In aqueous solutions of amphiphiles the reorientation dynamics of a part of the water molecules is much slower than in bulk water. In chapter 10 we will show that the number of slower water molecules scales with the number of hydrophobic groups in the solution. Such a dependence strongly suggests that the slower water molecules are those that solvate the hydrophobic moieties of the amphiphile. In this chapter we investigate in the underlying mechanism of the retardation of water molecules in the hydrophobic solvation shell. We find that OD-groups around the methyl groups of tetramethylurea (TMU) have a lower rate of jumps. This effect is highly correlated with a component of extremely slow spectral diffusion in these solutions. These results are consistent with recent Raman MCR experiments in which it was found that the structure of the hydrogen-bond network around hydrophobic groups is more ordered. From these observations we conclude that reduced translational motions hinder the approach of a new hydrogen-bonding partner close to hydrophobic groups, a process that is essential for a successful jump to happen. We show that for increasing temperatures this effect rapidly disappears.
7.1 Introduction

The concepts of ‘hydrophobic interaction’ and ‘hydrophobic hydration’ have gained a lot of use in the past decades, but what is the hydrophobic effect? The use of the terms may be considered questionable, as hydrophobic groups are rather lacking direct interaction with solvating water molecules. Instead, the driving mechanism behind processes that are associated with the hydrophobic effect, like aggregation, is rather found in the hydrogen-bonding structure and dynamics around the hydrophobe.

Water consists of an extended network by forming on average almost four hydrogen-bonds per water molecule. To accommodate a small hydrophobic particle, this network is able to elastically bend to form a cavity. For larger particle sizes, bending the network is not sufficient anymore and hydrogen-bonds are broken, thereby forming an interface [92, 11]. The first process is entropic in nature and depends on the volume of the particle, while the second process is enthalpic and depends on the surface of the cavity. It is found that the transition between the two mechanisms takes place for particle sizes of about 1 nm [11]. The detailed balance between the free energy of a number of hydrated small hydrophobic molecules or one hydrated large aggregate determines whether aggregation is favored or not. Since this balance is partly enthalpic in nature, the aggregation effects are expected to depend on the temperature. Such a temperature dependence has indeed been found empirically for systems in which hydrophobic aggregation plays a role, like protein folding [93, 94, 95].

The remarkable change in heat capacity for aqueous solutions of amphiphiles previously lead Frank and Evans to propose the existence of highly structured water around hydrophobic groups, for which they coined the term ‘icebergs’ [96]. Although the iceberg model was proposed already in the fifties, evidence for such a strongly increased structure of water around hydrophobic groups was not found [97]. Only a recent Raman spectroscopy study found some structure enhancement in solutions of alcohols in water [98]. Contrasting to the lacking evidence for induced structure of water, compelling evidence exists by NMR [99, 100, 101, 102], femtosecond infrared spectroscopy [28, 17], dielectric relaxation spectroscopy [103, 17, 104], classical molecular dynamics (MD) simulations [105, 106, 107] and ab initio MD simulations [108] that the reorientation of water in solutions of amphiphiles is slower than in bulk water. The magnitude of the retardation and the extent of the effect is however not agreed upon.

In recent two-dimensional infrared (2D-IR) spectroscopy studies it was found that water molecules show very slow spectral dynamics around the hydrophobic groups of tert-butyl alcohol (TBA), trimethylamine-N-oxide (TMAO) and tetramethylurea (TMU) [109, 110]. The partial slowing down of the spectral diffusion was found to be highly correlated to the slower reorientation dynamics in these solutions [110]. This correlation suggests a common origin, and points to a strong hindrance of water in its evolution to a bifurcated hydrogen bond structure near hydrophobic groups. The hindrance can be explained by a distortion of the hydrogen-bond network by the presence of the hydrophobic molecular groups, allowing for less translational motions and jump reorientation events.
To investigate this proposition, we performed infrared pump-probe experiments on a concentrated solution of TMU in isotopically diluted water. By exciting the OD stretch vibration of a subset of HDO molecules that form very weak hydrogen-bonds, we are able to obtain information on the spectral diffusion and orientational dynamics of this subset. First we compare the spectral diffusion for both neat water and aqueous solutions of TMU, after which we consider the reorientation of water molecules in both solutions. Finally we explore the temperature dependence of water reorientation in the TMU solution. All results combined are consistently interpreted with a detailed molecular picture of reorientation dynamics in the hydrophobic solvation shell.

7.2 EXPERIMENTAL

The details of the experiments performed in this chapter are identical to those described in section 6.2 of the previous chapter. Instead of neat isotopically dilutated water, we used a solution of TMU in isotopically diluted water. TMU was purchased from Sigma Aldrich (99.9 % pure) and added to 8 % D₂O in H₂O to obtain a solution of 6 molal (mol/kg solvent) TMU.

7.3 RESULTS AND INTERPRETATION

7.3.1 ISOTROPIC RESULTS AND SPECTRAL DIFFUSION

Fig. 7.1A shows the transient spectra obtained after excitation of the 6 molal TMU solution by the narrow band pump, centered at 2650 cm⁻¹, at room temperature (295K). At short delay times \( t \), the bleach is blue-shifted from the central absorption of the OD stretch band. For increasing \( t \), the bleach undergoes complicated dynamics. First it shifts to lower frequencies while increasing in amplitude, later it decays again to a thermalized ground state. From close examination of the transient spectra obtained for the delay times 7 ps and 50 ps it can be seen that the amplitude at 2480 cm⁻¹ is becoming more negative again after 7 ps. This can only be explained if the excitation is not decaying immediately to the thermalized ground state but is somewhat delayed. This is fully in agreement with previous findings on the thermalization dynamics in similar systems [23, 22, 28] (see also section 4.2.2).

The thermalization contribution is subtracted in a procedure identical to what was described in the previous chapter and section 4.3. From the resulting thermalization-free transient spectra we determined the first moment \( M_1 \) as a measure of the spectral diffusion in the sample. The results are shown in Fig. 7.1B for the TMU solution (triangles) and for neat 16% HDO:H₂O (squares). A similar determination of \( M_1 \) was done for measurements with a spectrally broad excitation pulse centered around the OD-stretch band maximum of 2500 cm⁻¹ (Fig. 7.1B).

The \( M_1 \) curves for the broad-excitation pulse are nearly flat, positioned at \( \sim2530 \text{ cm}^{-1} \) for neat 16% HDO:H₂O and blue-shifted by only a few wavenum-
Figure 7.1. (A) The isotropic transient spectra for a number of pump-probe delay times. For short delay times the transient spectra mainly show a bleach at blue frequencies. The bleach subsequently shifts to the red and decays. For long delay times the transient spectrum is the thermal difference spectrum. Please note that the increase of amplitude of the transient spectra between 7 and 100 ps at 2480 cm$^{-1}$ is indicative for a delayed heat ingrowth as discussed in the text. (B) The first moment determined from the heat corrected transient spectra of the TMU solution and neat 16% HDO:H$_2$O (see chapter 6) at 295K. The open markers are the first moments obtained from measurements for which the pump spectrum was spectrally broad and centered around the maximum of the OD stretch absorption band (2500 cm$^{-1}$). For both solutions there is fast spectral diffusion for short delay times, but for TMU the diffusion is not complete. Subsequent decay occurs by a much slower process.

7.3.2 Anisotropy Decay of Water Around TMU

Fig. 7.2 shows delay curves of the transient absorption at two different probe frequencies probed parallel and perpendicular to the pump polarization. In the first picosecond the relative amplitude decay of the parallel signal probed at
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Figure 7.2. Delay traces at two probe-frequencies probed parallel and perpendicular to the pump polarization, obtained with a narrow band pump (center frequency 2650 cm\(^{-1}\)) for a 6 molal solution of TMU in 16% HDO:H\(_2\)O at room temperature. In the first picosecond the signals at 2650 cm\(^{-1}\) show a fast decay, while at 2500 cm\(^{-1}\) there is a fast rise. For long delay times both parallel and perpendicular signals assume a value that remains constant till at least 100 ps. This static transient signal is the thermal difference response due to sample heating after the vibrational relaxation. The difference between the parallel and perpendicular signals are a measure for the reorientation dynamics.

2650 cm\(^{-1}\) is much larger than that of the perpendicular signal at 2650 cm\(^{-1}\). This shows that a large part of the initial anisotropy decays within the first picosecond. The parallel and perpendicular signals probed at 2500 cm\(^{-1}\) are crossing a few hundred femtoseconds after excitation. From this delay time onwards the anisotropy measured at this frequency is thus increasing, reaching a maximum somewhere between 0.5 ps and 1.5 ps after which it decays again.

We calculate the anisotropy dynamics (using equation Eq. (4.18)) after subtraction of the thermal contribution of the raw parallel and perpendicular transient spectra. The results for the TMU solution and for neat 16% HDO:H\(_2\)O, probed at the \(\nu = 0 \rightarrow 1\) transition and at the \(\nu = 1 \rightarrow 2\) transition, are shown in Fig. 7.3 for a sample temperature of 295K. There are two main differences between the results of the two samples. Firstly, for the TMU solution there is a frequency dependence of the anisotropy that is persistent for longer delays. This is the case for probe frequencies in both the \(\nu = 0 \rightarrow 1\) and \(\nu = 1 \rightarrow 2\) region. Secondly, after a fast decay in the first picosecond, the dynamics in the TMU solution show a much slower decay for the remaining anisotropy. At 8 ps the anisotropy is still quite large, implying that a large amount of orientation remains. The amplitude of this long-delay part is different for various probe frequencies.

We first consider the persistent frequency dependence. We recall from the previous chapter that for neat 16% HDO:H\(_2\)O the anisotropy dynamics after
Figure 7.3. Anisotropy dynamics following narrow-band excitation at 2650 cm$^{-1}$, probed at 2490, 2500, 2520, 2560 and 2600 cm$^{-1}$ (red to blue curves) in the $\nu = 0 \rightarrow 1$ region (upper figures) and at 2100, 2150, 2200, 2250 and 2300 cm$^{-1}$ in the $\nu = 1 \rightarrow 2$ region (lower figures). The samples used were 6 molal TMU (panel A and C) and neat 16% HDO:H$_2$O (panel B and D). The frequency dependence of the anisotropy is persistent for the TMU solution, while for neat water spectral equilibration removes the frequency dependence after 1 ps. The solid lines are guides to the eye.

$\sim$1.5 ps is completely independent on the probe frequency due to spectral diffusion by translational motions in the liquid. The persistence of the frequency dependence in the TMU solution shown in Fig. 7.3 thus indicates that the spectral diffusion is not completed at 8 ps. As a result, the anisotropy at different frequencies (high in the blue wing, low in the red wing, following a 2650 cm$^{-1}$ excitation) does not completely average out for delays < 8 ps.

The observation of such a persistent frequency dependence of the anisotropy agrees with the spectral diffusion curves we obtained from the analysis of the first moments $M_1$ of the transient spectra (Fig. 7.1). From that analysis we found that in neat 16% HDO:H$_2$O spectral diffusion is completed after $\sim$2 ps, while in the TMU solution a very slow component exists that has not yet de-
Figure 7.4. (A) Thermalization dynamics in a solution of 6m TMU at different lab temperatures. The slow component that is present at room temperature disappears almost entirely at 343K. For comparison the thermalization dynamics in neat water at 295K is shown (black curve). In neat water, the thermalization dynamics does not depend much on temperature (see section 4.3). (B) Dynamics of the first moment in a solution of 6m TMU at 295K and 343K after excitation at 2500 cm$^{-1}$ and 2650 cm$^{-1}$. The difference in endlevel at 295 is indicative for a very slow spectral diffusion component. At 343K, this component has disappeared and spectral diffusion is complete after a few picoseconds.

cayed at 8 ps. We discussed two main mechanisms for spectral diffusion: Angular jumps to a stronger hydrogen-bond configuration and translational motion to smaller values of $R_{OO}$. Both mechanisms eventually lead to a complete equilibration of the hydrogen-bond strength distribution and thus decay of $M_1$. The observation of incomplete spectral diffusion at delay times between 2 and 8 ps therefore implies that both mechanisms are altered.

A subset of the OD oscillators in the TMU solution thus have both a low rate of jumping and slow translational motions. As a result, the anisotropy of this subset decays much slower, as we indeed observe for delay times $t > 2$ ps. At early delays ($t < 2$ ps) the dynamics is in fact significantly faster than those following a broad excitation. A likely explanation is that both the fast reorientation component and the fast relaxation of $M_1$ of the TMU solution in the first $\sim$2 ps is mainly associated with OD oscillators outside the hydrophobic hydration shell. This is analogous to the dynamics observed for neat 16% HDO:H$_2$O.

We performed the same experiment at elevated temperatures. At every temperature we performed an additional determination of the thermalization dynamics using the method from section 4.3. The results are shown in Fig. 7.4A. At low temperatures the thermalization happens on two very distinct timescales, but for increasing temperatures the slow component disappears. After removing the thermalization contribution from the data we determine the dynamics of the first moment $M_1$. Fig. 7.1B shows the results for $T=295K$ and $T=343K$ for a
Figure 7.5. (A) Similar figure as Fig. 7.3A for 6 molal TMU at a sample temperature of 328K. The slow decaying part of the anisotropy has a smaller amplitude. In contrast to the results obtained at 295K, no frequency dependence for long delay times is observed. (B) The anisotropy values at 2.5 ps delay time are shown as a function of probe frequency for different temperatures. The frequency dependence that is observed for a sample temperature of 295K completely disappears at higher sample temperatures. For comparison the same plot is shown for neat 16% HDO:H2O at 295K. The solid lines are fits of a straight line to the frequency region 2485–2530 cm\(^{-1}\) to quantify the spectral dependence of the anisotropy as a function of time.

pump spectrum centered at 2500 cm\(^{-1}\) and 2650 cm\(^{-1}\). At room temperature the spectral diffusion seems to have come almost to a halt at 6 ps, while at 343K spectral diffusion is completed after a few picoseconds.

The reorientation dynamics obtained for the TMU solution at 328K are shown in Fig. 7.5A. In analogy to what we found for neat water in chapter 6, the anisotropy probed at 328K decays faster than that probed at 295K. However, we find that upon increasing the temperature the dynamics in the TMU hydration shell accelerates much more dramatically than in neat water. This finding is in agreement with previous work [17]. Additionally, the slow component of the spectral diffusion becomes faster and the frequency dependence of the anisotropy disappears. After \(\sim 2\) ps the anisotropy values are completely independent on the probe frequency. The temperature dependence of this anisotropy dispersion is further illustrated in Fig. 7.5B. In this figure the value of the anisotropy at different probe frequencies is shown for four sample temperatures and a pump-probe delay time of 2.5 ps. We further quantify the anisotropy dispersion by fitting a straight line to the anisotropy in the frequency domain 2485–2530 cm\(^{-1}\) at every delay time (solid lines in Fig. 7.5B). The slope of the fits are shown as a function of delay time in Fig. 7.6A for a number of temperatures. The non-vanishing endlevels at low temperature are indicative for the persistent frequency dependence of the anisotropy we found in Fig. 7.3. The values of the endlevels are shown in Fig. 7.6B for different temperatures. For comparison we also plotted the difference in endlevel of the dynamics of the first moment (see
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Figure 7.6. (A) Slope of a straight line fitted to the frequency dependent anisotropy (see Fig. 7.5B) as a function of delay time for different temperatures. For low temperatures the anisotropy is not equilibrated at 5 ps, resulting in the persistent slope. The solid lines are guides to the eye. The endlevels are a measure of inhomogeneity at long delay times and are plotted as a function of temperature in panel (B). For comparison the difference in endlevel of the first moment is plotted, which is a measure for incomplete spectral diffusion (see Fig. 7.4B). Both parameters are correlated and vanish for increasing temperatures.

In Fig. 7.7 we compare the anisotropy decay after excitation with a spectrally broad pump with the anisotropy decay after excitation with a spectrally narrow pump at 2650 cm\(^{-1}\) at a probe frequency of 2600 cm\(^{-1}\). The anisotropy decay following the narrow-band blue excitation is faster in the first picosecond than the anisotropy decay following the spectrally broad excitation: The anisotropy after 6 ps is independent of the excitation pulse used for this probe frequency. This loss of memory of excitation is present for all measured temperatures. The slow component represents the dynamics in the TMU solvation shell, in which spectral diffusion is very slow. Hence, as long as these oscillators are excited, irrespective by a spectrally broad pump or a narrow blue pump, these dynamics will be seen. This is a different situation from neat water, where spectral diffusion does play a role and a narrow blue excitation effectively speeds up the dynamics probed at 2600 cm\(^{-1}\). For the TMU solution, only the dynamics in the first few picoseconds becomes faster after a narrow blue excitation. These dynamics thus likely mainly represent OD oscillators outside the TMU solvation shell for which spectral diffusion is still fast and plays a dominant role in the dynamics.
Figure 7.7. Comparison of the anisotropy dynamics obtained with a spectrally narrow pump centered around 2650 cm$^{-1}$ (solid lines) and a spectrally broad pump centered around 2500 cm$^{-1}$ (dotted lines) at 295K and 343K. The probe frequency is 2600 cm$^{-1}$. Similar to what was found for neat 16% HDO:H$_2$O in chapter 6, at short delay times a faster anisotropy decay is observed after a spectrally narrow blue excitation. The amplitude of the slow reorientation process, however, is conserved: for a probe frequency of 2600 cm$^{-1}$ the anisotropy does not depend on the type of excitation anymore at 8 ps.

7.4 DISCUSSION

We find that spectral diffusion of the OD stretch vibration in a 6 molal solution of TMU in 16% HDO:H$_2$O has a very slow component that is not present in neat 16% HDO:H$_2$O (Fig. 7.1). This finding is in agreement with previous 2D-IR measurements on a similar system [109, 110]. Here we find that spectral diffusion also comes to an almost complete halt on the picosecond timescale of the experiment. Spectral diffusion can be due to excitation transfer and structural diffusion [43]. For the isotope dilution we used, the contribution of ( Förster) excitation transfer is small [26]. Others have proposed that slow spectral diffusion in aqueous solutions of amphiphiles determined by 2D-IR may be due to the different interaction strength of OD/OH groups with the hydrophilic group of the amphiphile and other water molecules [105, 106]. However, the number of OD/OH groups hydrogen-bonded to the carbonyl group of TMU is likely limited to only two or three, while previous studies found that as many as 12 OD groups per TMU molecule are affected [24, 17]. In addition, in solutions of urea water was found to be hardly affected at all [111], while this molecule has an identical carbonyl group.

The slower spectral diffusion therefore likely arises from slower structural diffusion and a decreased rate of jump reorientation events near the hydrophobic part of the molecule. Recent work using Raman spectroscopy revealed that water around the hydrophobic groups of tert-butyl alcohol is more structured [98]. The methyl groups of TMU are small enough to reside in cavities in the hydrogen-bond network without the need of breaking hydrogen-bonds [11]. The folding of the network around TMU likely leads to a stiffening of the hydrogen-bond network that causes structural diffusion to be severely hindered.
The slower reorientation dynamics is closely related to the slow component of the spectral diffusion, as is also demonstrated in Fig. 7.6. Water dynamics is dominated by the process of hydrogen-bond switching according to the jump-mechanism of reorientation [2]. The rate limiting step for jump reorientation events is the structural reorganization of the hydrogen-bond network to allow the approach of the new hydrogen-bonding partner [89]. Slower structural diffusion thus inevitably also leads to a decreased rate of jump reorientation events and hence slower dynamics.

The reorientation dynamics probed in the blue wing contains contributions of both OD oscillators outside the hydrophobic hydration shell and OD oscillators that are strongly affected by TMU. In comparison to anisotropy measurements with a broad excitation spectrum, the anisotropy at the blue shoulder is initially decaying much faster (Fig. 7.7). This is fully consistent with the interpretation above of the OD groups outside the hydrophobic hydration shell that jump to the red side of the spectrum and diffuse back to the blue side, similar to what we observed for neat water (Fig. 7.3). Structural diffusion is very slow for the OD oscillators that are affected by TMU and for these OD oscillators jumps occur at a much lower rate than in bulk water [108]. The anisotropy decay of these oscillators is therefore much slower, and is in the absence of spectral diffusion mainly probed in the blue wing.

In the case of excitation at 2650 cm\(^{-1}\), the anisotropy measured at low frequencies represents almost exclusively the response from OD oscillators that, after blue excitation, underwent relatively rapid spectral diffusion. These oscillators are thus not so much influenced by TMU. These structurally diffused oscillators either experienced a jump event or migrated from the blue side of the spectrum to the red side by structural diffusion. The decay of the anisotropy in the red wing is very similar to that of OD groups in neat water (Fig. 7.3).

Spectral diffusion leads to a complete randomization of the initially excited subset, after which the reorientation dynamics is independent on the probe frequency. For neat 16\% HDO:H\(_2\)O this is indeed what we find (Fig. 7.3) and chapter 6 elaborated more extensively on this frequency dependence for short delay times. In contrast to the results for neat 16\% HDO:H\(_2\)O, we find that the anisotropy dynamics in a 6 molal solution of TMU after excitation by the narrow-band pump pulse strongly depends on the probe frequency. Previous anisotropy measurements on aqueous TMU solutions did not show any frequency dependence for this concentration of TMU [24], but in those experiments the OD absorption band was homogeneously excited by a broad band pump.

At the TMU concentration used in our experiments, it is valid to question whether or not all water molecules are in the vicinity of a TMU molecule and whether a bimodal model as described above is justified [112, 105, 107]. There are a number of points to be taken into consideration to answer this question. TMU is found to aggregate at concentrations below 6 molal and it is therefore likely that nanopools of water exist between clusters of TMU molecules [113, 17, 107]. Water reorientation and spectral diffusion in these nanopools are likely similar to bulk water. Secondly, even water molecules in close vicinity of a TMU
molecule may posses an OD group of which the dynamics is hardly affected by
the presence of TMU. This will be the case if the OD group hydrogen-bonds
to a water molecule outside the TMU hydration shell or to the hydrophilic
group of the TMU. Finally, recent ab initio calculations on TMU solution do
suggest that even at concentrations as high as 11 molal, the water hydrogen-
bond network percolates through regions of accumulating TMU molecules [114].
The average number of hydrogen-bonds per water molecule in a solution of 5.5
molal TMU was found to be 3.6, only marginally smaller than the coordination
number in pure water (3.7). The hydrogen-bond network is thus maintained to
a large extent at such high concentrations and likely contains regions where the
reorientation proceeds similar as in bulk water.

A large increase in reorientation time around TMU has also in previous
fs-IR and dielectric relaxation experiments been found for relatively low con-
centrations of TMU [17, 24]. This large increase has been disputed by classical
molecular dynamics (MD) simulations [105, 106]. These simulations find a very
modest retardation factor at low concentrations of 1.5 that was assigned to a
shielding effect: OD/OH groups in the hydration shell of a hydrophobic group
have less potential new hydrogen-bond partners, resulting in a lower frequency
of jumps [105]. In this picture there is no collective effect like an enhancement
of the hydrogen-bond structure around the hydrophobe. Simulations based on
ab initio calculations did show an enhanced structure and much slower dynam-
ics of water molecules in the TMU hydration shell [108]. It was found that the
spectral diffusion of water around a hydrophobe contains three timescales of
spectral diffusion: 70 fs, 1 ps and >10 ps [108]. The slower dynamics was as-
signed to a (five-fold) decreased rate of hydrogen-bond jumps that was related
to the overcoordination of water molecules [108].

The slowing down of the water dynamics around hydrophobic groups seems
therefore not only due to the local excluded volume of the hydrophobic moiety.
The hydrogen-bond network is probably more globally jammed by accommo-
dating the hydrophobic molecule. The hydrogen-bond rearrangements leading
to reorientation is a collective process that requires the reorganization of mul-
tiple molecules [115, 61, 68, 86, 82]. The filling of the network cavities by the
hydrophobic moieties leads to a strong slowing down of the structural reorgani-
zation (spectral diffusion) and thus of the rate of formation of hydrogen-bond
configurations that would enable a successful reorientational jump.

In agreement with previous work [116, 17] we find that the slow reorienta-
tion around TMU strongly accelerates upon increasing the temperature. This
speed up probably finds its origin in the structural relaxation that becomes
much faster at higher temperatures. All hydrogen-bonds become weaker and
the formation of a cavity accommodating the hydrophobic groups has a much
less restrictive effect on the hydrogen-bond network. The improved ability of
the hydrogen-bond network to restructure, results in an increased rate of jumps
for OD oscillators next to the hydrophobic groups and therefore a faster decay
and spectral equilibration of the anisotropy (Fig. 7.7 and Fig. 7.6). This inter-
pretation is corroborated by ab initio calculations, where it was found that the
slowest timescale of both spectral diffusion and reorientation dynamics becomes
increasingly less important with increasing temperature [108].

7.5 Conclusions

We studied the reorientation of OD groups in a 6 molal solution of TMU in isotopically diluted water (16% HDO:H$_2$O). We used two-color infrared pump-probe spectroscopy to excite the blue wing of the OD stretch vibration and probe the $\nu = 0 \rightarrow 1$ and $\nu = 1 \rightarrow 2$ regions of this band. By exciting only OD oscillators with a blue resonance frequency, we selected those oscillators that have a very weak hydrogen-bond. We found that the spectral diffusion in the TMU solution has a slow component with a time constant $> 10$ ps. In addition, the reorientation dynamics show a persistent dependence on the probe frequency and hence hydrogen-bond strength of the OD oscillators. These results point at the presence of a less dynamic hydrogen-bond network that folds itself around the hydrophobic groups of the TMU molecule. The decreased ability of the network to restructure leads to much slower spectral diffusion. As a consequence, OD groups that form this cavity have a low rate of forming hydrogen-bond structures that would allow for a reorientational jump. At higher temperatures, the enhanced structuring of the hydrogen-bond network around the hydrophobic groups vanishes, leading to a strong acceleration of the spectral diffusion and the reorientation dynamics.