Molecular motions of water: The effect of charged and hydrophobic solutes
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5 Temperature dependence of water reorientation

We study the temperature dependence of the molecular reorientation of HDO molecules in H\textsubscript{2}O with polarization-resolved femtosecond mid-infrared pump-probe spectroscopy. With this technique we measure the decay time of the second order correlation function of the molecular reorientation. We find that the reorientation time changes from $4.8\pm0.3\ \text{ps}$ at 1 \textdegree C to $0.97\pm0.05\ \text{ps}$ at 70 \textdegree C. We compare the measurements with literature results of terahertz time-domain spectroscopy, where the Debye reorientation time is measured. From this comparison we obtain the ratio between the macroscopic Debye reorientation time and the first order microscopic reorientation time.

5.1 Introduction

The many anomalies of water find their origin in the structural arrangement of water, where water molecules form a connected network through hydrogen bonds. This network is not static, since molecular rearrangements take place continuously, typically on a picosecond ($10^{-12} \text{ s, ps}$) timescale. The reorientation of liquid water involves three distinct processes. First of all, there is very fast 'single molecule' rotation that occurs for a very small fraction of undercoordinated water molecules, i.e. molecules that have very few or no hydrogen bonds [186]. The second process is formed by the ultrafast librational motions of the OH groups that keep the hydrogen bonds intact [43, 80]. This process occurs on an ultrafast timescale ($<200 \text{ fs}$ [43,109]) and leads to a partial ($\sim20\%$) orientational scrambling. Recently, the temperature dependence of this librational contribution to the reorientation of liquid water was investigated in Ref. [109], where it was found that the relative contribution due to librational reorientation depends on the hydrogen bond strength, and that this dependence increases with temperature. The third process that can occur is the collective reorganization of the hydrogen-bond network, which involves the transient breaking and reformation of hydrogen bonds. In this Chapter, we focus our attention on this reorientation process. Numerical simulations recently showed that this reorientation of water molecules occurs in large-amplitude angular jumps (see Fig. 5.1), with a distribution of jump angles that is centered around $50^\circ$ [81, 83]. This jump model differs from the previously commonly accepted
picture of subsequent small-amplitude angular rearrangements, known as the diffusion model.

Figure 5.1. The molecular mechanism of water reorientation, following a jump mechanism (see Ref. [81]). After the approach of molecule C towards the hydrogen-bonded molecules A and B (left figure), a bifurcated state is formed, where molecule A is hydrogen-bonded both to molecule B and to molecule C (middle figure). After a large angle molecular jump, water molecule A, which was originally bonded to molecule B, is now bonded to molecule C.

Different experimental techniques have been employed to measure reorientation times of water molecules, like GHz dielectric relaxation (DR) [23], terahertz time-domain spectroscopy (THz-TDS) [139], nuclear magnetic resonance (NMR) [85, 97], optical Kerr-effect spectroscopy (OKE) [182] and femtosecond vibrational pump-probe spectroscopy (fs-IR) [109, 134, 157, 161]. Depending on how the observable is related to the angle between field and molecular dipole, these techniques are sensitive to the first or second order dipole correlation function [20]. DR and THz-TDS measurements probe the decay of

\[ C^{(1)}(t) = \langle P^{(1)}[\vec{M}(0) \cdot \vec{M}(t)] \rangle \propto e^{-t/\tau_D}, \]  

(5.1)

with \(P^{(1)}[x]\) the first order Legendre polynomial in \(x\), \(M(t)\) the total dipole moment of the system at time \(t\) and \(\tau_D\) the Debye relaxation time. The brackets \(\langle \ldots \rangle\) denote averaging of equilibrium initial conditions for the system, including angular displacement. The *macroscopic* Debye time \(\tau_D\) is related to the *microscopic* first order molecular reorientation time \(\tau_r^{(1)}\). Fs-IR, NMR and OKE probe the decay of

\[ C^{(2)}(t) = \langle P^{(2)}[\vec{\mu}_i(0) \cdot \vec{\mu}_i(t)] \rangle \propto e^{-t/\tau_r^{(2)}}, \]  

(5.2)

where \(P^{(2)}[x]\) is the second order Legendre polynomial in \(x\), \(\vec{\mu}_i(t)\) is the dipole moment of the \(i\)th molecule at time \(t\) and \(\tau_r^{(2)}\) denotes the second order reorientation time.

We use polarization-resolved femtosecond mid-IR vibrational pump-probe spectroscopy (fs-IR) to measure the second order orientational relaxation time
of HDO molecules in liquid H$_2$O solvent at temperatures from 1 to 70 °C. We compare our results for $\tau_{r}^{(2)}$ with literature values of $\tau_{D}$ from THz-TDS measurements [139] for H$_2$O for a similar temperature range. From this comparison we obtain the ratio between the macroscopic Debye time and the microscopic first order reorientation time. This ratio is a measure for the amount of dipole-dipole correlation between different water molecules and local field effects.

5.2 Experimental

We measure the decay of the anisotropy of the OD-stretch vibration of HDO dissolved in H$_2$O with polarization-resolved pump-probe spectroscopy. This technique uses two ultrafast infrared pulses (duration <150 fs), where the first (pump) pulse excites the OD-stretch vibration of a subset of HDO molecules. Mainly OD groups that are aligned in the same direction as the polarization of the pump pulse are excited. After a variable delay, a second (probe) pulse measures the number of excited OD groups. This is done for probe polarization parallel with respect to the pump polarization and probe polarization perpendicular to the pump polarization. The normalized difference between the parallel and perpendicular signal is the anisotropy parameter, whose time dependence reflects the orientational decay of the vibrationally tagged water molecules.

The fs-IR setup (see Chapter 3, Fig. 3.5) that is used for measurements of molecular reorientation dynamics employs a commercial Ti:sapphire regenerative amplified laser system (Spectra-Physics Hurricane) that delivers 800 nm pulses with a duration of ~110 fs with an energy of 1 mJ at a rate of 1 kHz. Part of this light is used to pump a white-light seeded optical parametric amplifier (OPA) based on a $\beta$-barium borate (BBO) crystal. The idler signal output from the OPA, with a wavelength of 2 $\mu$m, is frequency doubled in a second BBO crystal to 1 $\mu$m and then difference-frequency mixed with the remaining 800 nm light in a potassium niobate crystal (KNB). This produces ~5 $\mu$J of 4 $\mu$m (2500 cm$^{-1}$, resonant with the OD-stretch vibration) light with a pulse duration of ~150 fs.

The pump-probe experiment is conducted by sending part of the 4 $\mu$m light into the pump branch and part into the probe branch of the set-up. Both pump and probe pulses are focused onto the same spot in the sample. Every other pump pulse is blocked by a 500 Hz chopper, so that every consecutive probe pulse either experiences an excited or a non-excited sample. The difference between these consecutive signals gives the pump-induced change in absorption of the sample $\Delta\alpha$. A reference pulse that is focused on a different spot on the sample allows compensation for fluctuations in the probe intensity. The absorption of the probe and reference pulses is measured with a 2×32 liquid-nitrogen cooled mercury-cadmium-telluride (MCT) array spectrometer.
(Infrared Associates), resulting in $\Delta \alpha(\nu)$. A delay stage that controls the relative delay between pump and probe pulse is used to monitor the dynamics of the pump-induced change in absorption $\Delta \alpha(\nu, t)$, where $t$ is the pump-probe delay time.

To measure reorientation dynamics, a $\lambda/2$-plate is placed in the pump path in combination with a motor-controlled polarizer in the probe path after the sample. This makes it possible to detect the induced absorption for a probe polarization parallel to the pump polarization ($\Delta \alpha_\parallel$) and the signal measured with a probe polarization perpendicular to the pump ($\Delta \alpha_\perp$). We use $\Delta \alpha_\parallel$ and $\Delta \alpha_\perp$ to construct the isotropic signal, which is independent of reorientation: $\Delta \alpha_{\text{iso}} = \frac{1}{3}(\Delta \alpha_\parallel + 2\Delta \alpha_\perp)$. We also construct the anisotropic signal or anisotropy, which is independent of vibrational energy relaxation: $R = (\Delta \alpha_\parallel - \Delta \alpha_\perp)/3\Delta \alpha_{\text{iso}}$. $R(t)$, where $t$ is time, is proportional to the second order orientational correlation function $R(t) = \frac{2}{5}C^{(2)}(t)$. The exponential decay rate of $R(t)$ gives the second order reorientation time $\tau_r^{(2)}$ (see also Section 2.3).

The sample is a solution of 8% HDO in H$_2$O solvent (4% D$_2$O in H$_2$O). We use an isotopically diluted sample to avoid the decay of the anisotropy as a result of Förster energy transfer between the stretch vibrations, which quickly randomizes the orientation ($<100$ fs [183]). The study of the anisotropy of the OD vibration of HDO:H$_2$O has the advantage over the study of the OH vibration of HDO:D$_2$O that the vibrational relaxation of the OD vibration is slower (1.8 ps [75]) than that of the OH vibration (750 fs, [185]). The anisotropy dynamics can thus be measured over a longer time interval for the OD vibration than for the OH vibration. A shorter lifetime would introduce more noise to the anisotropic signal at a shorter pump-probe delay time. The sample is placed between CaF$_2$ windows that are separated by a 25 $\mu$m spacer. The sample cell is mounted in a temperature controlled sample holder with a Peltier element that allows cooling and heating.

### 5.3 Results and discussion

#### 5.3.1 Isotropic signal

To obtain the anisotropy dynamics of the excitation, the measured data $\Delta \alpha_\parallel$ and $\Delta \alpha_\perp$ have to be corrected for the time-dependent thermalization signal, as described in detail in Section 4.2.1. The time dynamics of this contribution to the signal can be obtained from a detailed investigation of the isotropic signal. In Fig. 5.2, the isotropic pump-induced absorption spectrum $\Delta \alpha_{\text{iso}}(\nu, t)$ is shown for a number of pump-probe delay times for temperatures of 10 °C (A) and 60 °C (B). The dip centered at $\sim$2500 cm$^{-1}$ is due to the bleach of the 0 $\rightarrow$ 1 transition of the OD-stretch vibration and stimulated emission from the first excited state. All data are modeled with the cascading energy relaxation
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model as described in Section 4.2.1 and Ref. [134]. In this model, the energy from the OD-stretch vibration is transferred through an intermediate state (presumably a bending mode) to a thermal end level (lower energy modes). The model contains two global fit parameters: $\tau_1$ (first excited state OD stretch $\rightarrow$ intermediate state) and $\tau_2$ (intermediate state $\rightarrow$ thermal end state). A least square fit is conducted for the whole spectrum at each delay time to find the two timescales. The fits to the data using this model are shown in Fig. 5.2 (solid lines). The quality of the fits is evident and the same over the entire temperature range, indicating that the vibrational relaxation mechanism is temperature-independent.

![Figure 5.2](image)

**Figure 5.2.** Pump-induced absorption spectrum $\Delta \alpha(\nu, t)$ at different delay times (0.5, 1, 2, 4 and 100 ps) for 10 °C (A) and 60 °C (B). The solid lines are fits to the model. A broadening is observed at higher temperature in accordance with linear absorption spectra.

The fit parameters, $\tau_1$ and $\tau_2$, are determined for all temperatures. In Fig. 5.3 the values of these parameters are presented as a function of temperature. The value of $\tau_1$ increases for increasing temperature, an effect that has also been observed for pure liquid water [95] and HDO in D$_2$O [185]. The slowing down of vibrational energy relaxation in pure H$_2$O and in HDO:D$_2$O with temperature is likely due to the decrease of the spectral overlap between the overtone of the bending mode and the excited stretch mode for increasing temperatures [87]. The decrease in spectral overlap is mainly caused by a blue shift of the stretch vibration for higher temperatures, which is in turn the result of a decrease in hydrogen bond strength [116]. For the OD-stretch vibration of HDO in H$_2$O, a similar blue shift of the stretch frequency occurs [37]. In the case of HDO:H$_2$O vibrational energy relaxation will follow a different relaxation path, since the overtone of the bending mode has a higher frequency than the OD stretch. The relaxation path for HDO:H$_2$O likely involves relaxation to the fundamental bend mode and additional excitation of lower energy modes, such as librations or hydrogen-bond stretching [39, 134]. The shift to higher frequencies of
the OD-stretch vibration with increasing temperature increases the energy gap to the bending mode, which likely forms the origin of the observed increase of \( \tau_1 \).

After the relaxation is complete, the energy of the pump pulse thermalizes, leading to an increase of the sample temperature by about 1 \(^\circ\)C. The spectrum observed at large delays (see Fig. 5.2 at a pump-probe delay time of 100 ps) represents the difference of the absorption at this elevated temperature and the absorption at the initial temperature (no pump excitation). We have measured the linear absorption spectra for a wide range of temperatures and verified that the frequency dependence of the thermal end level is in correspondence with the difference in the linear spectra of the elevated and initial temperature (see Fig. 5.4).

![Graph showing the values for \( \tau_1 \) and \( \tau_2 \) that were found using the fitting procedure (error bars represent 95 % confidence intervals). Upon increasing the temperature, \( \tau_1 \) increases, whereas \( \tau_2 \) decreases.](image)

The timescale \( \tau_2 \) represents the time constant of the relaxation of the intermediate state to low energy modes. In Fig. 5.3 it can be seen that \( \tau_2 \) becomes shorter for increasing temperature, which implies that there is an increased coupling of the intermediate level to lower frequency modes with increased temperature [115].

### 5.3.2 Anisotropic signal

In Fig. 5.5, the anisotropic decay data are shown for six different temperatures (5, 15, 30, 40, 50 and 70 \(^\circ\)C). The signal for each temperature is averaged
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![Graph](image)

**Figure 5.4.** The difference between linear spectra taken at temperature $T + 4 ^\circ C$ and linear spectra at temperature $T$ for $T$ between 1 and 61 °C. We estimated that our pump excitation dumps an amount of energy in the system to increase the temperature by about 1 °C. The differential spectrum from our pump-probe measurements is therefore in good quantitative agreement with the results from the linear spectra at different temperatures.

between 2475 and 2525 cm$^{-1}$. Clearly the anisotropy decays faster with increasing temperature. The anisotropy decays are fit to a mono-exponential function, resulting in a reorientation time $\tau_r^{(2)}$ that decreases from 4.8±0.3 ps at 1 °C to 2.6±0.1 ps at room temperature to 0.97±0.05 ps at 70 °C. Here, we do not take into account the orientational dynamics that occur in the first 200 fs (Förster transfer and librational motion). The observation of a decreasing orientational relaxation time for an increasing temperature agrees well with earlier observations using DR [23], THz-TDS [139] and NMR [85, 97] (see Fig. 5.6).

The observed speedup by a factor of 5 in the temperature range from 1 to 70 °C thus indicates a strong increase of the hydrogen-bond dynamics. This speedup can be explained from the overall weakening of the hydrogen bonds.

We compare our (second order, microscopic) fs-IR reorientation data with (first order, macroscopic) THz-TDS measurements for H$_2$O by Rønne and Keiding [139]. In an ideal first order correlation experiment one would measure the first order molecular correlation function $C_{i,j}^{(1)}(t) = \langle P^{(1)}[\vec{\mu}_i(0) \cdot \vec{\mu}_j(t)] \rangle$. However since THz-TDS measures the correlation function of the total dipole moment of the system $\vec{M}$, additional cross-correlation terms show up: $C_{i,j}^{(1)}(t) = \langle P^{(1)}[\vec{\mu}_i(0) \cdot \vec{\mu}_j(t)] \rangle$ (see also Eq. 5.1), where $i$ and $j$ represent different molecules. Due to these cross-correlations, (THz) dielectric relaxation measurements probe
Figure 5.5. The decay of the anisotropy vs. pump-probe delay time for different temperatures (5, 15, 30, 40, 50 and 70 °C), showing a clear decrease in reorientation time for higher temperature. The lines are mono-exponential fits to the data and yield the second order reorientation time $\tau_r^{(2)}(T)$.

Figure 5.6. The reorientation time as a function of temperature, as measured with fs-IR, THz-TDS (from Ref. [139]) and NMR (from Ref. [97]).

the macroscopic $\tau_D$ instead of the microscopic $\tau_r^{(1)}$. The amount of dipole-dipole correlation determines the ratio between $\tau_D$ and $\tau_r^{(1)}$. This ratio is furthermore determined by local field effects: The microscopic electric field that a water molecule experiences might be different from the applied macroscopic electric field. We use the following equation to extract the ratio
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\[ \kappa = \frac{\tau_{r}^{(1)}}{\tau_{D}} = \frac{\tau_{r}^{(1)}}{\tau_{r}^{(2)}} \cdot \frac{\tau_{r}^{(2)}}{\tau_{D}}. \]  

(5.3)

Here we use our experimental data for \( \tau_{r}^{(2)} \) and literature data for \( \tau_{D} \) from Ref. [139]. The ratio \( \tau_{r}^{(1)}/\tau_{r}^{(2)} \) is known from literature and has a value ranging from 2.5 - assuming reorientation behavior according to the jump model - to 3.0 - assuming diffusive reorientation [81]. The results are shown in Fig. 5.7 and give experimental evidence that the contribution of cross-correlation terms and local field effects is not very strong in neat water. We find a value of \( \kappa = 0.74 – 0.94 \), where the former represents the case of large-angular jump reorientation and the latter the case of diffusive reorientation. These values include a 3% uncertainty contribution that has been estimated from our experimental data. Theory and simulation have resulted in similar values of \( \kappa \approx 0.9 \) [20, 177] and \( \sim 0.7 \) [48], but also smaller values have been found such as 0.5 [83] or \( \sim 0.125 \) [6].

Many physical properties of water show an anomalous temperature dependence, examples of which are the density, viscosity and specific heat. In Fig. 5.7, the ratio \( \kappa = \tau_{r}^{(1)}/\tau_{D} \) is determined for the whole temperature range. It can be seen that the ratio is not temperature-dependent. We further observe that the ratio, where diffusive reorientation is assumed, and the ratio, where large-angular jump reorientation is assumed, are well-separated. This is a strong indication that the reorientation mechanism is not temperature-dependent, in accordance with recent simulation results [83]. It also confirms that the decay time of the correlation function as measured by fs-IR spectroscopy corresponds to the same collective reorientation process as is probed by (THz) dielectric relaxation measurements.

5.4 Conclusion

We used polarization-resolved femtosecond mid-IR pump-probe spectroscopy to measure the second order reorientation time of HDO molecules in liquid H\(_2\)O over a temperature range between 1 and 70 °C. In the isotropic (reorientation-free) data we see an increase of the relaxation time constant \( \tau_{1} \) and a decrease in the thermalization time constant \( \tau_{2} \). The anisotropic (relaxation-free) data show a fivefold decrease in reorientation time between 1 and 70 °C.

We compare the second order reorientation time \( \tau_{r}^{(2)} \) with THz time-domain spectroscopy measurements of \( \tau_{D} \) from Ref. [139]. These time constants are associated with the same collective reorientation process of hydrogen-bonded water molecules. From this comparison, we find that the ratio \( \tau_{r}^{(2)}/\tau_{D} \) does not depend on temperature, which indicates that the reorientation mechanism does not change with temperature. The ratio \( \kappa = \tau_{r}^{(1)}/\tau_{D} \) lies between 0.74 and
Figure 5.7. The temperature dependence of the ratio $\tau_\text{D}/\tau_\text{r}^{(1)}$, assuming large-angular jump reorientation.

0.94, which points towards a fairly weak effect of the dipole-dipole correlations of water molecules and local field effects on the Debye relaxation time $\tau_\text{D}$ in neat water.