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During the course of this grant, substantial progress in the investigation of dynamics and intermolecular interactions in supercritical fluids (SCFs) has been made. The project also included studies of liquids to provide understanding of the relationship between SCFs and normal liquids. The research utilized fast (ps) dynamical measurements of solutes in SCFs. The focus has been on experiments that can probe dynamics and interactions on the ground state potential surface. The first measurements of vibrational relaxation of polyatomic solutes in polyatomic SCFs have been made. These measurements are the first to examine dynamics near the SCF critical temperature. Previous vibrational dynamics measurements on systems, such as a diatomic in a rare gas, have been made far from the critical temperature. Measurements, such as fluorescence of large molecules, have also been conducted far from the critical temperature. Our vibrational relaxation experiments are performed using the ps infrared (IR) pump-probe method. As a precursor to future work, we have also made orientational relaxation polarization selective IR measurements in liquids and performed vibrational echo experiments in liquids.

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Final Technical Report: Ultrafast Nonlinear Optical Investigations of Supercritical Fluids (F49620-94-1-0141)

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During the course of this grant, substantial progress in the investigation of dynamics and intermolecular interactions in supercritical fluids (SCFs) has been made. The project also included studies of liquids to provide understanding of the relationship between SCFs and normal liquids.

The research utilized fast (ps) dynamical measurements of solutes in SCFs. The focus has been on experiments that can probe dynamics and interactions on the ground state potential surface. The first measurements of vibrational relaxation of polyatomic solutes in polyatomic SCFs have been made. These measurements are the first to examine dynamics near the SCF critical temperature. Previous vibrational dynamics measurements on systems, such as a diatomic in a rare gas, have been made far from the critical temperature. Measurements, such as fluorescence of large molecules, have also been conducted far from the critical temperature.

Our vibrational relaxation experiments are performed using the ps infrared (IR) pump-probe method. As a precursor to future work, we have also made orientational relaxation polarization selective IR measurements in liquids and performed vibrational echo experiments in liquids.

A. Vibrational Relaxation in SCFs Near the critical Temperature

We have examined the solute, tungsten hexacarbonyl ($W(CO)_6$) in supercritical carbon dioxide (CO_2) and ethane (C_2H_6). The ps IR pump-probe experiment measures the vibrational relaxation rate of the CO asymmetric stretching mode of $W(CO)_6$ at $\sim 1980\text{ cm}^{-1}$. In an IR pump-probe experiment, a ps IR source is tuned into the vibrational transition of interest. (see below for a description of the experiment setup). The short IR pulse is split into a strong pump pulse and a weak probe pulse. The pump pulse excites the CO asymmetric stretch of $W(CO)_6$. The probe monitors the flow of vibrational energy out of the mode. This energy can flow into modes of the solute and the solvent.

In the experiments in supercritical CO_2 , the temperature is held constant at a temperature T above the critical temperature, $T_c = 31\text{ }^\circ\text{C}$. The density is then varied over a wide range, i. e., 1 mol/l to 17 mol/l, by varying of pressure. To date, the density dependence of the vibrational relaxation has been examined at three temperatures, 33 $^\circ\text{C}$, 40 $^\circ\text{C}$, and 50 $^\circ\text{C}$. The density dependence of the vibrational spectrum was also measured for these densities and temperatures. The vibrational relaxation in ethane ($T_c = 32\text{ }^\circ\text{C}$) was measured as a function of density at 34 $^\circ\text{C}$.

At all temperatures, as the density is increased, the vibrational lifetime becomes faster. In CO_2 at 33 $^\circ\text{C}$, a dramatic trend was observed. When the density neared the critical density, 10.7 mol/l, the vibrational lifetime became independent of density. The region of density independence is very broad, spanning a range of density of ~ 2.5 . When

the temperature is increased to 40 °C, there is again a density independent region, but it spans a narrower range. By 50 °C, there is a continuous change in vibrational lifetime with density, with no density independent region. This behavior tracks the behavior of the anomalous compressibility that occurs near T_c . The results are mimicked in the behavior of the vibrational spectrum, which shifts to the red with increasing density, but displays regions of no change with density near T_c . In addition, the vibrational relaxation in ethane also displays a density independent range near the critical pressure. However, in ethane, this is narrower and the change in the vibrational lifetime is significantly greater outside of this range.

The results are dramatic and novel. Vibrational relaxation is intimately related to the local fluid structure and the intermolecular interactions. These experiments are providing completely new and unexpected insights into solute/SCF dynamics and interactions.

B. Vibrational Relaxation in Liquids

Studies were conducted on vibrational relaxation of $W(CO)_6$ (and $Cr(CO)_6$) in several liquids that will subsequently be studied as SCFs. Two of the solvents, CCl_4 and $CHCl_3$, gave results that demonstrate the importance density on vibrational relaxation even in liquids. The vibrational relaxation measurements were made as a function of temperature from the melting points (~230 K) to the boiling points (~340 K). These experiments are the first to directly measure the vibrational lifetime as a function of temperature of polyatomic molecules in polyatomic liquids.

In CCl_4 , the vibrational lifetime becomes shorter as the temperature is increased. However, in $CHCl_3$, the vibrational lifetime actually becomes longer as the temperature is increased. We refer to this as an "inverted" temperature dependence.

In trying to understand this effect, the first fully quantum mechanical theory of the vibrational relaxation of polyatomic molecules in polyatomic solvents was developed. Previous theories used classical formalisms which did not properly account for the role of high frequency vibrations in either the solute or the solvent. The new theory shows that an increase in temperature, which produces increased vibrational mode and increased low frequency continuum mode occupation numbers, will cause the vibrational lifetime to become shorter. However, the theory also contains terms that are not explicitly temperature dependent, but can be density dependent. This can be important since there is a decrease in liquid density that accompanies a temperature increase.

A change in density can affect the vibrational lifetime in two ways: through a change in the density of states of the low frequency continuum and through a change in the intermolecular interactions. Using detailed theoretical calculations of the instantaneous normal modes of CCl_4 and $CHCl_3$, performed with Prof. Tom Keyes of Boston University, it was determined that changes in the density of states were small and not responsible for the inverted temperature dependence. This led to an understanding of the importance of density on the strength of the intermolecular interactions responsible for vibrational relaxation and energy flow into the solvent. As the temperature increases, the density decreases. Thus, the average distance between molecular increases; the region of the intermolecular potential that is sampled changes. The increase in temperature causes the lifetime to become shorter while the decrease in density causes the lifetime to

become longer. Which effect is greater will determine whether the temperature dependence appears normal or inverted. Even if the temperature dependence appears normal, there are still density effects that reduce the magnitude of the apparent temperature dependence.

C. Vibrational Echoes in Liquids and Glasses

To date, this group is the only group in the world to conduct vibrational echo experiments on liquids, glasses, and proteins. The work on liquids directly ties into SCF studies. One class of molecules that are being studied as SCFs is alkanes. As a precursor to SCF studies, vibrational echo experiments on $W(CO)_6$ in 2-methylpentane (2MP) were performed.

The vibrational echo experiment is the IR vibrational analog of magnetic resonance spin echo and the optical spectroscopy photon echo. It is an optical coherence experiment that measures the vibrational homogeneous dephasing. Its importance is that it permits the determination of how fluctuating intermolecular interactions couple to the solute molecule. Therefore it is a probe of the solvent dynamics and how those dynamics are felt by the solute.

In a vibrational echo experiment, two IR pulses, tuned to the vibration of interest, are crossed in the sample. The time delay between the pulses is varied. A third IR pulse is emitted from the sample in a unique direction. The third pulse is the echo. It is measured as a function of the delay between the incoming pulses. The measured echo decay is the Fourier transform of the homogeneous vibrational line. It provides information on vibrational dephasing that is not available from conventional spectroscopy.

Vibrational echo decays of the CO asymmetric stretch of $W(CO)_6$ in 2-MP from 10K to 300K were measured. The homogeneous dephasing depends on three factors, the vibrational lifetime, the orientational relaxation and the pure dephasing (the energy level fluctuations). The full temperature dependence of each of these from the low temperature glass to the room temperature liquid were measured. The results provide a totally new view of intermolecular interactions and dynamics.

D. Experimental Apparatus

A flexible experimental apparatus for performing ps IR experiments on SCFs was developed. This apparatus was used for the pump-probe vibrational lifetime measurements briefly described above.

A considerable portion of the work done over the past two years was devoted to designing and constructing the SCF experimental setup. This is a highly complex system that has already been used to perform experiments that have never been attempted previously. The apparatus is composed of the laser system and the SCF handling and sample cell system.

The laser system is capable of making tunable IR pulses with pulse durations variable from ~10 ps to ~50 ps at 1 kHz rep. rate. (A second system making fs pulses is described below.) The laser is a mode-locked and Q-switched cavity dumped Nd:YAG. This laser has an output coupler that provides a train of ~100 ps pulses. This pulse train is doubled and used to pump a cavity dumped dye laser. The dye laser has a tunable wavelength output of ~10 μ J. The YAG laser is also cavity dumped, providing a ~1 mJ pulse. This pulse is doubled, and the left over 1.06 μ m light is doubled again. This second doubled pulse is used to pump a dye

amplifier, bringing the dye energy to $\sim 50 \mu\text{J}$. The first doubled pulse from the cavity dumped YAG and the amplified dye pulse are match in spot size and timing and directed into a LiIO_3 optical parametric amplifier. This provides the IR pulses for the experiments. By tuning the dye laser, the IR wavelength is tuned. The IR pulse is beam split and part is passed down a computer controlled variable delay line. This is the weak probe pulse. The strong pump pulse and the probe pulse are directed, counter propagating, into the SCF cell.

The heart of the sample handling system is the SCF cell and its control and measurement subsystems. The cell is made from a monel 400 body, gold o-rings, and CaF_2 windows. All components are highly resistant to corrosion. It can operate at pressures up to 10,000 psia and 500°C . This makes it possible to take almost any molecule into the supercritical state.

The cell is pressurized and the pressure is regulated by a microprocessor controlled syringe pump. In addition, the cell has a pressure sensor and two resistance thermometers. One thermometer is used for feedback to a fuzzy logic temperature controller. The other is used for precise temperature measurements. Spectroscopic measurements are made directly in the cell using an FT-IR. Kinematic bases allow mirrors to be dropped in and the IR output beam of the FT-IR to be directed through the cell. The IR is detected with a remote IR detector. It is possible to switch from making ps pump-probe measurements to measuring the spectrum in less than one minute.

The signal from the pump-probe experiment uses a sophisticated set of electronics that does shot-to-shot normalization at the experimental rep. rate of 1 kHz. The signal is recorded by computer.

A second IR system is in the final stages of development. This system generates pulses of variable duration from 70 fs to 1 ps. It operates at 1 kHz, generating $1 \mu\text{J}$ at $5 \mu\text{m}$. This fs system is based on a Ti:Sapphire laser. All components except the Ar^+ laser are made in house. The Ti:Sapphire oscillator is amplified in a regenerative amplifier pumped at 1 kHz by an intracavity doubled Q-switched YAG laser. A specially designed stretcher enables the pulse duration to vary from <100 fs to 1 ps.

The amplified Ti:Sapphire pulse is split in three. The first pulse is used to generate "white" light in a flowing liquid cell. This light is spectrally resolved. The appropriate wavelengths are directed into the first OPA stage, which is pumped by the second Ti:Sapphire pulse. The output is directed into a second OPA stage along with the third Ti:Sapphire pulse. The output of the second stage is a signal and idler in the near IR. These two frequency pulses are directed into a LiIO_3 OPA, which generates the IR used for experiments. The wavelength is tuned by changing the spectral portion of the white light directed into the first OPA stage.