Ultrafast Multi-dimensional Infrared Spectroscopy of Gases at Low and High Pressures
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I. Infrared Pump-Probe Experiments and Theoretical Descriptions of Dynamics and Interactions in Supercritical Fluids and Gases.

Temperature and density-dependent vibrational relaxation data for the ν_6 asymmetric stretch of WCO_6 in supercritical fluoroform (trifluoromethane, CHF_3) were conducted and compared to a recent theory developed by this group 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.

Infrared ps pump-probe experiments were conducted for the *P*, *Q*, and *R* rotational branches of the asymmetric CO stretching mode of tungsten hexacarbonyl ~1997 cm^{-1} in the collisionless gas phase. The pump-probe decays are tri-exponentials ~140 ps, 1.3 ns, and .100 ns in contrast to single exponential decays observed in supercritical fluids and liquid solvents. The 1.3 ns decay component is the vibrational energy relaxation (VER) time. The long component occurs following intramolecular VER into a distribution of low-frequency modes. After VER is complete, the *R* signal is 48%, the *Q* signal is 29%, and the *P* signal is -10% (absorption increase) compared to the $t = 0$ signal. These long-lived signals result from an increase in the occupation numbers of low-frequency modes (internal heating) that causes a shift of the vibrational spectrum. The fastest decay is produced by spectral diffusion. The spectrally narrow pump pulse burns a hole in the inhomogeneous ground state spectrum and generates a narrow spectral population in the excited state (excited state peak). The inhomogeneity arises from the distribution of occupation numbers of the low-frequency modes that produces different combination band spectral shifts. Spectral diffusion is caused by the time evolution of the complex low-frequency thermal vibrational wave packet. Two possible models for the spectral diffusion were evaluated, one in which spectral diffusion reduces the pump-probe signal by hole filling and broadening of the excited state peak, and one in which the spectral diffusion only broadens the excited state peak.

II. Hydrogen Bond Breaking in Alcohol Oligomers Probed with Multidimensional Stimulated Vibrational Echo Correlation Spectroscopy

Hydrogen bond population dynamics were extricated with exceptional detail using ultrafast (< 50 fs) infrared multidimensional stimulated vibrational echo correlation spectroscopy with full phase information and frequency resolved IR pump-probe experiments performed on the hydroxyl stretch of methanol-OD oligomers in CCl_4. Hydrogen bond breaking makes it possible to acquire data for times much greater than the hydroxyl stretch vibrational lifetime. The correlation spectra and detailed calculations demonstrated that vibrational relaxation leads to

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hydrogen bond breaking for oligomers that have hydroxyl stretch frequencies on the low energy (red) side of the hydroxyl stretch spectrum, the spectral region that is associated with the strongest hydrogen bonds. Frequency resolved pump-probe data support the conclusions drawn from the correlation spectra. Using a global fit to the pump-probe spectra, in conjunction with assignments made possible through the correlation spectra, it was demonstrated that the residual ground state and photoproduct of hydrogen bond breaking are prepared near their thermal equilibrium distribution. The spectrum of the hydrogen bond breaking photoproduct and the residual ground state approach the steady-state temperature difference spectrum on the 10's ps time scale, indicating the system thermalizes on this time scale.

III. Using Ultrafast Infrared Multidimensional Correlation Spectroscopy to Aid in Vibrational Spectral Peak Assignments

Ultrafast infrared heterodyne detected vibrational stimulated echoes with full phase information were used to obtain the vibrational correlation spectrum from a mixture of metal-carbonyl compounds. The linear absorption spectrum displays four peaks in the carbonyl stretching region. In the absence of knowledge of the molecules that make up the mixture, the absorption spectrum could arise from four molecules that each produces a single peak to one molecule with four peaks. In contrast, the correlation spectrum displays four peaks on the diagonal and off-diagonal peaks that make it straightforward to determine which peaks belong to a particular molecule. This is a demonstration of the ability of vibrational echo correlation spectroscopy to be used as an analytical tool to enhance the information obtained from convention infrared vibrational absorption spectroscopy.

IV. Vibrational Echo Correlation Experiments in the Gas Phase and Weak Transitions

The experiments performed previously were all done in liquid samples, which makes the sample cell simple. It also makes crossing the four invisible IR input beams used in the vibrational echo and pump-probe experiments, overlapping the vibrational echo pulse that emerges from the sample with the local oscillator beam, and aligning them through the monochromator relatively straightforward although nontrivial. In addition, all of the experiments were conducted either on strong vibrational transitions (metal carbonyls) or relatively strong transitions (hydrogen bonded hydroxyl stretches). We have now conducted the first true vibrational echo correlation spectroscopy experiments in a high-pressure gas cell, and we have conducted the first vibrational echo experiments on C-H stretching modes, which are very weak transitions.

The design, construction, and implementation of a high pressure infrared cell appropriate for performing vibrational echo correlation spectroscopy has been an on going endeavor. We are now successfully using the fourth iteration of the design with its associated equipment for the past several months. The cell has been tested to 10,000 psi. The cell can use either Teflon O-rings which are good to ~225 C or gold O-rings, which can be used too much higher temperatures. The difficulty with the cell design is that the four beams that go into and out of the cell come in at four angles. There must be sufficient clear aperture to get the beams in and out of the cell. Yet, because of the high pressure, the windows cannot have a large unsupported area. In addition, it is necessary to be able to position the cell very precisely and reproducibly because the crossing volume of the beans spans a depth of only ~400 μm. This creates another design

problem. The sample path length, that is the distance between the windows must be very small and changeable for different samples. We can go in steps from 100 μm to 400 μm. We are currently using Teflon O-rings. The cell is pressurized with a syringe pump. The pressure is monitored with a pressure transducer. The cell temperature is monitored with a thermometer inserted into the body of the cell near the sample region. The cell, valves, pressure transducer, tubing, etc. are all contained in an oven with heaters and a fan to circulate the air to achieve uniform temperature.

Vibrational echo correlation spectra were recorded in a high-pressure gas. The sample was (acetylacetonato)dicarbonylRhodium ($Rh(CO)_2(acac)$) in fluoroform at a pressure of 1400 psi. Data were obtained for the symmetric and antisymmetric CO stretches in the spectral region between ~1975 cm^{-1} and ~2125 cm^{-1} with T_w = 400 fs. The symmetric and antisymmetric CO stretches of $Rh(CO)_2acac$ have been studied in great detail in liquid and solid solutions using vibrational echo techniques. All of the features can be assigned in the correlation spectrum using diagrammatic perturbation theory.

The $Rh(CO)_2acac$ was used as a first sample to develop the ability to perform experiments in the gas cell. The ability to vary the density enables us to study high pressure gases and provides us with an important new handle. We can change the density at fixed temperature and we can change the temperature at fix density. The ability to study dynamical linewidths as a function of time, density (pressure), and temperature, will provide considerable insights into solute-solvent interactions and the structural evolution of gas phase molecules. We have taken a considerable amount of data on this sample, and from these first experiments we have learned the many new approaches necessary to deal with the added complexity of performing one of the most complex optical experiments on a sample that is anything but ideal. Metal carbonyls have some of the strongest IR transitions that exist. Thus, there study was an important first step. However, we are interested in organic molecules that have interesting intermolecular and intramolecular dynamics and interactions. We have also taken the first vibrational echo data on C-H stretching modes. The sample was n-hexane in CCl_4. The spectra were absolute value rather than true correlation spectra. With improvements in methodology now underway using a DURIP grant, we should be able to extend the vibrational echo correlation spectroscopy method to weak transitions.

V. Hydrogen Bond Dynamics in Water

Water is ubiquitous in nature. It has profound effects on diverse fields of science from astronomy to zoology. It is important in nature as a solid, a liquid, and a gas. The properties of water are dominated by the strong hydrogen bonds that form among water molecules. The hydrogen bonds give rise to hydrogen bonding networks that play a major role in both the structure and dynamics of water. In liquid water, the hydrogen bond networks are continually evolving in time. Hydrogen bonds break and new hydrogen bonds form. Structural evolution causes weak hydrogen bonds to become strong and strong hydrogen bonds to become weak.

For the first time, we have applied vibrational echo correlation spectroscopy *with full phase information* to the study of the dynamics of water. The OD hydroxyl stretch of low concentration HOD in H_2O is being studied in unprecedented detail. Through the study of water, we have improved our methods further in experimental technique, data processing technique and software, and theoretical analysis. By watching the changing peak shapes with increasing T_w, the structural evolution of the water hydrogen bond network can be quantified. To analyze the data

quantitatively is a major theoretical endeavor. It is composed of two parts. The first is the calculation of a frequency-frequency correlation function (FFCF). The FFCF provides the connection between the experimental observables and the microscopic details of molecules and their interactions and dynamics. The second is using the FFCF to calculate the vibrational echo correlation spectra and compare them to the data.

We collaborated with Professor James Skinner, University of Wisconsin at Madison. In the collaboration, he has developed a method for calculating FFCFs for standard water models. We developed the necessary diagrammatic perturbation theory machinery to calculate the water vibrational echo correlation spectra. We have calculated correlation spectra for three standard water models, TIP4P, SPC/E, and SPC-FQ. The agreement between the SPC-FQ simulation and the experimental FFCF is remarkable. SPC-FQ is the only one of the three simulations that uses a polarizable model of water. The other two simulations have fixed partial charges on the atoms that make up a water molecule. The SPC-FQ model has partial charges that vary in response to the electric field produced by surrounding water molecules with the sum of the partial charges always maintaining electrical neutrality on each molecule. Analysis of the simulations shows that the short time scale dynamics reflect very local changes in hydrogen bond lengths while the longest time scale dynamics arise from global hydrogen bond network evolution in involving making and breaking of hydrogen bonds. Water simulations are widely used in studies of chemistry, biology, geology, and other fields. For the first time we have very detailed tests of the adequacy of water simulations on a molecular level.

The types of experiments presented very briefly here give a greatly expanded picture of hydrogen bond dynamics in liquids and now beginning in gas phase clusters. Multidimensional vibrational echo correlation spectra with full phase information permit questions to be asked and answered that are not accessible by other methods.

Publications 12/01/2000 – 11/30/2004 (AFOSR Grant # F49620-01-1-0018)

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Ph.D. Theses of Students Supported by this Project

1. Vibrational dynamics in complex systems investigated with non-linear ultrafast infrared techniques
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2003

2. Vibrational dynamics in supercritical fluids and the collisionless gas phase
Daniel Jay Myers
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14. ABSTRACT
Infrared pump-probe experiments were used to study vibrational relaxation of polyatomic molecules in supercritical fluids and the gas phase. IR pump-probe experiments and theory were used to investigate hydrogen bond dynamics in oligomers of alcohols. Vibrational echo correlation spectroscopy (VECS) was developed and experiments were performed on molecules in liquids and gases. VECS is an ultrafast multidimensional approach that is in many respects the vibrational equivalent of multidimensional NMR. VECS experiments have been performed on molecules in liquids and gases. The OD hydroxyl stretch of HOD in water was studied and the results were compared to theoretical simulation models of water. The time evolution of the vibrational echo correlation spectrum reflects the structural evolution of the hydrogen bond networks in water. The experiments and theory provide detailed tests of water models. A gas cell for performing ultrafast infrared experiments was developed and the first vibrational echo correlation spectroscopy experiments were performed in the gas phase. VECS was also been demonstrated as a new type of analytical tool that can aid in sorting out congested vibrational spectra.

15. SUBJECT TERMS
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