Ultrafast vibrational dynamics of water

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Ultrafast Energy Equilibration in Hydrogen-Bonded Liquids

We have studied the equilibration dynamics of several alcohols following a local deposition of energy using time-resolved femtosecond mid-infrared pump-probe spectroscopy. The equilibration dynamics is monitored via the spectral response of the O-H stretch vibration. It is found that the equilibration leads to complicated changes of the absorption band of the O-H stretch vibration including a shift of the absorption band and a decrease of the absorption cross section. Interestingly, these spectral changes do not occur simultaneously, which indicates that they are associated with the equilibration dynamics of different low-frequency modes. We compare the equilibration dynamics of the alcohols with that of water and observe that the equilibration time strongly increases going from water to alcohols like methanol, ethanol and propanol. This means that water molecules can adapt much faster to a local deposition of energy than other hydrogen-bonding liquids.
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5.1 Introduction: water as solvent for (bio)chemical reactions

By a rearrangement of the water molecules in the surroundings of the reactive intermediates of chemical reactions, water is able to stabilize these intermediates and to lower the energy barrier for the reaction. The dynamics of chemical reactions in aqueous solution will be governed both by the dynamics of the solvation interactions and the rate at which water molecules can accept the energy dissipated in the reaction. The solvation dynamics of water has been investigated by probing the response of solvating water molecules to an electronic rearrangement in a dissolved dye molecule [39, 70]. The solvation dynamics were observed to consist of a fast inertial component with a time response of \( \approx 50 \) femtoseconds and two slower, diffusive components with subpicosecond response times.

Several theoretical studies have been performed on the role of liquid water as a solvent for different solutes, ranging from peptides and biomolecules [9, 74] to organic molecules [102] and HDO [76]. In Ref. [9] a combined quantum mechanical and classical mechanical (QM/MM) method is used. The active part of the system, for example an excited state, is treated quantum-mechanically, while the environment can be treated with molecular dynamics simulations. With this technique normal modes, potential energy surfaces and solvent-induced spectral shifts can be obtained. The importance of water as a solvent is also illustrated in Ref. [102] where the relaxation of vibrationally excited CH\(_3\)Cl molecules in water is studied. It was shown that a large number of water molecules participate in the redistribution of the vibrational energy. In Ref. [76] molecular dynamics simulations were used to investigate the rate and mechanism of the vibrational relaxation of HDO molecules dissolved in D\(_2\)O. In this study the OH-stretch was found to relax to the first overtone of the bending mode with a time constant of 7.5 ps. The excess energy of the bending mode will be accepted by the so-called bath modes, which are the low frequency modes, like rotations and translations of all molecules, but no time scale was given for this process of equilibration.

The outcome of molecular dynamics simulations on liquid water strongly depends on the modeling of the interactions between the water molecules [60]. Hence, there is a strong need for experimental information. In particular one would like to know the time scale on which low-frequency water modes, like librations and hydrogen-bond translations, respond to a local deposition of energy induced by a (bio)chemical reaction. In this respect, linear spectroscopic studies are not very informative due to the large inhomogeneity of aqueous systems. Therefore, nonlinear spectroscopic techniques using intense ultrashort pulses should be employed. Unfortunately, it is difficult to probe the response of low-frequency water modes directly on an ultrashort time scale. A solution to this problem is to follow a higher-frequency mode that is strongly coupled to these modes. For the case of the hydrogen bond, the OH-stretch vibration \( (\nu_{\text{OH}}) \) forms a suitable probe, because the frequency of the OH-stretch vibration depends linearly on the hydrogen-bond length [28, 67]. Hence, this
vibration can be used as a probe for low-frequency hydrogen-bond dynamics that in turn represent changes in orientation and position of the water molecules.

Until now not much is known about the time scale on which water molecules react to an ultrafast dissipation of energy. Vodopyanov performed saturation studies in which water and ethanol layers were excited with intense picosecond laser radiation [95, 96, 97, 98]. In these studies a blue shift of the OH–stretch absorption band was observed due to a rise in temperature after irradiation. From the intensity dependence of the saturation, the vibrational lifetime $T_1$ of the OH–stretch vibration of HDO dissolved in D$_2$O was estimated to be between 0.3 and 0.6 ps and the lifetime of the OH–stretch vibrations of pure H$_2$O was estimated to be <3 ps [98]. A major problem in these studies was that it was not possible to separate the time scale of the relaxation of the OH–stretch excitation from that of the full equilibration of the energy in the liquid. If the OH–stretch vibration relaxes to some non-thermal intermediate state, these time scales will be different. Recently, the vibrational lifetime $T_1$ of the OH–stretch vibration of HDO dissolved in D$_2$O was measured using femtosecond mid-infrared pulses and was found to have a value of 740 ± 20 femtoseconds at room temperature [108]. Since the system studied was a dilute solution of HDO, the temperature increase of the sample due to the relaxation was negligibly small and no information on the equilibration dynamics of the water was obtained.

Here we present a study on the equilibration dynamics of water and alcohols at room temperature following a local dissipation of energy. The equilibration dynamics are monitored by probing the spectral changes of the OH–stretch absorption band with femtosecond mid-infrared laser pulses. It is found that the equilibration dynamics in water is exceptionally fast in comparison to the alcohols.

5.2 Experimental

The setup used for the results presented in this chapter, is depicted in Figure 5.1. We use a Ti:Sapphire based laser system that delivers 800 nm, 1 mJ pulses at a repetition rate of 1 kHz and a duration of about 110 fs. All of the 800 nm light is sent into one optical parametrical amplification and generation (OPA/OPG) stage based on $\beta$-BaB$_2$O$_4$. Part of the pump light is converted into signal and idler pulses with a central wavelength for the signal of 1.1 $\mu$m. A beam splitter divides the signal pulses into two parts. The strongest part of the signal is used, together with the remaining 800 nm pump light, in a second parametric amplification process in a KTiOPO$_4$-crystal to generate pulses near 3 $\mu$m [15]. The pulses have typical energies of 15 $\mu$J, a FWHM duration of 220 fs and a spectral width of 80 cm$^{-1}$. The infrared pulses generated as described above (pump pulses) are focused into the sample and are used to excite a fraction of the molecules from the vibrational ground state to the $\nu_{\text{OH}} = 1$ state. Thereby energy is put into a specific degree of freedom.

By the same generation mechanism the second weaker part of the signal is con-
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**Figure 5.1.** Generation of mid-infrared laser pulses. See text for the description of the generation. BD: beam dump; LWP: long wave pass filter; BBO and KTP: crystals

... converted to pulses around 3 μm. These pulses have the same duration and spectral width as the pump pulses and an energy per pulse of approximately 1 μJ. They are also focused on the sample and are used to monitor the thermalization of the excitation of the pump pulse. The transmission of the probe and pump pulses through a 200 μm pinhole was typically 50%. The probe polarization was set at the magic angle with respect to the polarization of the pump pulse by means of a zero-order λ/2 plate.

We investigated the equilibration dynamics of pure water, methanol, ethanol and 1-propanol. The samples consisted of a thin layer of liquid (≈ 1 μm for water, 15 μm for the alcohols) between two sapphire windows. In order to avoid heating in the sample due to former excitation pulses, the sample was rotated. The temperature rise due to a single pump pulse is calculated to be approximately 30 K for water.

### 5.3 Results

The conventional infrared absorption spectrum of the OH–stretch band of water is depicted in the previous chapter, Figure 4.3. The absorption band has its maximum at 3410 cm\(^{-1}\) and has a width of 420 cm\(^{-1}\) at room temperature. It consists of two sub-bands stemming from the symmetric and antisymmetric stretching normal modes. In Figure 4.2, the transmission change \(\ln(T/T_0)\) as a function of delay time is shown for pure water. The molecules are excited with a pump pulse with a central frequency of \(\nu = 3250\) cm\(^{-1}\) and are probed at eight different frequencies. Let’s resume the observations from that figure. All displayed curves show a higher or lower final level of transmission for long delay times. This level remains constant on a very long time scale, which indicates that this level of transmission results from the complete thermalization of the system. Probing at the red side of the absorption band (upper two curves, left panel) shows an induced 1→2 absorption around \(t = 0\). At the blue side (upper two curves right panel) a bleaching peak is observed around \(t = 0\). For probe frequencies in the center of the absorption band (3200 and 3400 cm\(^{-1}\)), the
Results

Figure 5.2. Absorption spectrum of the OH–stretch vibration of pure ethanol. The maximum of the band is at 3330 cm\(^{-1}\). The pump and probe frequencies are indicated with arrows.

bleaching peak is overwhelmed by the thermalization effect.

Here, we compare the measured signals for water with results obtained for methanol, ethanol and 1-propanol for which the hydrogen-bond strength is similar to that of water. In Figure 5.2, the OH–stretch absorption spectrum of pure ethanol (C\(_2\)H\(_5\)OH) is presented. The absorption spectra of methanol (CH\(_3\)OH) and 1-propanol (C\(_3\)H\(_7\)OH) are very similar to that of ethanol. Again we pump at the center frequency of the band, which is at 3330 cm\(^{-1}\) for these three alcohols. The frequencies of the probe pulses (3150, 3265, 3310 and 3450 cm\(^{-1}\)) are indicated by arrows in Figure 5.2.

Figure 5.3 shows delay time scans for pure ethanol. The observed relaxation behavior is very similar to that of water. For Figure 5.3b and 5.3c, we again observe after a bleaching at \(t = 0\) and a decay at short delay times, a rise towards a permanent bleaching signal. Clearly, the same process of equilibration is observed as in water, but the time scale is dramatically different. In Figure 5.3d, the probe wavelength is in the red wing of the absorption band. We observe an induced \(\nu_{\text{OH}} = 1 \rightarrow 2\) absorption, followed by a rise to an increased level of transmission, as was observed for water in Figure 4.2 (upper curves, left panel). In Figure 5.3a, where the probe wavelength is in the blue wing of the OH–stretch absorption band, the observed signal decreases to a negative final value.
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Figure 5.3. Delay time scans for pure ethanol after excitation with a 3330 cm⁻¹ pump pulse. Transmission changes were recorded with probe pulses at the blue (a) 3450 cm⁻¹, center (b) 3310 cm⁻¹ and (c) 3265 cm⁻¹ and at the red (d) 3150 cm⁻¹ of the absorption band.
5.4 Kinetic modeling

The results are interpreted in the same way as in the previous chapter. The pump pulse excites molecules from the $\nu_{\text{OH}} = 0$ to the $\nu_{\text{OH}} = 1$ state. This excited population relaxes with a time constant $T_1$ to an intermediate level, which is the vibrational (OH-stretch) ground state combined with (an)other vibrational mode(s). The exact nature of the intermediate level is not crucial here. It is only essential that the intermediate level does not yet represent thermal equilibrium, implying that only very specific combination tones get directly excited by the relaxation of the OH-stretch vibration.

The relaxation of the intermediate level leads to a full thermalization, i.e. a redistribution of the energy over all degrees of freedom. This thermalization occurs with a time constant $\tau_{\text{eq}}$. After equilibration, the temperature of the sample is increased, which leads to weaker hydrogen bonds and therefore to a blue shift of the OH-stretch resonance frequency [28, 67]. As a result, the transmission at the center frequency and at the red side is strongly increased at longer delay times, while at the blue side of the OH-absorption band an induced absorption is observed (Figure 5.3d). By changing the pump intensity we found that the thermalization (equilibration) time does not depend on the amount of energy to be equilibrated.

**Table 5.1. Fit results for different hydrogen-bonding liquids**

<table>
<thead>
<tr>
<th></th>
<th>$T_1$(fs)</th>
<th>$\tau_{\text{eq}}$(ps)</th>
<th>$\tau_{\text{eq}}$(ps)</th>
<th>$\tau_{\text{eq}}$(ps)</th>
<th>$\tau_{\text{eq}}$(ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1→2</td>
<td>red</td>
<td>center</td>
<td>blue</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>260±20</td>
<td>0.55±0.05</td>
<td>0.55±0.05</td>
<td>0.55±0.05</td>
<td>0.55±0.05</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>250±100</td>
<td>1.5±0.5</td>
<td>-</td>
<td>7.0±0.5</td>
<td>-</td>
</tr>
<tr>
<td>C$_3$H$_5$OH</td>
<td>450±100</td>
<td>2.1±0.5</td>
<td>7±1</td>
<td>13±2</td>
<td>3.2±0.5</td>
</tr>
<tr>
<td>C$_3$H$_7$OH</td>
<td>500±100</td>
<td>3.0±0.5</td>
<td>-</td>
<td>15±2</td>
<td>-</td>
</tr>
</tbody>
</table>

We have fitted the data on the alcohols with the model presented in the previous chapter (see Section 4.4). We followed the same procedure to extract the parameters $T_1$ and $\tau_{\text{eq}}$. Because the measurement showing induced absorption, Figure 5.3d, is most sensitive to $T_1$, we fitted Eq. 4.4 to this measurement to extract both $T_1$ and $\tau_{\text{eq}}$. Due to the large contributions of the thermalization signals, the fitted $T_1$ was taken constant in fitting Figure 5.3a-c with Eq. 4.2. The results of the fits are shown in Table 5.1. The results for water are obtained in Chapter 4. In this table, 1→2, red, center and blue mean probing at 3150, 3265, 3310, and 3450 cm$^{-1}$, for ethanol. For methanol and 1-propanol 1→2 and center stand for 3150 and 3310 cm$^{-1}$, respectively.
5.5 Discussion

In our experiment the response of the OH-stretch vibration is used to monitor the equilibration process. This OH-stretch vibration is very sensitive to changes in the relative positions of the water and alcohol molecules. The observed blue shift of the OH-stretch absorption band and the decrease of the cross-section thus directly reflect the repositioning of the molecules that follows from the dissipation of energy.

5.5.1 Energy redistribution and repositioning

It should be noted that the equilibration involves two subsequent processes. The first process is formed by the energy redistribution in which the energy of the non-thermal intermediate level becomes thermally distributed over all degrees of freedom. After this redistribution the equilibration is not yet complete because putting energy in a particular degree of freedom does not imply that the coordinate corresponding to this degree of freedom instantaneously finds its new equilibrium position. For instance, if a molecule is excited with a short pulse to a dissociative potential, it still takes some time, determined by the time scale of the nuclear motion, before the molecule is really dissociated. In a similar fashion it takes some time after the energy has been redistributed before the low-frequency translational and rotational degrees of freedom have acquired their new equilibrium positions. Hence, after the first process of energy redistribution, the equilibration involves a second process in which the molecules reposition at their new equilibrium positions. This repositioning of the molecules is directly observed in our experiment, since this process affects the cross section and spectral position of the OH-stretch absorption band.

The question arises whether the energy redistribution or the repositioning forms the rate-limiting step of the overall equilibration. It is to be expected that the three-dimensional hydrogen-bonded network of water allows for a much faster redistribution of energy than the one-dimensional hydrogen bonded chains [40, 45, 82] of methanol, ethanol and propanol. Hence, if the energy redistribution would form the rate-limiting step of the equilibration, water is expected to show a faster equilibration than the three alcohols, as indeed is observed. However, in that case the three alcohols are expected to have very similar equilibration times, which is certainly not the case. If on the other hand, the repositioning of the molecules forms the rate-limiting step of the equilibration, the equilibration rate is expected to scale inversely with the mass of the molecules. This agrees quite well with the observation that the equilibration time constant increases going from water to methanol, ethanol and propanol. If the overall equilibration time is indeed determined by the rate of the repositioning of the molecules, the time scales of the equilibration of water, methanol, ethanol and propanol should correlate with those observed in dielectric relaxation and rotational correlation experiments.

Dielectric relaxation measurements [3, 42] on the pure liquids show Debye relax-
Discussion

Discussion

Relaxation times of about 8 ps for water, 50 ps for methanol, about 160 ps for pure ethanol and about 320 ps for 1-propanol. Debye relaxation times calculated from NMR spectroscopy yield about 10 ps for water [3, 6], 41 ps for methanol [19], 190 ps for ethanol [19] and 560 ps for 2-propanol [19]. Hence, dielectric relaxation measurements show a very similar increase in time constant going from water to methanol to ethanol to 1-propanol as we observe for the equilibration. This strongly suggests that at least for the alcohols the repositioning of the molecules forms the rate-limiting step in the equilibration. However, for the fastest liquid, being liquid water, the rate of equilibration could still be limited by the rate of energy redistribution.

It should be noted that, although the trend matches, the absolute values of the Debye relaxation time and the equilibration time do not match. Here it should be realized that reorientation, as it is measured in Debye relaxation and rotational correlation experiments, and thermalization are not defined in the same way. The repositioning of the molecules in a thermalization process mainly involves a small change (a few degrees) in the angle the hydrogen-bond makes between donor and acceptor groups to make an appreciable difference in absorption cross section. In NMR and dielectric relaxation measurements, reorientation times are defined on the basis of a rotation of the whole molecule; rotation angles are in this case more in the order of 90 degrees. Hence, it is not surprising that the time scales measured for the equilibration process are much shorter than the Debye relaxation and orientational relaxation time constants.

5.5.2 Low frequency hydrogen-bond modes

A striking difference between the equilibration of the alcohols and liquid water is the frequency dependence of the equilibration time. For the alcohols the equilibration time constant strongly depends on the probe frequency, in the wings of the OH-stretch absorption band the equilibration time constant is much shorter than in the center of the absorption band. In contrast, for water the equilibration time constant is the same at all frequencies. A closer look at the fits to the alcohol data also shows that the equilibration process is not truly singly exponential, in the early stages of the equilibration the equilibration is somewhat faster than the fitted exponential function and at longer times the equilibration is somewhat slower than the fitted function.

The frequency dependence of the fitted equilibration time constant and the non-exponential character of the equilibration of the alcohols indicates that at least two time scales are involved in the equilibration process of the alcohols, i.e. in the repositioning of the molecules. It should be realized that shifts of the absorption spectrum will much more affect the transmission measured in the wings of the absorption than in the center, whereas a decrease in the absorption cross-section will have a similar effect on all probe frequencies. The fact that the fitted equilibration time constant is much shorter in the wings (Figures 5.2a,d) than in the center (Figures 5.2b,c) thus indicates that the blue shift of the absorption band occurs on a shorter time scale.
than the decrease of the absorption cross-section.

The total picture is now as follows. After the energy has been redistributed over all degrees of freedom, the coordinates of the low-frequency modes should find their new equilibrium positions. The most obvious candidate low-frequency mode that could influence the position of the OH-stretch band would be the hydrogen-bond stretching vibration. However, the blue shift of the OH-stretch band due to lengthening of the hydrogen-bond, can only be due to thermal expansion, which is a process that takes place on nano- or microsecond time-scales. Hence, the stretching of the hydrogen bond is not responsible for the fast blue shift of the stretch band.

The only coordinates that can be responsible for both the decrease in cross section as well as the blue shift of the OH-stretch band are the hydrogen-bond bending and librational coordinates. Both affect the angle between the OH-group and the O-H···O hydrogen-bond. Apparently, the first small change of this angle, which affects the charge density on the hydrogen atom and hydrogen bond acceptor oxygen atom, leads to the blue shift. A further change in the hydrogen-bond bending coordinate decreases the amount in which the OH-groups on different alcohol molecules are in line. Thereby the conjugation of the OH-stretch vibrations is reduced which leads to a decrease of the absorption cross-section.

For water the equilibration time hardly depends on the probe frequency which strongly suggests that for water the rate of equilibration is not limited by the rate at which the water molecules attain their new positions in the liquid but rather by the rate of energy redistribution. Hence for water the observed equilibration time constant is mainly determined by the relaxation rate of the non-thermal intermediate state. This means that the observed time scale of \( \approx 0.55 \) ps presents an upper limit for the time scale on which the molecules in liquid water reposition following a dissipation of energy.

### 5.6 Conclusions

Using two-color femtosecond mid-infrared pump-probe spectroscopy, we investigated the equilibration dynamics of water, methanol, ethanol and 1-propanol, following a local deposition of energy. In the experiments, the OH-stretch vibration is excited that relaxes to a non-thermal intermediate state, which is formed by specific combination tone(s) of excited intra- and intermolecular vibrations. The relaxation of this non-thermal intermediate state leads to a complete (thermal) equilibration of the energy. The dynamics of the latter equilibration process is monitored via the spectral response of the OH-stretch vibration. We observe that the equilibration leads to a blue shift of the OH-stretch absorption band and a decrease of the absorption cross section. Using a kinetic modeling of the experimental data we find that the time constants of equilibration of water, methanol, ethanol and 1-propanol are 0.55, 1.5-7, 2.1-13 and 3.0-15 ps, respectively. The equilibration time scale increases with increasing
molecular mass, which indicates that for the alcohols the rate of equilibration is determined by the rate at which the molecules can change their relative orientations and positions in the liquid.

For the alcohols the frequency dependence of the equilibration time constant suggests that the blue shift of the absorption band is much faster than the decrease in absorption cross-section. The hydrogen-bond bending coordinate is responsible for both processes.

For water, we observe a very short equilibration time constant of 0.55 ps, which, in contrast to the alcohols, hardly depends on frequency. This suggests that for water the equilibration rate is not determined by the repositioning of the molecules (as for the alcohols) but rather by the rate of energy relaxation from a non-thermal intermediate state. Hence, the reposition of the molecules in liquid water probably occurs on a time scale that is shorter than 0.55 ps. This means that water can adapt extremely fast, much faster than alcohols, to a deposition of energy.