Infrared Free Induction Decay of Liquid Water Molecules

Robert A. Crowell, Gary R. Holtom, and X. Sunney Xie*

Environmental Molecular Sciences Laboratory, Pacific Northwest Laboratory, P.O. Box 999, Mail Stop K2-14, Richland, Washington 99352

Received: October 31, 1994; In Final Form: January 3, 1995

The infrared vibrational quantum beats of monomeric liquid water molecules dissolved in deuterated methylene chloride are directly observed at room temperature by up-converting the free induction decay generated with a new femtosecond infrared optical parametric oscillator operated near 3 μm.

Introduction

The importance of water as a universal and unique solvent for chemical and biological reactions has continued to stimulate experimental,1–4 theoretical, and computational5 efforts toward understanding the structure and dynamics of liquid water. Femtosecond spectroscopic measurements have shown that the ultrafast dynamics (≤100 fs) of liquid water play an important role in aqueous phase chemical reactions.1 The femtosecond dynamics of liquid water have recently been extensively studied by time dependent Stoke shift1,2 and optical Kerr effect3 experiments. The former measures the dielectric relaxation while the latter probes the low frequency modes in liquids. In this Letter we report our initial effort on femtosecond infrared spectroscopy of liquid water. Complementary to the previous techniques, femtosecond infrared experiments will provide structural as well as dynamical information on liquid water.

A monomeric liquid water molecule has two infrared absorption bands in the 3 μm region due to its symmetric and asymmetric stretching vibrations. These bands are particularly sensitive to the hydrogen bond structure. In neat liquid water these bands are significantly red shifted and broadened due to the hydrogen-bonded network.6 Picosecond hole burning experiments in this spectral region have suggested that such a broad band is inhomogeneously broadened, due to distinctly different hydrogen-bonded structures.7

Infrared nonlinear experiments with multiple pulse sequences, such as infrared photon echoes, will allow the removal of the inhomogeneous broadening and permit the measurement of the homogeneous line width. Recently, infrared echo8 and Raman echo9 experiments have been demonstrated on molecular liquids. However, such an experiment has not been performed on liquid water due to the lack of suitable femtosecond sources. For example, a 50 fs pulse at 3 μm is needed to coherently excite the entire inhomogeneously broadened band of liquid water.

We have recently constructed a stable femtosecond infrared source around 3 μm using a synchronously pumped OPO and OPA combination. The details of this system will be described elsewhere.10 Pertinent to this Letter are the schematic of the OPO and the detection system shown in Figure 1. The OPO is synchronously pumped with the 80 fs pulse train (1.3 W average power, 76 MHz, 817 nm center wavelength) from a mode-locked Ti:sapphire laser (modified Coherent Mira Basic). An antireflection coated KTP crystal (1 mm) is cut and oriented for noncritical phase matching (Θ = 90°, φ = 0°). The cavity is made resonant with the signal beam at 1.16 μm. It is composed of two 10 cm radius mirrors, one high reflector, and a 5% output coupler. The cavity is dispersion compensated with a pair of SF-10 prisms. The signal beam has an output of 320 mW and 65 fs, which is not used in the experiment. The idler beam is simultaneously generated at 2.8 μm and is collected through a sapphire substrate mirror. It has a pulse energy of 0.2 nJ and a 120 fs pulse width (sech² pulse shape). The idler beam is 1.3 times the transform limit for a sech² pulse. The cavity length is actively stabilized, which keeps intensity fluctuations less than 1%.

The idler beam from the OPO is passed unfocused through the sample, generating the FID. The transmitted beam (containing the FID) is then temporally resolved by an up-conversion technique. As shown in Figure 1, the Ti:sapphire pulse train (OPO pump residual, 817 nm center frequency, 120 fs pulse width, and 300 mW average power) is used to time gate the infrared FID. The infrared beam transmitted through the sample is focused onto a 0.3 mm LiIO₃ up-conversion crystal (type I phase matching) together with the gating beam in a noncollinear geometry. The bandwidth of the up-conversion is about 150 cm⁻¹. The sum frequency light at 628 nm is detected with a photomultiplier tube (Hamamatsu R928) and lock-in amplifier (Stanford Research System SR850 DSP) combination as a function of the time delay of the gating beam. The instrumental response function is the cross correlation of the 817 nm and 2.8 μm beams and is measured by removing the sample from the 2.8 μm beam path.

The sample is doubly deionized water dissolved in 99.95% deuterated methylene chloride (Aldrich) at a concentration of 0.05 M. The solvent was used without any further purification. The infrared spectrum indicates no water cluster formation at this concentration. Higher concentrations (> 0.5 M) result in a broad absorption at longer wavelength due to hydrogen bond formation. The sample is placed in a 2 mm path length cell with CaF₂ windows and has an optical density of 1.1 at the absorption maximum. The experiment was conducted in an environment that was vigorously purged with dry nitrogen to minimize complications from water vapor.

Experimental Section

Extending the femtosecond OPO technology12 to the water spectroscopic region, we have constructed a new femtosecond
Results and Discussions

The solid line in Figure 2 shows the FTIR absorption spectrum of the sample. The 3600 cm\(^{-1}\) peak is assigned to the symmetric stretching, and the 3685 cm\(^{-1}\) peak is assigned to the asymmetric stretching of the water molecules. The dashed line in Figure 2 shows the spectrum of the excitation pulses from the OPO, which clearly have enough bandwidth to coherently excite the two vibrational modes of the solute water molecules.

Figure 3A shows the up-converted infrared FID (solid line) and the instrumental response function (dashed line, FWHM of 180 fs). The transmitted infrared radiation first follows the instrumental function and then has the distinct first recurrence at 370 fs. The two vibrational modes of water molecule radiate coherently, resulting in quantum beats. The 370 fs time delay corresponds to the 90 cm\(^{-1}\) splitting of the peaks in the infrared spectrum of Figure 2. The solid line in Figure 3B shows the semilogarithmic plot of the same data. We have directly measured the vibrational quantum beats of solution phase water molecules at room temperature.

It is important to note that the temporal behavior of the femtosecond pulses passing through the sample has been changed. Upon transmission through the sample the pulses become significantly temporally broadened. Such a phenomenon has been previously observed in infrared pump-probe experiments,\(^{13}\) as well as in sum frequency generation experiments on surfaces.\(^{14}\) In these experiments, there was only one vibrational band being excited. The temporal broadening of the infrared pulses has been attributed to the FID. In the time domain the FID can be described as follows. A short pulse coherently excites the molecular vibrations. The induced macroscopic polarization (FID) radiates and decays with a time constant equal to the inverse of the absorption line width. The FID, propagating collinearly with the input pulse, destructively interferes with the input pulse (during the pulse duration) which results in an energy loss of the input beam (absorption) and a variation in the temporal behavior of the transmitted beam. The fact that there are two vibrational modes coherently excited in water molecules results in the intensity beating behavior of the FID in Figure 3.

In the frequency domain, the water absorption shown in Figure 2 acts as a spectral filter for the input pulse spectrum. On the basis of this simple picture, we have simulated the observed transmitted signal. If the transform limited input pulses are assumed, the E-field spectrum of the input pulse, \(E_{in}(\omega)\), is the square root of the intensity spectrum in Figure 2.
measurement can allow more accurate measurement of the correlation function which would be otherwise hard to obtain by analyzing the details of absorption spectra. Such a linear experiment cannot be used to separate the homogeneous and inhomogeneous contributions to the absorption line shape. Nonlinear experiments such as infrared photon echoes are needed to extract the homogeneous line shape from the inhomogeneously broadened lines. We have constructed an OPA system to produce infrared pulses with energies sufficient to perform nonlinear experiments. Our results reported in this Letter indicate that the dephasing time is significantly longer than the pulse width. This initial experiment shows the promise for using multiple infrared pulse sequences to conduct femtosecond nonlinear vibrational spectroscopy in order to unscramble the complex molecular interactions and dynamics in liquid water.

Acknowledgment. This work was performed at the Pacific Northwest Laboratory under the auspices of the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy. Pacific Northwest Laboratory is a multiprogram national laboratory operated for the Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

References and Notes