOWLEDGMENTS

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