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14. ABSTRACT
Both experimental and theoretical methods were employed to gain a molecular level understanding of vibrational energy flow and solute-solvent interactions in supercritical fluids (SCF) as a function of temperature and pressure. Infrared (IR) ps pump-probe experiments and vibrational absorption spectroscopy were employed to study the vibrational dynamics of solutes in a variety of supercritical fluids. The SCF solvents were ethane, fluoroform, and carbon dioxide. Pump-probe (transient absorption) experiments were used to directly follow the relaxation of vibrational energy as a function of the density at fixed temperature and the temperature at fixed density in SCF solvents. Vibrational spectra were used to observe the spectroscopic shifts of vibrational peaks as a function of density and temperature. Detailed theory was developed to describe the density and temperature dependence of vibrational relaxation. The theory was able to reproduce the experimental results with considerable accuracy using a minimal number of parameters.

15. SUBJECT TERMS

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FINAL REPORT: Grant Number: F49620-97-1-0061

PRINCIPAL INVESTIGATOR: Professor Michael D. Fayer

INSTITUTION: Department of Chemistry, Stanford University

GRANT TITLE: Ultrafast Nonlinear Optical Investigations of Supercritical Fluids

AWARD PERIOD: 1/15/1997 - 11/30/2000 (Total funding period)

OBJECTIVES: To gain an understanding of vibrational dynamics of complex molecules in supercritical fluids as a function of temperature and pressure. To use the nature of vibrational energy flow as a probe of solute-solvent interactions in supercritical fluid solvents. To develop new methods for the investigation of solute-solvent interactions in supercritical fluids. To develop theoretical descriptions of density and temperature dependence of vibrational energy relaxation as a function of density and pressure in supercritical fluids.

APPROACH:

This program used both experimental and theoretical methods to gain a molecular level understanding of vibrational energy flow and solute-solvent interactions in supercritical fluids (SCF) as a function of temperature and pressure. Infrared (IR) ps pump-probe experiments and vibrational absorption spectroscopy were employed to study the vibrational dynamics of solutes in a variety of supercritical fluids. Pump-probe (transient absorption) experiments were used to directly follow the relaxation of vibrational energy as a function of the density at fixed temperature and the temperature at fixed density in SCF solvents. Vibrational spectra were used to observe the spectroscopic shifts of vibrational peaks as a function of density and temperature. Detailed theory was developed to describe the density and temperature dependence of vibrational relaxation.

ACCOMPLISHMENTS:

The project, entitled, "Ultrafast Nonlinear Optical Investigations of Supercritical Fluids" focused on the nature of solute-solvent interactions in supercritical fluids by examining vibrational energy relaxation as a function of SCF density and temperature. A

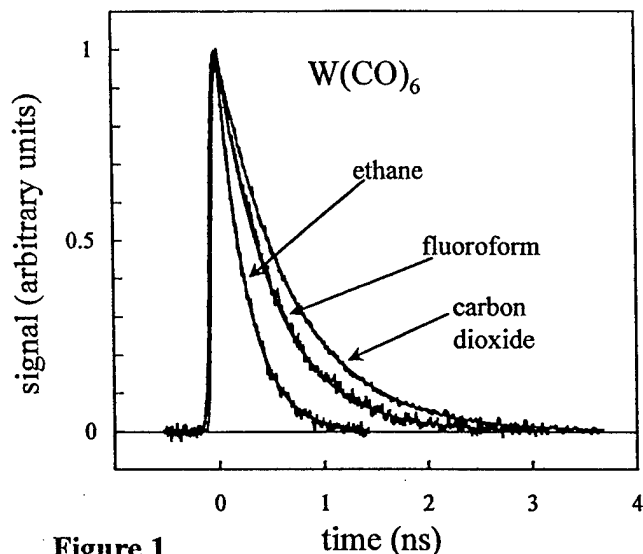


Figure 1 vibrational relaxation of the CO asymmetric stretching mode of the solute, $W(CO)_6$, in several different polyatomic supercritical solvents (ethane, carbon dioxide, and fluoroform), in argon, and in the collisionless gas phase. Figure 1 shows typical pump-probe data.

In all three SCF polyatomic solvents studied, the vibrational lifetime decreases with increasing density at constant temperature (see below). The lifetimes show a significant dependence on the solvent, with the lifetimes shortest in ethane and longest in carbon dioxide. The spectral peak positions of the $W(CO)_6$ asymmetric CO stretching vibration in the three solvents shift with density in a manner similar to the trends observed for the lifetimes.

list of publications is given below.

Vibrational lifetimes were measured directly using ps pump-probe experiments. The experiments are the first to measure vibrational lifetimes of polyatomic molecules in polyatomic SCFs. Experimental and theoretical results were presented for

The vibrational lifetime vs. temperature data at fixed solvent density display a remarkable solvent-dependent behavior. The vibrational relaxation with ethane as the solvent actually slows down with increasing temperature for a significant range of temperatures above T_c . (Figure 3 below shows data in ethane as a function of temperature at the critical density.) At sufficiently high temperature, the trend changes direction, and the lifetime decreases with further increases in temperature. The inverted temperature dependence does not occur when the solvent is CO_2 . The lifetime decreases as the temperature is increased above T_c .

The theory that was developed to explain the vibrational relaxation data in

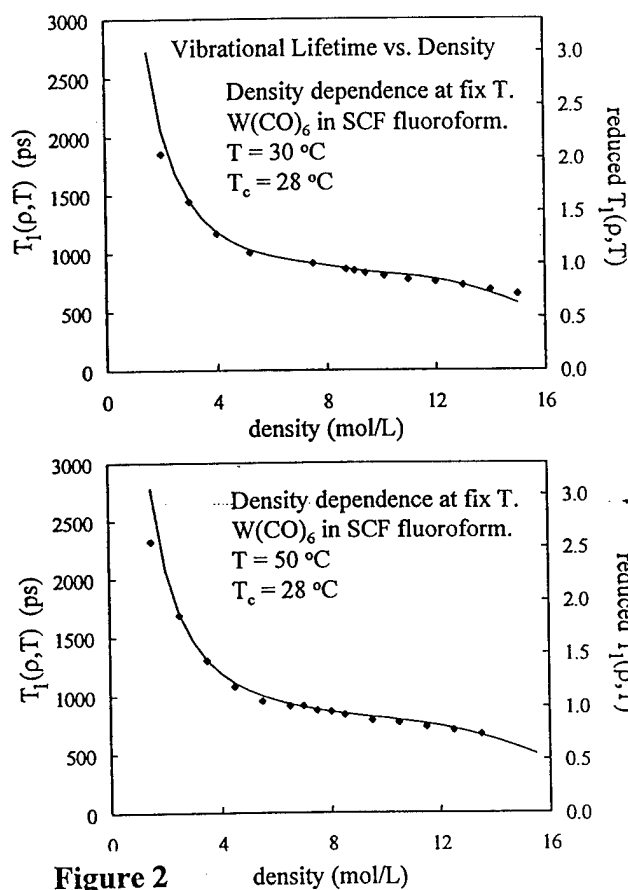


Figure 2

supercritical fluids is based on relations between the microscopic events and bulk solvent properties given by accurately known equations of state. Figure 2 shows density dependent data at two temperatures. The solid lines through the data were calculated with the theory we developed. The theory has a minimum of free parameters to fit: a scaling factor to account for various constants, the Fourier transform

frequency, ω , which corresponds to the energy deposited into the solvent in the

vibrational relaxation process, and the hard sphere diameter of the solvent, which is heavily constrained. All three variables were optimized once (the solvent diameter once for each solvent) and then fixed. The Egelstaff quantum correction is used to account for the calculation of a classical force-force correlation function. In the data presented in fig. 2, the upper calculated curve has two adjustable parameters, the scaling factor, which does not influence the shape of the curve, and the fluoroform hard sphere radius. ω was obtained from the fit to data in ethane. The hard sphere radius was obtained from low

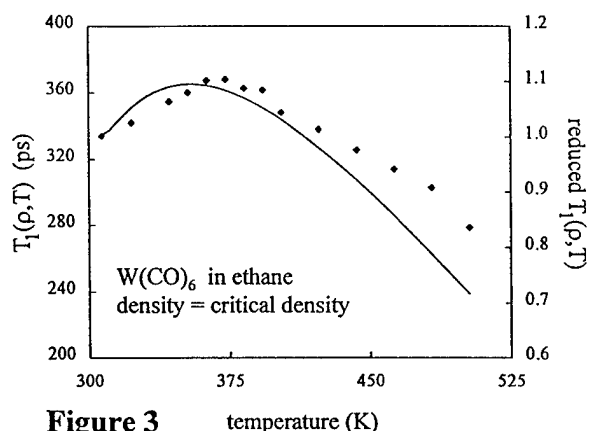


Figure 3 temperature (K)

temperature crystal structure data and adjusted to account for the large temperature change. The calculated curve through the data in the lower panel has no adjustable parameters. Overall, the agreement between theory and experiment is remarkably good. The theory can do a very respectable job of reproducing the density dependence at fixed temperature. It is also able to reproduce the temperature dependence at fixed density. Of particular importance is the theoretical reproduction of the inverted temperature dependence in ethane and the lack of an inverted region in CO_2 . Figure 3 shows the calculated temperature dependence with no adjustable parameters. While the calculation is not perfect, it captures the novel behavior of the data with almost quantitative accuracy.

Studying vibrational dynamics in supercritical fluids can aid in understanding the vibrational relaxation process as well as providing insights into the nature of solute-

solvent interactions in supercritical fluids. One important result that emerged from the studies is the success of the theory to describe the data over a range of solvents, densities, and temperatures. The theory contains details of the solvent through the input of thermodynamic and hydrodynamic parameters obtained from the solvent's equation of state. However, the solute-solvent spatial distribution, which comes into the theory through the solute-solvent direct correlation function, is obtained with a hard sphere description. Therefore, it is possible to describe the data without invoking attractive solute-solvent interactions, which can give rise to local density augmentation (solute-solvent clustering). Other theoretical treatments can describe some of these same data using attractive solute-solvent interactions.

Local density augmentation is a common theme in the description of many experiments. It is a topic of a great deal of current research on supercritical fluids. The appearance of mild changes in experimental observables with large changes in density around the critical density is often ascribed to local density augmentation. The experiments presented here exhibit the type of behavior that might be explained by solute-solvent clustering. The theoretical analysis demonstrates that the vibrational relaxation experiments can be described with a theory that does not include attractive solute-solvent interactions and local density augmentation. This is an area of rapid growth in understanding. The work conducted under this grant has made a major contribution to increasing understanding of this important subject.

In the course of conducting the vibrational relaxation studies as a function of density in SCFs, it was necessary to know the zero density (gas phase) vibrational lifetime of the 2000 cm^{-1} asymmetric stretching mode of the solute, $\text{W}(\text{CO})_6$. The

important issues in SCFs involve the solute-solvent contribution to vibrational relaxation. The zero density value of the lifetime is necessary so that it can be removed from the density dependence of the lifetime. For this reason, measurements were performed on $\text{W}(\text{CO})_6$ in the gas phase. In all the experiments conducted in three SCFs over a very wide range of densities and in a wide variety of liquids, the vibrational decay of the 2000 cm^{-1} asymmetric stretching mode of $\text{W}(\text{CO})_6$ is always a single exponential (see fig. 1). This proved not to be the case in the gas phase.

The decay in the gas phase is a tri-exponential. Briefly, the gas phase dynamics reveal an intramolecular vibrational relaxation/redistribution lifetime of $1.28 \pm 0.1\text{ ns}$, as well as the presence of faster (140 ps) and slower ($>100\text{ ns}$) components. The slower component is attributed to a heating-induced spectral shift of the CO stretch. The fast component results from the time evolution of the superposition state created by thermally populated low frequency vibrational modes. The slow and fast components are strictly gas phase phenomena, and both disappear upon addition of sufficiently high pressures of argon. The observation of the fast component is a fundamentally new effect that has important implications for understanding the microscopic nature of energy flow in gas phase polyatomic molecules.

PUBLICATIONS:

“Vibrational Relaxation in Supercritical Fluids Near the Critical Point,” Binny J. Cherayil and M. D. Fayer, *J. Chem. Phys.* 107, 7642-7650 (1997).

“Vibrational Lifetimes and Vibrational Line Positions in Polyatomic Supercritical Fluids Near the Critical Point,” R. S. Urdahl, D. J. Myers, K. D. Rector, P. H. Davis, B. J. Cherayil, and M. D. Fayer, *J. Chem. Phys.*, 107, 3747-3157 (1997).

“Temperature Dependence of Vibrational Lifetimes at the Critical Density in Supercritical Mixtures,” D. J. Myers, R. S. Urdahl, Binny J. Cherayil and M. D. Fayer, *J. Chem. Phys.* 107, 9741-9748 (1997).

“Temperature Dependent Vibrational Lifetimes in Supercritical Fluids Near the Critical Point,” D. J. Myers, Shirley Chen, Motoyuki Shigeiwa, Binny J. Cherayil and M. D. Fayer, *J. Chem. Phys.* 109, 5971-5979 (1998).

“Density Dependent Vibrational Relaxation in Supercritical Fluids,” D. J. Myers, Motoyuki Shigeiwa, M. D. Fayer, and Binny J. Cherayil, *Chem. Phys. Lett.* 313, 592-599 (1999).

“Non-exponential Relaxation of a Single Quantum Vibrational Excitation of a Large Molecule in Collision Free Gas Phase at Elevated Temperature,” D. J. Myers, Motoyuki Shigeiwa, M. D. Fayer, and R. Silbey, *Chem. Phys. Lett.* 312, 399-406 (1999).

“Vibrational Lifetimes and Spectral Shifts in Supercritical Fluids as a Function of Density: Experiments and Theory,” D. J. Myers, Motoyuki Shigeiwa, M. D. Fayer, and Binny J. Cherayil, *J. Phys. Chem.* 104, 2402-2414 (2000).

DISCLOSURES AND PATENTS:

None