Love and fear of water: Water dynamics around charged and apolar solutes
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Experimental Study of the Jump-Reorientation of Water

Molecular dynamics simulations showed that the largest contribution to the reorientation of water molecules is formed by hydrogen-bond switching events, in which a water molecule breaks a hydrogen-bond and forms a new one with another water molecule. This change of hydrogen-bonding partners was found to happen over large sudden jumps rather than in a continuous fashion. We use pump-probe spectroscopy on the OD-stretch vibration of HDO molecules in water to measure the reorientation of the vector along the transition dipole of this vibrational mode. We find experimental evidence that supports the jump mechanism of water reorientation. We also find that for increasing temperatures both the rate of spectral diffusion and the reorientation dynamics become faster. The activation energy that we obtain from the spectral diffusion data is $2.6 \pm 0.5$ kcal/mol.
6.1 Introduction

The hydrogen-bond network of water is both robust and dynamic at the same time. The binding energy of a hydrogen bond is 5.0 kcal/mol, about one twentieth of the OH covalent bond energy and still well above the energy of thermal fluctuations at room temperature. This does not mean that hydrogen-bonds do not easily break. Water molecules switch hydrogen-bonding partners at a rate of $0.3 \text{ps}^{-1}$ [61, 2, 68, 82, 3]. In this concerted process, the hydrogen-bond is never completely broken, but the hydroxyl group rather forms an intermediate bifurcated hydrogen-bond to the oxygen atoms of two nearby water molecules [2]. It was found that this transition state lowers the activation energy of a hydrogen-bond switch to about 3.1–3.5 kcal/mol [83, 84, 85, 86, 87, 88].

The transition through the bifurcated state happens on a timescale of 100 fs and involves a large angular jump of the hydroxyl group [2]. Classical molecular dynamics (MD) simulations found this process to be the main contributor to the molecular reorientation of water [2, 86]. For increasing temperatures the reorientation of water has been found to become faster and it is therefore likely that the jump mechanism speeds up. This chapter aims at obtaining more knowledge on the jumping process and its temperature dependence.

The stretching vibration of the hydroxyl groups is particularly sensitive to its chemical environment and offers an ideal probe of the hydrogen-bond network. A strong hydrogen-bond leads to a red-shift of the resonance frequency of the OH stretch vibration, whereas a weak hydrogen-bond leads to a blue-shift. The transition state of a molecular jump can be regarded as a very weak hydrogen-bond [89]. The evolution from a linear hydrogen bond to the bifurcated transition state is therefore accompanied by a large change in vibrational frequency. Therefore there exists an intimate relation between the reorientation of water and spectral diffusion of the OH stretch vibrational frequency.

We use the strong coupling of the hydrogen-bond to the OH stretch vibration to study the jump reorientation of water molecules at different temperatures. To this end, we performed two-color infrared pump-probe spectroscopy on neat (isotopically diluted, 8% D₂O in H₂O) liquid water. By using a narrow-band excitation pulse positioned the blue wing of the OD stretch vibrational band, we excite the stretch vibration of a subset of OD groups that donate very weak hydrogen-bonds. These OD groups have a much higher chance of being within a few hundred femtoseconds from a reorientational jump compared to OD groups that donate hydrogen-bonds of average strength [89]. We first analyze the isotropic response, including spectral diffusion. Subsequently we consider the reorientation dynamics of OD groups with different hydrogen-bond strengths, first at room temperature and finally for elevated temperatures.

6.2 Experimental

The measurements in this chapter were performed using the two-color setup described in section 3.1.2 with the central frequency of the probe spectrum
6.3 Experimental Study of the Jump-Reorientation of Water 91

tuned to 2200 cm\(^{-1}\), 2550 cm\(^{-1}\) or 3000 cm\(^{-1}\). For some of the measurements we used a spectrally broad pump pulse (full width half maximum (FWHM) 200 cm\(^{-1}\)), tuned to the center of the OD stretch band at 2500 cm\(^{-1}\). Such a spectral shape of the pump assures a homogeneous excitation of OD oscillators over the whole absorption band. For most measurements we used a spectrally narrow pump pulse (FWHM 60 cm\(^{-1}\)) to selectively excite a part of the OD-stretch oscillators in their first excited state. With the center frequency tuned to the blue shoulder of the absorption band (eg. 2650 cm\(^{-1}\)), preferably OD groups that have a very weak hydrogen-bond will excited. To make pulses with such a narrow spectrum, the idler coming from the TOPAS was frequency doubled to \(\sim 1000\) nm using a BBO crystal of 4 mm thickness. We thereby used the narrow acceptance bandwidth of the crystal to generate pulses that are spectrally more narrow. To generate mid-infrared pulses we performed difference frequency mixing of this pulse with 1 mJ pulses of 800 nm in a lithiumniobate crystal with a length of 10 mm. The use of this relatively long crystal was to narrow the spectral bandwidth even further. The generated light pulses that we eventually obtained had a pulse energy of 16 \(\mu\)J.

We used D\(_2\)O (99.9 % pure, Sigma Aldrich) and millipore water to make isotopically diluted water samples (8 mol\% D\(_2\)O in H\(_2\)O). We used this isotope ratio to obtain an optimal contrast between the signal from the OD-stretch vibration and the undesired thermalization of excited OH-stretch vibrations. Resonant Förster energy transfer is at this HDO concentration still quite limited [26]. The sample cell consisted of a stainless steel ring with two calcium fluoride windows (0.5 mm), pressed against each other with a 25 \(\mu\)m spacer in between. For the temperature dependent measurements we used a peltier element with dedicated controller to heat up the aluminium base plate of the sample cell. A thermocouple attached to the sample cell was used to maintain a constant temperature (\(\Delta T \approx \pm 1\) K) in the temperature range between 295K and 343K.

6.3 Results and Discussion

6.3.1 Thermalization Dynamics and Spectral Diffusion

The isotropic transient spectra are constructed from the parallel and perpendicular data using Eq. (4.2) and are shown in Fig. 6.1. The transient spectra for short delay times show a bleach at blue frequencies. With increasing delay times this bleach shifts to lower frequencies and decays. The frequency shift within the first picosecond is attributed to fast spectral diffusion of the excited oscillators. After 30 ps the spectrum is not changing anymore with further increasing delay time within the experimentally accessible range (1 ns). This quasi-static spectrum is the thermal difference spectrum elaborated on in section 4.3.

Immediately after excitation, the thermal difference spectrum is already relatively large with respect to the excited state response. Previous measurements on the same system with a spectrally broad pump centered around the center of the OD stretch band (2500 cm\(^{-1}\)) yielded a thermal difference spectrum...
Figure 6.1. Raw isotropic transient spectra for pump-probe delay times between 0.09 ps (red line) and 50 ps (purple line). At short delay times the transient spectra mainly show a bleach at frequencies $>2450 \text{ cm}^{-1}$. The bleach subsequently shifts to the red and decays. At long delay times the transient spectrum takes the form of a thermal difference spectrum.

with a relatively smaller amplitude (data not shown, [24]). In principle this could be due to very fast relaxation of OD oscillators within the first hundred femtoseconds or so. This would require a strong coupling between those OD oscillators and their environment. However, since the pump spectrum is tuned to the blue side of the OD-stretch spectrum, the excited subset of OD oscillators rather contains weakly coupled oscillators. More likely is that the pump also excites OH oscillators which are relaxing with a time constant of $\approx 200 \text{ fs}$ [74]. Although $2650 \text{ cm}^{-1}$ is far off from the OH-stretch maximum at $3400 \text{ cm}^{-1}$, the cross section of the OH vibrations is non-zero due to the large amplitude of the band and inhomogeneous broadening. Since the OD-stretch band is pumped off-center, the relative contribution of the OH-stretch excitation is non-negligible and leads to a fast thermal response. More details on this collateral excitation can be found in section 2.2.

To obtain the reorientation dynamics using Eq. (4.18) we need to subtract the heating contribution from the parallel and perpendicular data. In previous work this was achieved by fitting a kinetic relaxation model to the isotropic data. As we have pointed out above, though, the transient spectra in Fig. 6.1 contain highly non-trivial thermalization dynamics. In addition, the excited state contribution is complicated due to the spectral diffusion. This renders the use of a simple kinetic model close to impossible. Therefore, we obtained the thermalization dynamics by probing the large thermal difference spectrum at the shoulder of the OH-stretch band at $3000 \text{ cm}^{-1}$ (details are described in section 4.3). At this frequency there is no contribution of the excited OD oscillators and the thermalization dynamics can be measured directly. These dynamics are used to subtract the thermal difference spectrum from the data of Fig. 6.1. An additional advantage of this method is that no assumptions need to be made on the rate and mechanism of the relaxation of the OD vibrations.
6.3 Experimental Study of the Jump-Reorientation of Water

Figure 6.2. (A) Isotropic transient spectra from which the thermalization component is subtracted. The first moment of the spectra is plotted in panel (B) for sample temperatures of 295K and 343K. The time evolution of the first moment reflects the spectral diffusion in the samples. At delay times >1 ps an equilibrium is reached. At 343K the spectral diffusion is faster and the center of the band is blue-shifted by 20 cm$^{-1}$.

The isotropic data obtained after subtraction of the thermal difference spectrum are shown in Fig. 6.2A. The spectral diffusion is apparent as a red-shift of the spectral maximum and the zero-crossing with increasing delay times. To quantify the spectral diffusion we evaluate the first moment $M_1$ of the negative (bleaching) part of the heat-corrected transient spectra. The first moments are plotted as a function of the pump probe delay time in Fig. 6.2B. In anticipation to the temperature dependent measurements presented later in this chapter, $M_1$ is shown for sample temperatures 295K and 343K. The first thing to notice is that within a few hundred femtoseconds $M_1$ has already relaxed to $\sim 2560$ cm$^{-1}$. The decay progresses still further in the subsequent 1.5 ps and equilibrates at 2530 cm$^{-1}$. At 343K the endlevel of $M_1$ is higher and the decay is somewhat faster than at 295K.

Before we interpret the dynamics of the $M_1$ decays we explain why it does not start at 2650 cm$^{-1}$, the maximum of the excitation spectrum. The OD stretch band is an inhomogeneously broadened collection of homogeneous lorentzian lineshapes, the number density of which falls of in the wings. The overlap of the spectrum of the excitation pulse at 2650 cm$^{-1}$ with the the lineshapes of OD oscillators red-shifted from 2650 cm$^{-1}$ is larger than that with OD oscillators that are resonant at 2650 cm$^{-1}$. As a result, the maximum of the number density of excited OD oscillators is at 2610 cm$^{-1}$ (see also section 2.2).

The excited OD oscillators have high frequencies, meaning that they donate a very weak hydrogen-bond. There are two main molecular configurations corresponding to a weak hydrogen-bond: Either 1) the hydrogen-bonding (OD-O) angle between the vector pointing along the OD covalent bond and the oxygen-
oxygen vector is large, or 2) the oxygen-oxygen distance \( R_{OO} \) of the two water molecules involved in the hydrogen-bond is large [60].

From classical MD simulations it is known that for the excited subensemble in this experiment more than 20% of the OD oscillators is within 125 fs from a molecular jump [86]. In comparison, for an excitation around the OD stretch absorption maximum this is less than 5%. Therefore, the excited subset exists of two groups with different near future events: shortly after excitation either 1) evolves to the bifurcated state, resulting in a rapid successful jump over a large angle to a new hydrogen-bonding partner or switches back to its original hydrogen-bonding partner in an unsuccessful jump, or 2) ordinary structural diffusion leads to a gradual evolution to stronger hydrogen-bonds.

Let us now consider how these hydrogen-bond configurations and structural dynamics influence our observables. In case the OD group was at the time of excitation close to a transition state, it will either rapidly switch back to its current hydrogen-bonding partner or jump. In either case, in the final state the hydrogen-bond is much more linear (and hence stronger) and the resonance frequency of the OD oscillator thus quickly decreases. As a result, these processes lead to fast spectral diffusion to lower frequencies. The typical time associated with a reorientation jump are on the order of a few hundred femtoseconds [2, 4] and we associate this process with the very fast decay of \( M_1 \) that we find in Fig. 6.2B.

In other cases, the OD oscillator was donating a weak hydrogen-bond due to its large oxygen-oxygen distance \( R_{OO} \) and will remain wobbling in the librational cone of its current hydrogen-bonding partner. It will not be much restricted by its coulomb interaction with the nearest water molecule [60] and has a lot of freedom to wobble: its librational cone is large [89]. While wobbling, its hydrogen-bond strength will on average remain weak and the wobbling thus has a limited contribution to spectral diffusion. For the oscillator to spectrally diffuse to lower frequencies, the \( R_{OO} \) distance should become smaller. This can happen by translational motions that occur in pure liquid water on a \( \sim 1 \) ps timescale [66, 63, 65, 68, 67, 64, 60]. Such an initially blue-excited OD oscillator thus likely remains to give a response at blue frequencies within the first picosecond. This process is associated with the slower decay of \( M_1 \) in Fig. 6.2B.

### 6.3.2 REORIENTATION DYNAMICS AT ROOM TEMPERATURE

After subtraction of the thermal component of the parallel and perpendicular transient spectra we calculated the anisotropy dynamics at various probe frequencies using Eq. (4.18). The results are shown in Fig. 6.3A. The anisotropy in the first picosecond shows a strong dependence on the probe frequency, while for longer delay times the dynamics are completely frequency independent.

The low values of the initial anisotropy and subsequent rise in the first picosecond that we find for low probe frequencies (eg. 2500 cm\(^{-1}\)) is a feature that requires cautious consideration. This feature finds its origin in a frequency dependence of the anisotropy. To understand the observed frequency dependence in detail, we need to consider all contributions to the transient spectra carefully.
6.3 Experimental Study of the Jump-Reorientation of Water

Figure 6.3. Anisotropy dynamics of OD groups in neat HDO:H$_2$O. For these measurements the sample was excited with a narrow band pump at 2650 cm$^{-1}$. (A) Probe frequencies in the $\nu = 0 \rightarrow 1$ region (2490, 2500, 2520, 2560 and 2600 cm$^{-1}$, red to blue curves). For short delay times the anisotropy has a strong dependence on the probe-frequency, which disappears entirely after 1 ps. The anisotropy at 2600 cm$^{-1}$ initially decays significantly faster than 2.5 ps, the timescale of reorientation found using a spectrally broad pump centered around 2500 cm$^{-1}$ [22]. (B) Probe frequencies in the $\nu = 1 \rightarrow 2$ region (2100, 2150, 2200, 2250 and 2300 cm$^{-1}$, red to blue curves). The anisotropy dynamics show no dependence on the probe frequency and decay with a time constant of 2.3 ± 0.2 ps.

The total transient spectrum is a combination of a (negative) bleaching signal at the $\nu = 0 \rightarrow 1$ transition frequencies and a (positive) induced absorption signal at the $\nu = 1 \rightarrow 2$ transition frequencies. Due to the anharmonicity of the OH-stretch vibration the induced absorption is red-shifted about 200 cm$^{-1}$ with respect to the bleach. Therefore a considerable spectral region exists in which both features overlap. As a result, the total measured transient absorption at 2500 cm$^{-1}$ is in fact the sum of the bleach at 2500 cm$^{-1}$ and the blue wing of the induced absorption. The blue wing of the induced absorption is the $\nu = 1 \rightarrow 2$ response of weakly hydrogen-bonded oscillators that have a ground-state absorption at 2700 cm$^{-1}$, while the bleach at 2500 cm$^{-1}$ rather represents the $\nu = 0 \rightarrow 1$ response of OD oscillators with an average hydrogen-bond strength. If the reorientation dynamics is the same for any hydrogen-bond strength of the OD oscillators, the anisotropy at any probe frequency of either the bleach or induced absorption would be the same for a given delay time. Addition of the two signals would not make any difference. If however the reorientation dynamics does change with oscillator strength and thus probe frequency, the anisotropy at 2500 cm$^{-1}$ is a non-trivial combination of both the reorientation dynamics of OD oscillators that absorb at the blue wing of the linear spectrum ($\nu = 0 \rightarrow 1$) and those that absorb at the center of the linear spectrum ($\nu = 1 \rightarrow 2$). More specific, the anisotropy at 2500 cm$^{-1}$ is the sum of the reorientation dynamics of the $\nu = 0 \rightarrow 1$ and $\nu = 1 \rightarrow 2$ response, weighted to their isotropic spectral
amplitude. At probe frequencies where the total isotropic response is zero, this weighted sum leads to an asymptotic behavior of the anisotropy. The small (and even negative) values for the anisotropy at 2500 cm$^{-1}$ in Fig. 6.3A are thus artificial, but do represent an anisotropy that decreases with decreasing frequency. A formal description of this interference effect is found in the appendix 6.A.

The complicated competition within the bleaching of the OD stretch band can be avoided by probing the red wing of the induced absorption only. This approach comes at a cost: For a subset of oscillators with $\nu = 0 \rightarrow 1$ resonances at one single frequency there is a distribution of $\nu = 1 \rightarrow 2$ frequencies. The absence of a unique mapping results in a smearing effect that partly averages out spectral differences in reorientation dynamics. The anisotropy dynamics measured between 2100 cm$^{-1}$ and 2300 cm$^{-1}$ using the same spectrally narrow excitation pulse centered around 2650 cm$^{-1}$ are shown in Fig. 6.3B. To obtain these results we used the same method of subtraction of the thermalization contribution. These probe frequencies cover the red wing of the induced absorption part of the transient spectrum: Since the anharmonic shift is about 200 cm$^{-1}$, the oscillators probed at 2300 cm$^{-1}$ approximately correspond to the oscillators probed at 2500 cm$^{-1}$. Between 2100 cm$^{-1}$ and 2300 cm$^{-1}$ we observe no significant frequency dependence in the reorientation dynamics. It should be noted, though, that the initial value of the anisotropy $R_0$ at 2300 cm$^{-1}$ is lower than $R_0$ at 2600 cm$^{-1}$.

The frequency dependence of the anisotropy following a narrow-band blue excitation is consistent with earlier work [90]. Previous fs-IR studies found that the reorientation time of OD groups in a similar solution is $2.5 \pm 0.1$ ps and is independent on the probe frequency [22]. Those experiments were performed with a spectrally broad pump, centered around the maximum of the OD-stretch band at 2500 cm$^{-1}$. For the subset excitation used in the present experiment, we observe that the dynamics of the anisotropy at different frequencies is governed by an interplay of the reorientational jumps and the structural diffusion. Librational motions also lead to a decay of the anisotropy, but is completed within hundred femtoseconds [89, 91], and therefore only shows in our results as a lower starting value of the anisotropy (Fig. 6.3). This loss of orientation originates from the wobbling motion of an OD group while keeping its hydrogen-bond intact. Librational motions do not contribute to spectral diffusion, since the hydrogen-bond strength remains similar.

For the interpretation of the subsequent anisotropy dynamics we will again consider the different configurations and structural dynamics of weakly hydrogen-bonded oscillators described in the previous section. We find that at very short delay times the anisotropy is lower on the red side than on the blue side of the spectrum (Fig. 6.3). This difference can be fully understood by the jump reorientation of blue-excited OD oscillators. Classical molecular dynamics (MD) studies have shown that more than 20% of such weakly hydrogen-bonded OD groups are within 125 fs of an orientational jump to a new hydrogen-bonding partner [86]. Such a jump event requires a large angular change of the OD group that leads to an almost complete decay of
the anisotropy [2]. As we have argued in the previous section, a jump event is accompanied with fast spectral diffusion of the OD oscillator to lower frequencies. These OD oscillators therefore have little contribution to the reorientation dynamics probed at 2600 cm\(^{-1}\) immediately after their jump. They rather dominate the signal at lower frequencies, eg. 2500 cm\(^{-1}\), where initially no OD oscillators were excited at all. The anisotropy measured in the first few hundred femtoseconds at 2500 cm\(^{-1}\) thus mostly represents OD oscillators that lost part of their orientation in a jump. As a consequence, the anisotropy at red probe frequencies is initially lower than the anisotropy at 2600 cm\(^{-1}\). For the anisotropy measured at 2500 cm\(^{-1}\) this effect is magnified by the competition between the bleach and the induced absorption at these frequencies, which was described above. A better comparison is obtained if we compare the anisotropy dynamics at 2600 cm\(^{-1}\) with those probed at 2300 cm\(^{-1}\) (Fig. 6.3). The response measured at 2300 cm\(^{-1}\) corresponds to the \(\nu = 1 \rightarrow 2\) transition of oscillators that absorb at 2500 cm\(^{-1}\). The anisotropy indeed shows a lower value in the first picosecond.

The second contribution to the anisotropy dynamics comes from structural diffusion by the variation of oxygen-oxygen distances \(R_{OO}\) [43]. As a result, \(R_{OO}\) decreases for those OD groups that initially had a large value of the oxygen-oxygen distance, thereby spectrally shifting the resonance frequency of those oscillators to lower frequencies. This shift we found as the \(\sim 1\) ps decay component in the spectral diffusion represented by the first moment in Fig. 6.2B. The process of the structural diffusion process will thus 'feed' the red side of the spectrum with oscillators that still possess relatively a lot of orientation. Conversely, there are oscillators that made a rapid orientational and spectral jump from the blue wing of the spectrum to 2500 cm\(^{-1}\). By the slower spectral diffusion process of translational motions, these oscillators diffuse back to the blue wing. Since they lost all their orientation already in the first few hundred femtoseconds, their contribution to the anisotropy measured at the blue side of the spectrum leads to a decay. Translational motions thus wash away any remaining memory of the out-of-equilibrium excitation, causing the anisotropy curves for all probe frequencies to become identical after \(\sim 1.5\) ps. After spectral diffusion is completed, the anisotropy is therefore independent on the spectral position of the excited OD oscillators.

The subsequent reorientation dynamics after spectral equilibration is not different from the anisotropy dynamics after a homogeneous excitation by a spectrally broad pump. These dynamics are dominated by the large angular jump hydrogen-bond switching and frame reorientation [2]. From an exponential fit to the data for delay times larger than 2 ps we indeed find a time constant of the anisotropy decay of 2.4 ± 0.3 ps. This time constant is in excellent agreement with previous findings on the reorientation of OD groups in isotopically diluted water (2.5 ps) [22].
Figure 6.4. (A) Similar figure as Fig. 6.3A (identical probe frequencies) for a sample temperature of 328K. The reorientation dynamics in neat 16% HDO:H$_2$O is faster than that at 295K. (B) Anisotropy decay probed at 2600 cm$^{-1}$ after excitation with a spectrally narrow pump centered around 2650 cm$^{-1}$ (solid lines) and anisotropy decay after excitation with a spectrally broad pump centered around 2500 cm$^{-1}$ (dotted lines) at 295K and 343K. The anisotropy decays faster in case the sample is pumped at 2650 cm$^{-1}$ compared to when the sample is excited with a spectrally broad pump. This also holds for elevated temperatures: although increasing the sample temperature speeds up the reorientation dynamics, pumping the blue wing of the OD-stretch band makes the anisotropy decay still faster.

Figure 6.5. Anisotropy decay probed at 2500 cm$^{-1}$ (A) and at 2600 cm$^{-1}$ (B) after excitation by a spectrally narrow pump centered around 2650 cm$^{-1}$, at a sample temperature of 295K (circles), 313K (triangles), 328K (squares) and 343K (diamonds). For increasing temperatures the dynamics become faster.
6.3 Experimental Study of the Jump-Reorientation of Water

6.3.3 Reorientation Dynamics at Elevated Temperature

All anisotropy results that we considered until this point were obtained at room temperature. We will now compare the frequency dependent measurements for neat 16\% HDO:H$_2$O at different temperatures. It should be noted that the vibrational lifetime $T_1$ of the OD-stretch vibration becomes longer for increasing temperature [88, 35]. A longer $T_1$ makes the determination of the anisotropy at longer delay times even more accurate.

Fig. 6.4A shows the frequency dependent reorientation dynamics obtained at $T = 328\,K$. The pump spectrum is again centered around 2650 cm$^{-1}$ with a FWHM of 60 cm$^{-1}$. We compare these data to the results obtained at room temperature (295K) presented in Fig. 6.3. The most clear difference is that the relaxation at all frequencies is significantly faster at 328K than at 295K. In Fig. 6.4B we compare the anisotropy dynamics obtained for a spectrally broad excitation and a narrow blue excitation at different temperatures. The probe frequency used is 2600 cm$^{-1}$, but it should be noted that for a broad excitation pulse the anisotropy decay does not significantly depend on the probe frequency [22]. At both 295K and 328K, the orientational relaxation after excitation with a spectrally narrow pump at 2650 cm$^{-1}$ is faster than after excitation with a spectrally broad pump. Independent on the type of excitation pulse used, the reorientation dynamics becomes faster at elevated temperatures. The anisotropy decays at 2500 cm$^{-1}$ and 2600 cm$^{-1}$ are shown in Fig. 6.5 for all sample temperatures measured.

The equilibration of the frequency dependence of the anisotropy in the first picosecond is faster at 328K compared to the data measured at 295K. This is quantified by fitting a straight line to the frequency dependent anisotropy at every delay time. The slope as function of delay time is shown in Fig. 6.7A for a number of temperatures. We compare these plots with the dynamics of the first moment in Fig. 6.7B. The first moments are obtained by the method described in section 6.3.1. We fitted mono-exponential functions to the data (solid lines), of which the decay constants are presented in Fig. 6.7 for all measured temperatures. The results show a strong correlation between the spectral diffusion and anisotropy equilibration, both becoming faster for increasing temperature.

In the previous section we found that the anisotropy decay following excitation with a spectrally narrow pump at 2650 cm$^{-1}$ are governed by an interplay of the reorientational jumps and spectral equilibration. For increasing temperatures, both components will become faster. Water reorientation by jumps is an activated process and thus this process becomes more frequent at elevated temperatures [88]. The rate limiting step of a jump event to occur is the approach of a new potential hydrogen-bonding partner. This process is sped up by faster structural diffusion and thus the frequency of jumps increases. $R_{OO}$ distances become on average slightly larger at higher temperatures, as is also illustrated by the higher endlevel of the first moment at 343K in Fig. 6.2B. Fig. 6.7 demonstrates that structural diffusion becomes faster (see also [87]),
resulting in a faster equilibration of the anisotropy as a function of probe frequency. Due to the increased rate of the jumps and the accelerated spectral diffusion, the average reorientation speeds up. From the decay constants of spectral diffusion and the anisotropy equilibration we can determine the activation energy of these processes (fitted lines in Fig. 6.7). Both methods yield a value of $11 \pm 2$ kJ/mol, or $2.6 \pm 0.5$ kcal/mol. This value is in reasonable agreement with previous findings of 3.1–3.5 kcal/mol [83, 84, 85, 86, 87, 88].

6.4 Conclusions

We studied the reorientation dynamics of OD groups in isotopically diluted water at different temperatures after excitation by a narrow-band pump pulse, spectrally centered around 2650 cm$^{-1}$. This pump excites a subset of those OD oscillators that donate a weak hydrogen-bond. This subset offers a good probe of the hydrogen-bond switching process for two reasons: these OD oscillators have an increased probability of being close to an orientational jump event that results in a hydrogen-bond switch, and for short delay times the signal response at the red side of the spectrum will reveal the oscillators that have just experienced such a hydrogen-bond switch. We find that a few hundred femtoseconds after excitation the hydrogen-bond switching leads to a lower anisotropy at low frequencies compared to high frequencies. This spectral dependence of the

Figure 6.6. (A) The time-dependent slope of a straight line fitted to the frequency dependent anisotropy between 2485 cm$^{-1}$ and 2530 cm$^{-1}$ (see inset for the fits to the data taken at 295K). The vanishing of the slope at long delay times implies that full spectral equilibration has taken place. The solid lines are mono-exponential fits to the data. (B) Dynamics of the first moment $M_1$ obtained at different temperatures. The plots are vertically displaced such that they decay to a vanishing difference $\Delta \nu$ between $M_1$ at a given delay time and $M_1$ of the equilibrium spectrum that is reached after several picoseconds (see Fig. 6.2). The solid lines are mono-exponential fits to the data.
6.4 Experimental Study of the Jump-Reorientation of Water 101

Figure 6.7. Natural logarithm of the decay rates that were obtained from an exponential fit to the dynamics of the first moment (circles) and slope of the frequency dependent anisotropy (triangles) from Fig. 6.7, as a function of inverse temperature. The activation energy that was found by taking the slope of a linear fit through the points is $11 \pm 2$ kJ/mol.

Anisotropy vanishes on a 1 ps time scale due to structural diffusion. After equilibration, the reorientation dynamics is governed by the interplay of structural diffusion and hydrogen-bond switching events and are the same as found after homogeneous excitation of the absorption band. For elevated temperatures we find that both the spectral diffusion and the reorientation become faster. We find an activation energy of hydrogen-bond switching of $2.6 \pm 0.5$ kcal/mol.
6.A Appendix: Narrow Pump and Anisotropy

In this appendix we will describe in detail the amplification effect of a frequency dependence in the anisotropy dynamics that may occur following a narrow-band blue excitation. We assume a similar excitation spectrum as used in the experiment, with a FWHM of 60 cm$^{-1}$ and centered around 2650 cm$^{-1}$. We recall from chapter 4 that the isotropic transient spectra may be written as the product of the population dynamics $N(t)$, reflecting the vibrational decay of the excitation, and the excited state transient absorption spectrum $\sigma(\nu)$ (Eq. (4.12)). Furthermore, we restate that $\sigma(\nu)$ consist of a negative contribution $\sigma_{01}(\nu)$ due to stimulated emission and ground state depletion (the bleach) at the $\nu_s = 0 \rightarrow 1$ transition frequency and a positive contribution $\sigma_{12}(\nu)$ due to excited state absorption at the $\nu_s = 1 \rightarrow 2$ transition frequency. The heat corrected isotropic transient spectra for a single species solution can thus be written as,

$$\Delta \alpha_{iso}(\nu, t) = N(t)\sigma(\nu) = N(t)(\sigma_{01}(\nu) + \sigma_{12}(\nu))$$ (6.1)

However, the absorption spectrum of OD-oscillators in isotopically diluted water is inhomogeneously broadened: oscillators with stronger or weaker hydrogen-bonds have their resonance frequency at different positions in the absorption band. In case of a narrow band excitation pulse with its center frequency at the blue side of the OD-stretch band, mainly those OD-oscillators are excited that have a weak hydrogen-bond. This results in a blue-shifted transient response of both $\sigma_{01}(\nu)$ and $\sigma_{12}(\nu)$ at time zero. Due to spectral diffusion, $\sigma_{01}$ and $\sigma_{12}$ have a time dependence and will eventually assume their equilibrium shape.

For simplicity we consider a gaussian shape for the bleach with central frequency $\nu_c^0$ at time zero, exponentially relaxing to $\nu_c^\infty$ due to spectral diffusion with rate $k_s$. The spectral contribution of the bleach $\sigma_{01}(\nu, t)$ to the total transient absorption can then be written as,

$$\sigma_{01}(\nu, t) = Ae^{-\frac{(\nu - \nu_c(t))^2}{2\Sigma^2}}$$ (6.2)

where $A$ is the amplitude of the response and $\Sigma$ the width of the gauss. We ignored here the fact that a narrow excitation also leads to a time dependent broadening of $\Sigma$. The time-dependent center frequency $\nu_c(t)$ can be written as,

$$\nu_c(t) = (\nu_c^0 - \nu_c^\infty)e^{-k_st} + \nu_c^\infty$$ (6.3)

A similar relation can be derived for the spectral contribution of the induced absorption $\sigma_{12}(\nu, t)$, for which the sign of the amplitude will be different and the center frequency is shifted to the red side of the spectrum by the anharmonicity (180 cm$^{-1}$). Using Eq. (4.4) and using the expression for the anisotropy of Eq. (4.3) yields,

$$R_m(\nu, t) = \frac{\sigma_{01}(\nu, t)R_{01}(\nu, t) + \sigma_{12}(\nu, t)R_{12}(\nu, t)}{\sigma_{01}(\nu, t) + \sigma_{12}(\nu, t)}$$ (6.4)

The subscript $m$ of the anisotropy $R_m$ is added as a reminder that this parameter represents the measured anisotropy as opposed to the actual anisotropy.
Figure 6.8. A simulation of the artefact that arises in the measured anisotropy dynamics in case the OD stretch vibration in isotopically diluted water is inhomogeneously excited by a narrow band pump centered at the blue shoulder of the absorption band. The solid black lines are the actual anisotropy dynamics at 2500 cm$^{-1}$ (lower line) and 2600 cm$^{-1}$ (upper line). The dashed-dotted lines are the anisotropy dynamics that were calculated as they would be measured for equidistant frequencies (step size 12.5 cm$^{-1}$) between 2500 cm$^{-1}$ (lowest curve) and 2600 cm$^{-1}$ (uppermost curve).

$R_{01}$ and $R_{12}$. We explicitly took the anisotropy different for the bleach and the induced absorption. This is necessary because at a given frequency $\nu$ the spectral response of the bleach arises from different oscillators than the spectral response of the induced absorption, due to the anharmonicity of the OD stretch vibration. An oscillators that contributes to the bleach at 2500 cm$^{-1}$, therefore also contributes to the induced absorption at 2320 cm$^{-1}$. In terms of the associated reorientation dynamics we write this as,

$$R_{12}(\nu, t) = R_{01}(\nu + 180, t)$$

(6.5)

In case there is no frequency dependence in the anisotropy, the equality in Eq. (6.5) is trivial and $R_m(\nu, t)$ reduces to $R_{01}(t)$. For the experiment in this chapter, the anisotropy in fact does depend on the probe frequency. In line to what we found we define the frequency dependence as,

$$R_{01}(\nu, t) = \frac{2}{5} (0.25e^{-0.4t} + 0.15\rho e^{-3t}) \begin{cases} 
\rho = 0 & (\nu < 2500) \\
\rho = \frac{\nu-2500}{100} & (2500 < \nu < 2600) \\
\rho = 1 & (\nu > 2600) 
\end{cases}$$

(6.6)

We calculated $R_m(\nu, t)$ according to Eq. (6.4) for values of the spectral diffusion parameters that are describing a physical example of actually measured data presented in chapter 7. The results are plotted in Fig. 6.8 for a number of probe-frequencies. The black lines represent the actual anisotropy of the bleach at 2500 cm$^{-1}$ and 2650 cm$^{-1}$. As can be seen, the amplitude of $R_m$
is heavily suppressed for short delay times, especially at frequencies close to $2500\text{ cm}^{-1}$ where an asymptotic behavior seems to be present. This behavior follows from the nominator of Eq. (6.4) than can become very small for frequencies at which $\sigma_{01}(\nu, t) \sim \sigma_{12}(\nu, t)$. Due to the difference between $R_{01}(\nu, t)$ and $R_{12}(\nu, t)$, the nominator is not necessarily small at these frequencies. This effect disappears for longer delay times for two reasons. 1) The definition of the anisotropy implicitly assumed a convergence of $R_{01}(\nu, t)$ and $R_{12}(\nu, t)$ and 2) the zero-crossing of $\sigma(\nu, t)$ shifts to frequencies lower than $2500\text{ cm}^{-1}$, thereby diminishing the artefact. Both of these points are related to spectral diffusion. In case spectral diffusion would not be complete within the timescale of the experiment, $R_{01}(\nu, t)$ and $R_{12}(\nu, t)$ would not converge with a residual frequency dependence as a result.