

Reorientation of HDO in liquid H₂O at different temperatures: comparison of first and second order correlation functions

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We study the temperature dependence of the molecular reorientation of HDO molecules in H₂O 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 ± 0.3 ps at 1 °C to 0.97 ± 0.05 ps at 70 °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 Debye reorientation time and the first order single molecule reorientation time.

I. 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} s, ps) timescale. The reorientation of liquid water involves two distinct processes. The first process is formed by the ultrafast librational motions of the OH groups that keep the hydrogen bonds intact [1, 2]. This process occurs on an ultrafast timescale (< 200 fs [1, 3]) and leads to a partial ($\sim 20\%$) orientational scrambling. The second process is formed by the complete reorientation of the water molecules involving the breaking and reformation of hydrogen bonds. Numerical simulations showed that reorientation of water molecules occurs in large-amplitude angular jumps. This jump model differs from the previously commonly accepted picture of subsequent small-amplitude angular rearrangements, known as the diffusion model [4].

Different experimental techniques have been employed to measure reorientation times of water molecules, most notably dielectric relaxation (DR) [5], Terahertz time domain spectroscopy (THz-TDS) [6], nuclear magnetic resonance (NMR) [7, 8], optical Kerr-effect spectroscopy (OKE) [9] and femtosecond vibrational pump-probe spectroscopy (fs-IR) [3, 10–12]. 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 [13]. DR and THz-TDS measurements probe the decay of

$$C^{(1)}(t) = \langle P_1[\vec{M}(0) \cdot \vec{M}(t)] \rangle \propto e^{-t/\tau_D} \quad , \quad (1)$$

with $P_1[x]$ the first order Legendre polynomial in x , $M(t)$ the total dipole moment of the system at time t and

τ_D the Debye relaxation time. The brackets $\langle \dots \rangle$ denote averaging of equilibrium initial conditions for the system, including angular displacement. The macroscopic Debye time τ_D is related to the first order molecular reorientation time $\tau_r^{(1)}$. Fs-IR, NMR and OKE probe the decay of

$$C^{(2)}(t) = \langle P_2[\vec{\mu}_i(0) \cdot \vec{\mu}_i(t)] \rangle \propto e^{-t/\tau_r^{(2)}} \quad , \quad (2)$$

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 H₂O solvent at temperatures from 1 to 70 °C. We compare our results for $\tau_r^{(2)}$ with literature values of τ_D from THz-TDS measurements [6] for H₂O 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 coupling between different water molecules.

II. EXPERIMENTAL

We measure the dynamics of the anisotropy of the OD stretch vibration of HDO dissolved in H₂O with polarization-resolved pump-probe spectroscopy. The fs-IR setup 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 ~ 100 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 β -barium borate (BBO) crystal. The idler signal output from the OPA, with a wavelength of 2 μm ,

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is frequency doubled in a second BBO crystal to 1 μm and then difference-frequency mixed with the remaining 800 nm light in a potassium niobate crystal (KNB). This produces $\sim 5 \mu\text{J}$ of 4 μm (2500 cm^{-1} , resonant with the OD stretch vibration) light with a pulse duration of $\sim 150 \text{ fs}$.

The pump-probe experiment is conducted by sending part of the 4 μm 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 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 probe intensity. Absorption of probe pulse and reference pulse is measured with a 2×32 liquid-nitrogen cooled mercury-cadmium-telluride (MCT) array spectrometer, resulting in $\Delta\alpha(\omega)$. 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 $\Delta\alpha(\omega, t)$, 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: $\Delta\alpha_{iso} = \frac{1}{3}(\Delta\alpha_{\parallel} + 2\Delta\alpha_{\perp})$. We also construct the anisotropic signal, which is independent of vibrational energy relaxation: $R = (\Delta\alpha_{\parallel} - \Delta\alpha_{\perp})/3\Delta\alpha_{iso}$. $R(t)$, where t is again the pump-probe delay 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 $\tau_r^{(2)}$.

The sample is a solution of 8% HDO in H_2O solvent (4% D_2O in H_2O). 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 ($< 100 \text{ fs}$ [14]). The study of the anisotropy of the OD vibration of HDO: H_2O has the advantage over the study of the OH vibration of HDO: D_2O that the vibrational relaxation of the OD vibration is slower (1.8 ps [15]) than that of the OH vibration (750 fs, [16]). As the anisotropy signal is inversely proportional to the isotropic signal, 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 make the anisotropic

signal diverge at a shorter pump-probe delay time. Since we fit the anisotropic signal to an exponentially decaying function to extract the reorientation time, we need a longer lifetime in order to make a reliable fit. The sample is placed between CaF_2 windows that are separated by a 25 μm spacer. The sample cell is mounted in a temperature controlled sample holder with a Peltier element that allows cooling and heating.

III. RESULTS AND DISCUSSION

A. 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. The time dynamics of this contribution to the signal can be obtained from a detailed investigation of the isotropic signal. In figure 1, the isotropic pump-induced absorption spectrum $\Delta\alpha_{iso}(\omega, t)$ is shown for a number of pump-probe delay times for temperatures of 10 $^{\circ}\text{C}$ (A) and 60 $^{\circ}\text{C}$ (B). The dip centered at $\sim 2500 \text{ cm}^{-1}$ 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 energy relaxation model as in ref [10]. 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 main fit parameters: τ_1 (first excited state OD stretch \rightarrow intermediate state) and τ^* (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 that constitute the best fit. The fits to the data using this model are shown in figure 1 (solid lines). The quality of the fits is evident and the same over the entire temperature range, indicating that the relaxation mechanism is temperature-independent.

The fit parameters, τ_1 and τ^* , are determined for all temperatures. In figure 2 the values of these parameters are presented as a function of temperature. The value of τ_1 increases for increasing temperature, which is comparable to the case of pure liquid water [17] and the case of HDO in D_2O [16]. The slowing down of vibrational energy relaxation in pure H_2O and in HDO: D_2O 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 [18]. The decrease in spectral overlap is mainly caused by a blue shift of the stretch vibration for higher temperatures, which is the result of a decrease in hydrogen bond strength [19]. For the OD stretch vibration of HDO in H_2O , a similar blue shift of the stretch frequency occurs [20]. In the case of HDO: H_2O vibrational energy relaxation will follow a different relaxation path, since the overtone

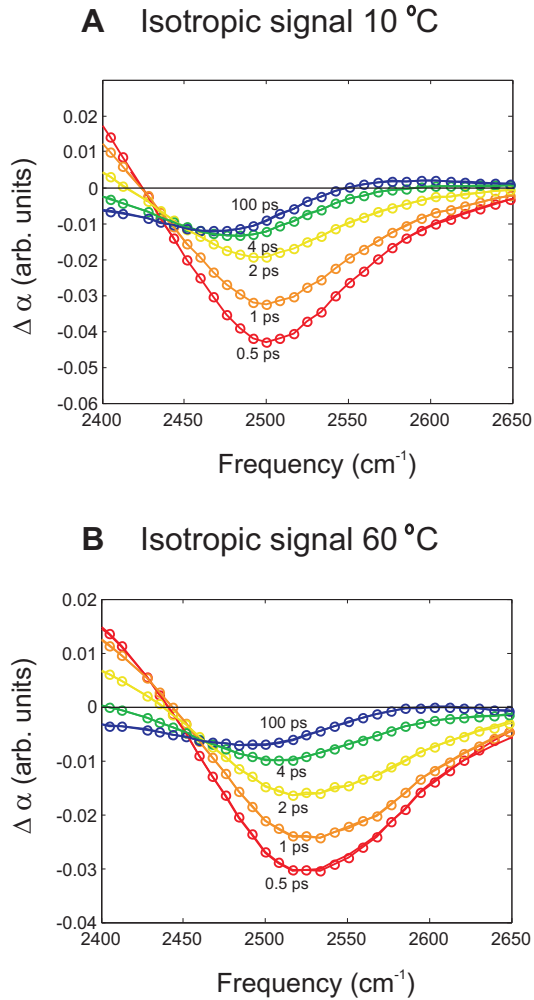


FIG. 1: Pump-induced absorption spectrum $\Delta\alpha(\omega, t)$ at different delay times (0.5, 1, 2, 4 and 100 ps) for 10 °C (A) and 60 °C (B). The solid lines are fits to the model. A broadening is observed at higher temperature in accordance with linear spectra.

of the bending mode has a higher frequency than the OD stretch. The relaxation path for HDO:H₂O likely involves relaxation to the fundamental bend mode and additional excitation of lower energy modes, such as librations or hydrogen bond stretching [10, 21]. 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 τ_1 .

After the relaxation is complete, the energy of the pump pulse thermalizes, leading to an increase of the sample temperature by a few Kelvin. The spectrum observed at large delays (see Figure 1 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. The timescale τ^* indicates how fast low energy modes are excited by the relaxation of the intermediate level. In figure 2 it can be seen that τ^* becomes faster for increasing temperature. This effect shows that there is an increased coupling of the intermediate level to lower frequency modes with increased temperature [22].

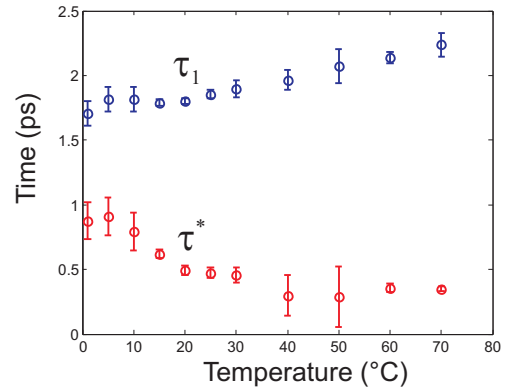


FIG. 2: The values for τ_1 and τ^* that were found using the fitting procedure (error bars represent 95 % confidence intervals). With temperature τ_1 increases, whereas τ^* decreases.

B. Anisotropic signal

In figure 3, the anisotropic decay data are shown for six different temperatures (5, 15, 30, 40, 50 and 70 °C). The signal for each temperature is averaged between 2475 and 2525 cm⁻¹. Clearly the anisotropy decays faster with increasing temperature. The anisotropy decays are fitted 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 0.97 ± 0.05 ps at 70 °C. This faster orientational relaxation for higher temperatures agrees well with earlier observations using DR [5], THz-TDS [6], NMR [7, 8] and OKE [9].

Recently, the temperature dependence of the librational contribution to the reorientation of liquid water was investigated [3]. It was found that this reorientation contribution depends on frequency, and that this frequency dependence increases with temperature [3]. The reorientation of liquid water on the longer time scale results from the global reorganization of the hydrogen-bond network, and involves the transient breaking and reformation of hydrogen bonds [4]. The observed acceleration by a factor of 5 in the temperature range from 1 to 70 °C thus indicates a strong acceleration of the hydrogen-bond dynamics. This acceleration can be

explained from the overall weakening of the hydrogen bonds.

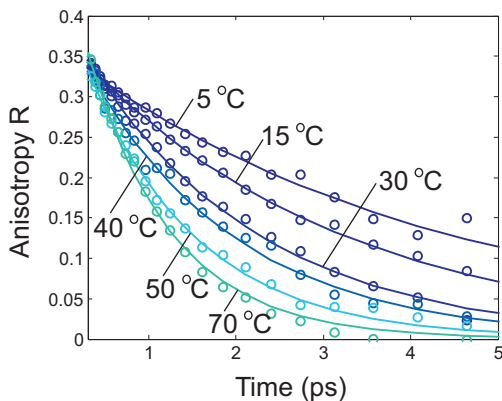


FIG. 3: The decay of the anisotropy vs. pump-probe delay time for different temperatures (5, 15, 30, 40, 50 and 70 °C), showing a clear decrease in reorientation time for higher temperature. The lines are mono-exponential fits to the data and yield $\tau_r^{(2)}(T)$.

We compare our (second order) fs-IR reorientation data with (first order) THz-TDS measurements for H₂O by Rønne and Keiding [6]. In an ideal first order correlation experiment one would measure the first order molecular correlation function $C_{i,i}^{(1)}(t) = \langle P_1[\vec{\mu}_i(0) \cdot \vec{\mu}_i(t)] \rangle$. However, due to dipole-dipole interaction 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. 1), where i and j represent different molecules. Due to these cross-correlations, first order correlation function measurements probe the macroscopic τ_D instead of the microscopic $\tau_r^{(1)}$. The amount of dipole-dipole coupling determines the ratio between τ_D and $\tau_r^{(1)}$. We use the following equation to extract this ratio:

$$\kappa = \frac{\tau_r^{(1)}}{\tau_D} = \frac{\tau_r^{(1)}}{\tau_r^{(2)}} \cdot \frac{\tau_r^{(2)}}{\tau_D}. \quad (3)$$

Here we use our experimental data for $\tau_r^{(2)}$ and literature data for τ_D from Ref. [6]. 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 [4]. The results are shown in figure 4 and give experimental evidence that the contribution of cross-correlation terms is not very strong. 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 $\kappa \sim 0.9$ [13, 23] and 0.7 [24], but also smaller values have been found such as 0.5 [25] or 0.125

[26].

Many physical properties of water show an anomalous temperature dependence, examples of which are the density, viscosity and specific heat. In figure 4, 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 [25].

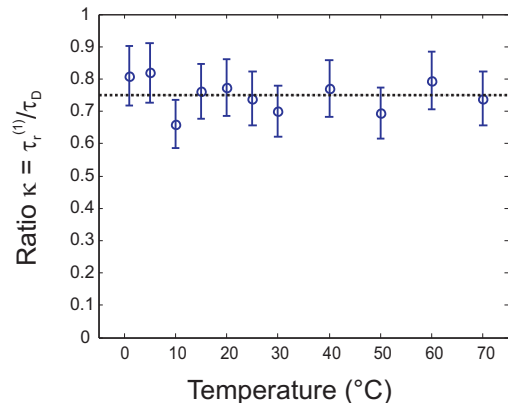


FIG. 4: The temperature dependence of the ratio $\tau_D/\tau_r^{(1)}$, assuming diffusive reorientation (blue) and large-angular jump reorientation (green).

IV. CONCLUSIONS

We have used polarization-resolved femtosecond mid-IR pump-probe spectroscopy to measure the second order reorientation time of HDO molecules in liquid H₂O over a temperature range between 1 and 70 °C. In the isotropic (reorientation-free) data we see an increase in relaxation time to the intermediate state and a decrease in thermalization time to the thermal end level. The anisotropic (relaxation-free) data shows a fivefold decrease in reorientation time between 1 and 70 °C.

We compare our results of the second order reorientation time $\tau_r^{(2)}$ with THz time domain spectroscopy measurements [6] of τ_D . From the comparison we find a ratio $\kappa = \tau_r^{(1)}/\tau_D$ between 0.74 and 0.94. This ratio points towards a fairly weak effect of dipole-dipole coupling between different water molecules on reorientation dynamics. From the temperature dependence of the ratio, we find a strong indication that the reorientation mechanism does not depend on temperature.

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- [1] C.J. Fecko et al., *J. Chem. Phys.* 122 (2005), 054506
- [2] D. Laage and J.T. Hynes, *Chem. Phys. Lett.* 433 (2006), 80
- [3] D.E. Moilanen et al., *Proc. Natl. Acad. Sci USA* 105 (2008), 5295
- [4] D. Laage and J.T. Hynes, *Science* 311 (2006), 832
- [5] R. Buchner, J. Barthel, J. Stauber, *Chem. Phys. Lett.* 306 (1999), 57
- [6] C. Rønne and S. R. Keiding, *J. Mol. Liq.* 101 (2002), 199
- [7] E. Lang and H.-D. Lüdemann, *J. Chem. Phys.* 67 (1977), 718
- [8] R. Ludwig, F. Weinhold and T.C. Farrar, *J. Chem. Phys.* 103, 6941 (1995)
- [9] K. Winkler et al., *J. Chem. Phys.* 113 (2000), 4674 (2000)
- [10] Y.L.A. Rezus and H.J. Bakker, *J. Chem. Phys.* 123 (2005), 114502
- [11] T. Steinel et al., *J. Phys. Chem. A* 108 (2004), 10957
- [12] H.S. Tan, I.R. Piletic and M.D. Fayer, *J. Chem. Phys.* 122 (2005), 174501
- [13] C.J.F. Böttcher, *Theory of*
- [14] S. Woutersen and H.J. Bakker, *Nature* 402 (1999), 507
- [15] M.F. Kropman et al., *J. Phys. Chem. A* 105 (2001), 4622
- [16] S. Woutersen et al., *Phys. Rev. Lett.* 81 (1998), 1106
- [17] A.J. Lock and H.J. Bakker, *J. Chem. Phys.* 117 (2002), 1708
- [18] C.P. Lawrence and J.L. Skinner, *J. Chem. Phys.* 119 (2003), 3840
- [19] A. Novak, *Struct. Bonding (Berlin)* 18 (1974), 177
- [20] S.A. Corcelli and J.L. Skinner, *J. Phys. Chem. A* 109 (2005), 6154
- [21] J.C. Deàk et al. *J. Phys. Chem. A*, 104 (2000), 4866
- [22] A. Nitzan and J. Jortner, *Mol. Phys.* 25 (1973), 713 *Electric Polarization; Elsevier (Amsterdam), Vol 2, 1978*
- [23] A. Wallqvist, B.J. Berne, *J. Phys. Chem.* 97 (1993), 13841
- [24] S.H. Glarum, *J. Chem. Phys.* 33, 1371 (1960)
- [25] D. Laage and J.T. Hynes, *J. Phys. Chem. B* 112, 14230 (2008)
- [26] B. Bagchi, *Chem. Rev.* 105 (2005), 3197
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