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Vibrational Relaxation of the Bending Mode of HDO in Liquid D_2O

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The vibrational relaxation of the bending mode of HDO in liquid D_2O has been studied using time-resolved mid-infrared pump−probe spectroscopy. At short delays, the transient spectrum clearly shows the $v = 1 \rightarrow 2$ induced absorption and $v = 1 \rightarrow 0$ bleaching and stimulated emission, whereas at long delays, the transient spectrum is dominated by the spectral changes caused by the temperature increase in the sample after vibrational relaxation. From the decay of the $v = 1 \rightarrow 2$ induced absorption, we obtain an estimate of 390 ± 50 fs for the vibrational lifetime, in surprisingly good agreement with recent theoretical predictions. In the $v = 0 \rightarrow 1$ frequency region, the decay of the absorption change involves a second, slower component, which suggests that after vibrational relaxation the system is not yet in thermal equilibrium.

I. Introduction

Vibrational energy relaxation plays an important role in condensed-phase chemistry, and this holds in particular for liquid water. Many experimental[1−19] and theoretical[20−25] studies have therefore been devoted to the vibrational relaxation of liquid water. For practical reasons, most of these studies were concerned with the HDO molecule in dilute D_2O or H_2O solution. Compared to liquid H_2O, such dilute isotopic solutions have the important advantage that the HDO molecules are sufficiently far apart for their interaction to be negligible. Experimental work has focused mainly on the OH- and OD-stretching modes of HDO, which are relatively easily accessible to time-resolved nonlinear spectroscopic investigations because of their high absorption cross sections and frequencies. The first experimental estimates of the OH-stretch vibrational lifetime of HDO in D_2O were obtained by Vodopyanov[1] and Graener et al.[2] in 1991. In subsequent years, these studies were followed by experiments with improved temporal resolution[4−8,16] and measurements of the OD-stretching mode relaxation of HDO in H_2O.[9,17−19]

Whereas theory and experiment progressed more or less in parallel for the stretching modes of HDO in D_2O, the situation is different for the bending mode. Several theoretical predictions for the bending-mode lifetime HDO in D_2O have been reported,[20−23] the most recent and accurate value being 380 fs,[23] but as yet it has not been determined experimentally. Here, we study the vibrational relaxation of the bending mode of HDO in D_2O using infrared pump−probe spectroscopy, extending our previous work on the H_2O bending mode.[26] The HDO bending mode has a frequency of 1460 cm^{-1},[27] by far the lowest of the three intramolecular vibrations of the HDO molecule, the OH and OD-stretching frequencies being 3395 and 2510 cm^{-1}. Consequently, vibrational relaxation of the bending mode cannot involve intramolecular energy transfer, like it does for the OH-stretching mode,[8,16,21−23] and must occur completely through energy transfer to modes of the surrounding bath. This renders the bending-mode relaxation an interesting probe of the intermolecular interactions in liquid water.

II. Experimental Section

In our experiments, we resonantly excite the HDO bending mode, and monitor the subsequent vibrational relaxation process by measuring the frequency-dependent absorption change as a function of delay time. Our optical setup is based on the design reported by Hamm et al.[28] The output of a commercial amplified Ti:sapphire laser system (1 mJ, 100 fs) is used to pump an optical parametric amplifier based on BBO, resulting in signal+idler energies of typically 100 μJ. Subsequent difference-frequency generation of signal and idler in $AgGaS_2$ results in mid-infrared pulses, which at 1450 cm^{-1} have a duration of ∼200 fs, an energy of 1 μJ, and a bandwidth of ∼150 cm^{-1} (fwhm). A small fraction of the mid-infrared pulses is split off with a wedged BaF_2 window to obtain probe and reference pulses, the remainder is used as the pump pulse. The pump and probe pulses are focused and overlapped in the sample by means of a 100 mm off-axis parabolic mirror (focal diameters of ∼400 and ∼250 μm for pump and probe, respectively) and transient absorption changes are measured by frequency-dispersed detection of the probe and reference pulses using a 2 × 32 HgCdTe array detector. The polarizations of the pump and probe pulses are at the magic angle ($\arctan\sqrt{2}$) to eliminate effects of orientational relaxation and/or resonant energy transfer. Isotopic HDO:D_2O solutions are prepared by mixing appropriate amounts of H_2O (HPLC grade, Sigma-Aldrich) and D_2O (>99.9%D, Apollo Scientific). The experiments are carried out at room temperature, on samples kept between two 2 mm thick CaF_2 windows separated by a 50 μm Teflon spacer. The contribution of the solvent and the windows to the transient signals is determined by replacing the HDO:D_2O sample by pure D_2O. We find that this contribution is negligible for all delays outside the region where pump and probe have temporal overlap.

III. Results and Discussion

Figure 1 shows the infrared absorption spectrum of a 6 M solution of HDO in D_2O. The bending frequencies of HDO and

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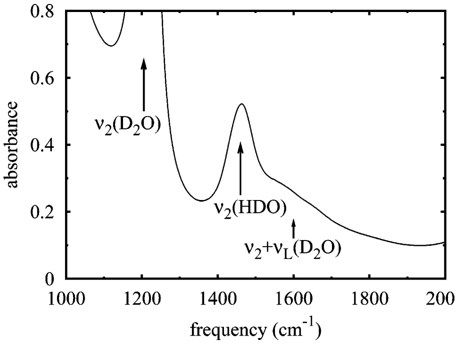

Figure 1. Infrared absorption spectrum of a 6 M solution of HDO in D_2O. The arrows indicate the frequencies of the D_2O and HDO bending modes, and of the bending + libration combination mode of D_2O.

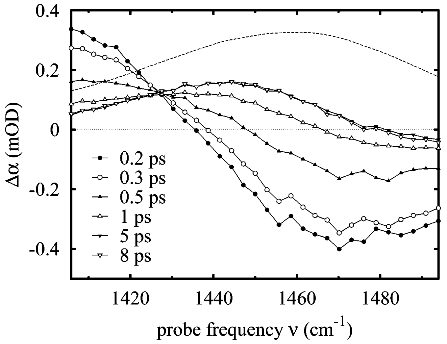

Figure 2. Connected points: transient absorption change after excitation of the HDO bending mode of a 6 M solution of HDO in D_2O, for several values of the pump−probe delay. Dashed curve: absorption spectrum of the sample (scaled).

D_2O have been indicated by arrows. The shoulder at ~1600 cm^{-1} is due to the bend + libration ($\nu_2 + \nu_L$) combination mode of D_2O[29] and the hardly visible peak at ~1650 cm^{-1} to the bending mode absorption of H_2O (present in a concentration of 0.2 M). Figure 2 shows the transient absorption change observed for a 6 M solution of HDO in D_2O, for several delays with respect to the pump pulse. The dotted line represents the absorption spectrum of the sample. At short delays, the transient absorption change is negative around the $v = 0 \rightarrow 1$ transition frequency (from 1440 to 1490 cm^{-1}) due to bleaching of $v = 0 \rightarrow 1$ transition and $1 \rightarrow 0$ stimulated emission and positive at lower frequencies (from 1405 to 1435 cm^{-1}) due to $1 \rightarrow 2$ excited-state absorption. Within a few picoseconds, vibrational relaxation causes both the excited-state absorption and the stimulated emission/bleaching features to vanish. It may be pointed out that, since the power spectrum of the pump pulse is much broader than the absorption band of the bending mode, no hole burning occurs, and spectral diffusion is not observable in our experiments. The residual signal remains essentially constant for delay times after ~5 ps and can be explained by the increase in temperature that occurs after vibrational relaxation (the subsequent diffusion of heat out of the focus takes place on a μs time scale).

We have confirmed this by measuring the steady-state absorption spectrum of the sample at 299 and 310 K. Figure 3 shows the difference spectrum $\alpha_{310K} - \alpha_{299K}$. This difference spectrum agrees well with previous measurements of the steady-state infrared spectrum of HDO:D_2O, which have shown that, with increasing temperature, the absorption band of the bending mode shifts to lower frequency.[30] The lowering of the center frequency of the bending mode with increasing temperature is due to the decrease of the average hydrogen-bond strength with temperature: in contrast to the stretching modes, the bending-mode frequency increases with hydrogen-bond strength, since hydrogen bonding steepens the potential-energy curve of the bending mode.[31]

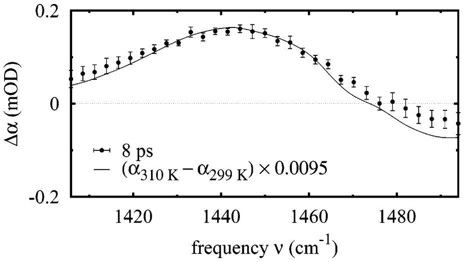

Figure 3. Points: transient absorption change 8 ps after excitation of the HDO bending mode of a 6 M solution of HDO in D_2O. Curve: difference between the steady-state absorption spectra at 310 and 299 K, multiplied by 0.0095.

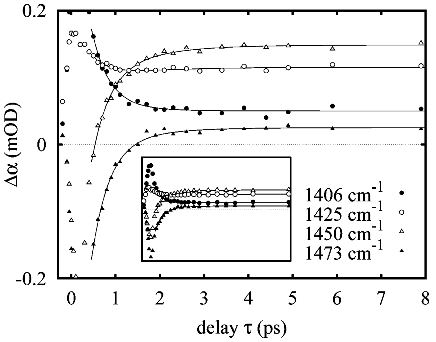

Figure 4. Transient absorption change as a function of pump−probe delay, for several probing frequencies. The solid curves are the result of a simultaneous least-squares fit of eq 1 to the decays at all probing frequencies. The inset shows the same data the same x-scale and full y-scale.

Comparison of the temperature-difference spectrum with the transient absorption change at 8 ps (shown as the points in Figure 3) confirms that the long-term absorption change is caused by the temperature increase following the vibrational relaxation. Comparing the transient spectrum at 8 ps with the difference spectrum $\alpha_{310K} - \alpha_{299K}$, we find that a scaling factor of 0.0095 is needed (see Figure 3). From steady-state absorption spectra recorded at several temperatures, we find that only the amplitude (and not the shape) of the temperature-difference spectrum changes with the magnitude of the temperature increase. Hence, we can derive a temperature increase of $(310-299) \times 0.0095 = 0.1$ K from the transient spectrum. From the experimental parameters (focal diameter ~400 μm, energy ~1 μJ, sample thickness 50 μm), one can obtain an order-of-magnitude estimate for the temperature increase by assuming that the energy is homogeneously distributed over a cylinder with a height equal to the sample thickness and a diameter equal to that of the pump focus. This results in an estimate of 0.03 K, which is of the same order of magnitude as the temperature increase of 0.1 K observed in the transient spectrum at long delays. Taking into account the Gaussian beam shapes of the pump pulse (and hence of the temperature distribution) and of the probing pulse, one obtains a more accurate estimate of 0.05 K. The discrepancy between this estimate and the observed value can well be accounted for by the uncertainties in the experimental parameters.

The pump−probe delay dependence of the absorption change is shown in Figure 4 for several probing frequencies. The decay of the $v = 1 \rightarrow 2$ induced absorption can be described by a single-exponential decay, see Figure 5. We find that in the data at frequencies in the $v = 0 \rightarrow 1$ region, in addition to a rapidly

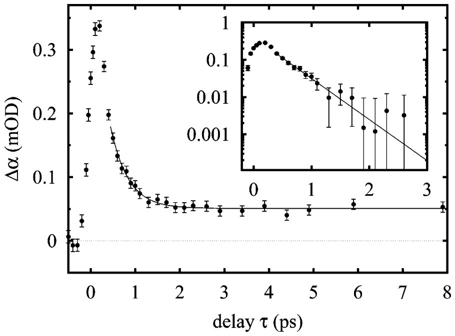

Figure 5. Transient absorption change as a function of pump−probe delay, at a probing frequency of 1406 cm^{-1}. The solid curve is a single-exponential decay with a time constant of 390 fs. The inset shows the same data, with the long-term background subtracted.

decaying component a small, more slowly decaying component is present. We assign the fast initial decay of the positive and negative transient absorption changes to the vibrational relaxation of the $v = 1$ state of the HDO bending mode. The presence of a small-amplitude, slower component in the decay suggests that after the vibrational relaxation of the bending mode, the system is not yet in thermal equilibrium, and that a second relaxation process takes place. Since the amplitude of the slow component is small, its time constant cannot be determined very accurately from our data. If the equilibration process after the T_1 relaxation is described by an exponential decay (with a time constant τ_{eq}), then the delay- and frequency-dependent absorption change can be calculated using a simple rate-equation model.[32] If we denote the equilibrium absorption spectrum by $\alpha_0(\nu)$, the $v = 1 \rightarrow 2$ spectrum by $\alpha_1(\nu)$, the spectrum of the system in the nonequilibrium state directly after vibrational relaxation by $\alpha_*(\nu)$, and the spectrum in the final thermal equilibrium (at a higher temperature) by $\alpha_T(\nu)$, then the absorption change is given by

$$\Delta\alpha(\nu,\tau) = \delta\alpha_1(\nu)e^{-k_1\tau} + \delta\alpha_*(\nu)\frac{k_1}{k_1 - k_{eq}}(e^{-k_{eq}\tau} - e^{-k_1\tau}) + \delta\alpha_T(\nu)\frac{k_1(1 - e^{-k_{eq}\tau}) - k_{eq}(1 - e^{-k_1\tau})}{k_1 - k_{eq}} \quad (1)$$

where $k_1 = 1/T_1$ and $k_{eq} = 1/\tau_{eq}$, and the amplitudes are

$$\delta\alpha_1(\nu) = \alpha_1(\nu) - \alpha_0(\nu)$$

$$\delta\alpha_*(\nu) = \alpha_*(\nu) - \alpha_0(\nu)$$

$$\delta\alpha_T(\nu) = \alpha_T(\nu) - \alpha_0(\nu)$$

Equation 1 shows that the decay of the absorption change is given by a biexponential function, with the amplitudes of the two exponentials depending on the probing frequency ν. We performed a simultaneous least-squares fit of eq 1 to the transients at all 32 probing frequencies, using the same values for the two time constants T_1 and τ_{eq} at every frequency. From the fit, we find time constants of $T_1 = 390 \pm 50$ fs and $\tau_{eq} = 1.2 \pm 0.4$ ps. The result of the fit is shown for several probing frequencies as the solid lines in Figure 4. Only data points for delay values larger than 0.4 ps were used in the fit, to ensure that artifacts around zero delay (coherent coupling[33] and/or Kerr effect[34]) do not influence the result. To confirm this, we also performed a fit using only delay values larger than 0.5 ps and found no significant differences in the values for the two time constants. The amplitudes $\delta\alpha_1(\nu)$, $\delta\alpha_*(\nu)$, and $\delta\alpha_T(\nu)$ obtained from the fit are shown in Figure 6.

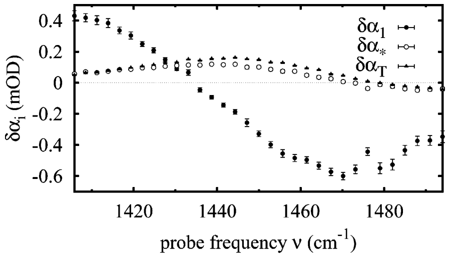

Figure 6. Amplitudes $\delta\alpha_1(\nu)$, $\delta\alpha_*(\nu)$, and $\delta\alpha_T(\nu)$ (see eq 1) obtained from the least-squares fit procedure described in the text.

The second relaxation process cannot involve an intramolecular mode, since the bending mode has the lowest frequency of the three intramolecular modes of the HDO molecule. Interestingly, the 1.2 ps value found here is similar to the time scale of the hydrogen-bond equilibration process observed in MD simulations[19] and in time-resolved measurements of the OH-stretching[6,35] and OD-stretching modes[17−19] of HDO in D_2O. In these studies, time constants of ∼1.5 and ∼1 ps were found for the equilibration of the hydrogen-bond network after vibrational relaxation of the OD- and OH-stretching modes, respectively.[6,18] The similarity of these time scales to the 1.2 ps found here suggests the possibility that the bending-mode relaxation leads to a disturbance of the hydrogen-bond network (involving stretching, rather than dissociation of hydrogen bonds, as the HDO bending-mode energy is well below the hydrogen-bond dissociation energy) which equilibrates in the same way as the disturbance created after relaxation of the OD-stretching and OH-stretching modes.

In a recent experiment on the vibrational relaxation of the bending mode of liquid H_2O, a vibrational lifetime of 170 fs was found for this mode.[36] This fast vibrational relaxation was explained by a strong coupling to the librations of H_2O, which have a significant spectral density at the H_2O bending frequency.[37] The fact that the vibrational relaxation of the bending mode of HDO in liquid D_2O is slower is probably due to the fact that the spectral density of the D_2O librations at the HDO bending frequency is very small.[38] This small spectral density at the HDO bending frequency also explains why, in contrast to liquid H_2O,[36] no direct excitation of D_2O librations is observed in our experiment.

The T_1 value of 390 fs for HDO in D_2O found here agrees surprisingly well with the most recent theoretical prediction of 380 fs by Lawrence and Skinner.[23] In view of the substantially bigger discrepancy between their theoretical value for OH-stretching T_1 and the experimental value (2.3 and ∼1 ps, respectively), the extremely good agreement between theory and experiment for the bending mode could to some extent be coincidental. In this respect, it is also interesting to point out that the bending-mode T_1 of H_2O in an isotopic H_2O:HDO:D_2O mixture[26] is the same (within experimental error) as that of HDO:D_2O, whereas the calculated spectral density of the fluctuating coupling causing the vibrational relaxation decreases by a factor of roughly 2 going from the HDO to the H_2O bending frequency.[23]

IV. Conclusion

In summary, we have determined the lifetime of the HDO bending mode in liquid D_2O using mid-infrared pump−probe spectroscopy. We found a T_1 value of 390 fs, which agrees well with recent theoretical predictions. We also found evidence for a thermalization process after the vibrational relaxation, which takes place with a time constant of approximately 1.2 ps.

We believe the experiments reported here open the way to new spectroscopic experiments investigating the dynamics of liquid water. A particular advantage of the bending mode as compared to the stretching modes of the water molecule is that the bending absorption bands of H_2O, HDO, and D_2O are cleanly separated. As a consequence, each of these molecular species can be separately excited and probed in isotopic H_2O:HDO:D_2O mixtures.

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