Water in confinement: ultrafast dynamics of water in reverse micelles

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Chapter 4

Inhomogeneous dynamics in confined water nanodroplets

The effect of confinement on the dynamical properties of liquid water was studied by mid-infrared ultrafast pump-probe spectroscopy on HDO:D$_2$O in reverse micelles. By preparing water-containing reverse micelles of different well-defined sizes, we varied the degree of geometric confinement in water nanodroplets with radii ranging from 0.2 to 4.5 nm. We find that water molecules located near the interface confining the droplet exhibit slower vibrational energy relaxation and have a different spectral absorption than those located in the droplet core. As a result, we can measure the orientational dynamics of these different types of water with high selectivity. We observe that the water molecules in the core show similar orientational dynamics as bulk water and that the water layer solvating the interface is highly immobile.

4.1 Introduction

There are many examples in the fields of biology [95, 96], geochemistry [116], tribology [16] and nanofluidics [102], where water molecules are not present as a bulk liquid, but in small numbers and confined geometries. The presence of an interface is known to influence the structure and dynamics of liquid water. By steady-state surface-sensitive techniques like x-ray diffraction it was shown that near a surface ordering of water molecules into layers occurs [28, 103, 124], which extends several molecular diameters into the liquid. In the case of small water droplets the confinement is three-dimensional, and the overall structure and dynamics of the water may be affected.

A suitable model system for studying confined water nanodroplets are reverse micelles [34, 79]. A solution of nanometre-sized droplets forms when preparing an emulsion of water in an apolar solvent by addition of a surfactant. We used the anionic lipid surfactant AOT (Sodium bis(2-ethylhexyl) sulfosuccinate, see Fig. 3.1), which is known to form micelles that are reasonably monodisperse (~15%) [1, 112]. The size of the water droplets can be easily
varied by changing the molar water-to-AOT ratio, conventionally denoted by the parameter $w_0 = [H_2O]/[AOT]$.

An important question is whether micelle contained water can be regarded as a two-component system where the water molecules at the micellar surface show different properties from water molecules in the core of the micelles. In previous studies two-component models have been used successfully to describe both the linear absorption [49,51] and the vibrational energy relaxation [30,99] of confined water. As for the structural hydrogen bond rearrangements of liquid water, the effects of nanoconfinement are under much debate. So far, no inhomogeneities were observed in the molecular orientational motions of the water molecules throughout the droplets [99], while such inhomogeneities have been predicted by molecular dynamics simulations [43]. A decrease in the average mobility of water in nanodroplets has been observed by several techniques [56,111,122,127], although so far no distinction could be made between water molecules at the surface layers of the droplets and those in the core. From these studies it therefore remained unclear whether the mobility of water in nanodroplets decreases overall, or that molecules located near the surface and in the core of the droplets show different dynamical behaviour. Here, we use spectrally resolved ultrafast mid-infrared pump-probe spectroscopy on the O–H stretch vibration of isotopically diluted water (HDO in D$_2$O) contained in reverse micelles. In these experiments we observe separately the contributions of core and interfacial water molecules, and find that the molecular mobilities are remarkably different.

4.2 Materials and Methods

Reverse micelle samples were studied with droplet radii of 0.2-4.5 nm, corresponding to clusters of 50-80,000 water molecules ($w_0 = 2, 4, 7, 12, 17, 20, 40$). These micelles were prepared by adding AOT and water at the appropriate concentrations to an apolar solvent of n-octane. We performed ultrafast mid-infrared pump-probe spectroscopy on the O–H stretch vibration of diluted HDO in D$_2$O. We use isotopically diluted water samples to prevent the signals to be affected by intermolecular resonant energy transfer of the O–H stretch vibrations. The transmitted probe beam is split into components polarised parallel ($\Delta\alpha_\parallel$) and perpendicular ($\Delta\alpha_\perp$) with respect to the pump polarisation, and both components are spectrally resolved simultaneously on a nitrogen-cooled HgCdTe detector array using a polychromator. We construct an isotropic absorbance change and anisotropy parameter (Eq. 1.5 and Eq. 1.6) from these polarisation components as described in chapter 1.

4.3 Results and Discussion

The structural dynamics of water can be studied through the dynamics of the O–H stretch vibrational frequencies of the molecules, because these frequencies strongly correlate with the strength of the hydrogen-bonds [78,104]. Compared
to bulk water, we find the hydrogen bond dynamics of confined water to be strikingly different. We measured the transient spectral response of both bulk water and a $w_0 = 7$ micelle ($n_{\text{water}} \approx 425$) when pumping at the blue wing of the O–H stretch spectrum (mainly exciting weakly hydrogen-bonded molecules), and at the red wing (mainly exciting strongly hydrogen-bonded molecules). The pump-induced transmission changes at 2 ps time-delay are shown in Fig. 4.1.

From the left panel of Fig. 4.1 we see that for bulk water, irrespective of which subset of water molecules was initially excited, the pump-probe spectra become identical very rapidly (within 1 ps). This fast spectral diffusion shows that rapid fluctuations within the hydrogen bond network cause a fast interconversion of strong and weak hydrogen bonds [52,92]. As a result, the excited subset of molecules quickly reaches its spectral equilibrium distribution. This sharply contrasts with the case of water confined in a nanodroplet, as shown in the right panel of Fig. 4.1. Here, the pump-probe spectra obtained with different pump frequencies remain shifted with respect to each other, even at long delays (>10 ps). The confined liquid apparently contains spectrally separated subsets of OH oscillators that do not interchange their absorption frequencies on a picosecond timescale, which suggests that water molecules within the nanodroplets experience different local hydrogen bonding over long time scales.

The observed inhomogeneity in the dynamics of the confined water molecules can be further investigated by studying their vibrational relaxation, which is known to depend strongly on the local hydrogen bonding [78]. In studies on neat (not isotopically diluted) water, it is shown that the vibrational relaxation rate increases with micelle size [30,37] (see chapter 6). This work can however
only reveal the average dynamics of the water molecules, because of the rapid intermolecular energy transfer occurring in neat H$_2$O [29,37]. Fig. 4.2 shows the vibrational relaxation measured for isotopically diluted water in nanodroplets. The decay is clearly multi-exponential (as opposed to bulk HDO in D$_2$O) and dependent on micelle size. We find from a global fit to all delay curves of measurements on 7 samples of different micelle sizes (32 probe frequencies / sample), that the dynamics can be well described by a model of two components with different vibrational relaxation time-constants $T_1$. Although we observe a slight frequency dependence in the relaxation rate of the slow component, we did not include this frequency dependence to limit the number of fit-parameters. In the fit, the relative amplitudes of each component is allowed to vary both with absorption frequency and size of the reverse micelle. Fig. 4.3 shows the obtained spectral amplitudes for two sizes of micelles. The blue-shifted component has $T_1=2.8$ ps for all droplet sizes. For the red-shifted component $T_1$ decreases from 1.0 ps for the smallest droplet to 0.7 ps for the largest droplet. The obtained results for the fit parameters are give in Table 4.1 of the Appendix.

As we lower the surface-to-volume ratio of the water droplets by increasing their size, the amplitude of the slow component in the vibrational relaxation strongly decreases, as illustrated in the top right panel of Fig. 4.3. For micelles having $w_0 > 10$ we find a decrease of the relative fraction of the slow component $f_{\text{slow}}$ consistent with a $1/w_0$ dependence ($\propto w_0^{-\alpha}$, $\alpha = 0.85 \pm 0.25$). Since the micelle radius varies linearly with $w_0$ in this size regime [112], the fraction of the
4.3 Water dynamics in anionic micelles

Figure 4.3. Spectral amplitudes of the core (fast) and interfacial (slow) components in the vibrational relaxation for water in two sizes of reverse micelles, obtained from a global fit to the data. The top right panel shows the relative core and interfacial fractions, which are obtained by spectrally integrating the positive (bleaching) part of the spectrum for each of the two components. Error bars are put at those fractions where the $\chi^2$-value of the global fit doubles its minimised value (keeping the interfacial vibrational lifetime fixed). In the Appendix we give the spectral amplitudes for core and interfacial components of all studied samples (Fig. 4.5).

The slow component is in fact inversely proportional to the radius of the droplet, just like the surface-to-volume ratio of a sphere. This strongly suggests that the slow component is associated with water molecules at the droplet interface. Assuming a dependence of the slow-component proportional to $1/w_0$, we find a prefactor to this term of $3.3 \pm 0.3$. If we neglect differences in the absorption cross-section of the core and interfacial molecules, this factor suggests a surface coordination of 6-7 hydrogen-bonds per surfactant molecule. This number of hydrogen bonds is consistent with the fact that there are the six lone electron pairs located at the oxygens of the sulfonate anion of the AOT surfactant molecule, which can accept one hydrogen bond each. We thus assign the slow component to interfacial water and the fast component to core water.

For the smaller micelles ($w_0 < 10$) we observe that the amplitude of the interfacial component does not follow a $1/w_0$ proportionality, but increases more slowly with decreasing $w_0$. This deviation is also found in molecular dynamics simulations [43]. In fact, for all micelles studied, the dependence on $w_0$ of the interfacial component agrees well with the calculated number of molecules.
within the first solvation layer of the micelle cavity. The simulations show that for the smallest micelles the interface is strongly curved, the surfactant molecules are less hydrated and pack more closely. Therefore the density of water molecules located at the interface decreases, explaining the deviation from the approximate $3/w_0$-dependence for the smaller micelles ($w_0 < 10$).

The spectrum of the interfacial component is blue-shifted with respect to the core component, as seen in Fig. 4.3, which points to a weakening of the hydrogen bonds of these molecules [37]. The OH···O hydrogen bond is known to weaken if it is not parallel to the OH-bond [104,126], and this configuration is likely to occur at a micellar interface. The local binding structure of the interfacial water depends on the hydrophilic interactions with the surfactant molecules and their counter-ions [57], and on packing constraints. The near-tetrahedral hydrogen-bond network that exists for bulk water will be disrupted at the interface, and non-directional and possibly bifurcated hydrogen bonds may form here.

The core water molecules have an average hydrogen-bonding that is slightly weaker compared to bulk water, as can be concluded from the missing red wing in the spectrum of the core component. This red wing recovers in going from $w_0=12$ to 40 and the vibrational relaxation rate approaches the bulk value only at about $w_0=40$. Therefore, water with full bulk-like character only starts to appear in a cluster of at least 2000 water molecules ($w_0=12$) and bulk-like molecules fully dominate the dynamics over molecules with interfacial character at clusters larger than 80,000 molecules ($w_0=40$). Note that the sodium counter-ions of the AOT surfactant molecules are not expected to have a large influence on the dynamics of the core component, since they mainly associate with the anionic head groups and are only partly solvated [57] (see also chapter 3.7). In addition, it has been found that the effect of sodium cations on the dynamics of bulk water is very small [94].

In order to obtain information on the molecular motions of the core and interfacial water, we measured the decay of the anisotropy in the orientation of the pump-excited OH-groups. Preferentially O–H stretch oscillators parallel to the pump polarisation will absorb, causing different transmissions for probe light polarised parallel and perpendicular to the pump polarisation. The decay of the relative difference of these two signals gives direct information on the angular motions of the OH-groups of the water molecules.

Fig. 4.4 shows four anisotropy decay curves for different absorption frequencies and two different micelle sizes (anisotropy decay curves for all studied samples are displayed in Fig. 4.6 in the Appendix). When the interfacial component dominates, which is the case at the blue absorption frequencies of especially the smallest nanodroplets, the anisotropy parameter decays very slowly over time scales larger than 20 ps. The water layer solvating the interface is apparently highly immobile, despite the fact that these molecules are more weakly hydro-

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Faeder et al. define the interfacial fraction as those molecules located within 0.5 nm distance from the reverse micelle cavity boundary. The present work shows the same micelle size-dependence for this fraction, but by an absolute fraction 20 percent lower, likely because it does not include any OH-groups forming hydrogen bonds to other water molecules.
Figure 4.4. Comparison of the anisotropy decay of the O–H stretch vibration at two different probe frequencies for an intermediate size micelle of $w_0=7$ (top panel), and a comparison of the orientational relaxation for two different reverse micelles sizes ($w_0=2,17$) at a single probe wavelength of $3513 \text{ cm}^{-1}$ (bottom panel).

A quite peculiar anisotropy decay can be observed at frequencies where we find both core and interfacial water, as illustrated by the decay curve for the $w_0=17$ micelle in Fig. 4.4. Directly after excitation we observe an anisotropy decay with an associated time constant close to that of bulk water, but the decay quickly levels off and even rises from about 2 ps onwards. This effect can be understood in terms of the different vibrational relaxation time-constants associated with core and interfacial water. Since only excited molecules contribute to the observed anisotropy and the vibrations of the interfacial water decay more slowly, the relative contribution of interfacial water to the signal will increase in time. As time progresses the anisotropy parameter increasingly reflects the slowly decaying anisotropy of the interfacial molecules. This explains the recovery of the value of the anisotropy parameter at later delays.

The observed anisotropy curves can be well described by a model in which the previously determined core and interfacial water fractions have different re-orientational time-constants $\tau$, as shown by the curves in Fig. 4.4 obtained from

\[ w_0=7 \quad (n_{\text{water}}=425) \]

\[ w_0=2 \quad (n_{\text{water}}=50) \]

\[ w_0=17 \quad (n_{\text{water}}=6000) \]
a global fit. We find that the core water reorients on a time scale close to that of bulk water \[48,92\] (\(\tau_{\text{core}} = 2 - 4\) ps), while the interfacial water is immobile on our experimentally accessible time scales (\(\tau_{\text{interface}} > 15\) ps).

In recent anisotropy relaxation measurements on the OD hydroxyl stretch of water by Piletic et al. it was also found that the orientational mobility of the molecules strongly changes when the micelle size decreases \[99, 122\]. The authors of this work however do not observe an inhomogeneity in the orientational relaxation throughout the droplet, and conclude that the hydrogen bond structural rearrangements of confined water are best described within a framework in which all molecules are treated equivalently. These conclusions contrast our observations presented above. A possible reason that the orientational motions of the two sorts of water can be distinguished in this study is the experimental advantage that we measure the dynamics spectrally resolved over the entire frequency range of the O–H stretch absorption band. The competition between the core and interfacial contributions to the anisotropy is most obvious in larger micelles at relatively blue absorption frequencies. In these cases one can observe most clearly the transition from a case in which the anisotropy is dominated by a large amount of core molecules, to a case in which the interfacial molecules dominate at later delays in view of their longer vibrational lifetime and blue absorption frequency (see Fig. 4.4). In addition, the OH band is more strongly inhomogeneously broadened than the OD band, which allows for a better spectral distinction of different species, i.e. the water in the core and at the interface of the micelle.

The observation of slow orientational dynamics for the interfacial water molecules is supported by recent molecular dynamics simulations on micellar systems \[9, 43\]. These studies have suggested that water molecules can remain bound to micellar surfaces for more than 100 ps. Other calculations show that the ionic-dipole interaction between the surfactant and its solvating water molecules is strong \[35\], leading to a local ordering and density increase of water molecules close to the surfactant molecules \[43\]. Also the sodium counter-ions, which mainly associate with the sulfonate anionic head groups at the interface, will influence the dynamical properties of neighbouring water \[57\].

Core and interfacial water molecules show strongly different orientational mobilities, which has to be explained from their different intermolecular interactions and very different geometric arrangements. Molecular reorientation involves the subsequent breaking and formation of hydrogen bonds. Interestingly, the activation energy for this process is not the same as the hydrogen bond binding energy, as is apparent from the fact that interfacial water has a smaller hydrogen bond binding energy, yet shows a slower molecular reorientation. For core water molecules (as for bulk water) the activation energy for reorientation is substantially lowered, because these molecules can break a hydrogen bond while simultaneously forming a new bond with another water molecule \[74\]. For interfacial water this process appears to be sterically hindered because these molecules are hydrogen bonded to a heavy immobile surfactant molecule. Because of this geometric effect, weakly hydrogen bonded molecules can experience a slow reorientation and slow hydrogen bond dynamics, even
though their hydrogen bond binding energy is relatively small.

In conclusion, we studied the vibrational and rotational dynamics of water molecules contained in water nanodroplets using femtosecond transient vibrational spectroscopy. We find that we can distinguish core and interfacial water on the basis of their different vibrational lifetimes. The orientational motions of the water molecules turn out to be strongly inhomogeneous in the droplet. Even for small micelles, the water molecules in the core reorient on a similar time-scale as bulk liquid water. Therefore, nano-confinement has a negligible effect on the orientational mobility of water molecules in the core of the droplets. We find the water at the interface to be highly immobile, in spite of the fact that their hydrogen bonding is weaker compared to molecules in the core of the droplets.

4.4 Appendix

4.4.1 Kinetic Modeling

In describing the vibrational relaxation, we perform a global fit to the delay curves of the rotation free signal of measurements on seven samples of different micelle sizes (32 probe frequencies/sample). The dynamics is well described by a model of two components with different time-constants. The slow component, assigned to interfacial water molecules, is assumed to have an associated vibrational relaxation time constant that is equal for all sizes of micelles. The fast component, assigned to core water molecules, may vary its time constant with micelle size. We thus separate the rotation free signal into two contributions from core and interfacial OH-oscillators:

\[
\Delta \alpha_{\text{RF}}(\omega, t) = \Delta \alpha_{\text{RF,core}}(\omega, t) + \Delta \alpha_{\text{RF,interface}}(\omega, t),
\]

\[
\Delta \alpha_{\text{RF,core}}(\omega, t) = \sigma_{\text{PP,core}}(\omega) e^{-t/T_{\text{core}}},
\]

\[
\Delta \alpha_{\text{RF,interface}}(\omega, t) = \sigma_{\text{PP,interface}}(\omega) e^{-t/T_{\text{interface}}}.\tag{4.1}
\]

Because of heating of the sample caused by the intense pump pulse, we measure a small thermal signal (0.1-5 percent of the total transmission change, depending on frequency and micelle size) in the pump-induced absorbance changes. This signal is modelled to grow in at the vibrational relaxation rate to the level of absorption change that is measured at \(\sim 10\) times the average vibrational relaxation time constant for each micelle (i.e. at 20, 15, 12, 10, 10, 9, 9 ps for \(w_0=2, 4, 7, 12, 17, 20, 40\), resp.) At these delay times the population induced transmission changes are negligible and only the thermal signal is present. The thermal signal is subsequently subtracted from the original signals \(\Delta \alpha_{\text{RF}}, \Delta \alpha_{\parallel}\) and \(\Delta \alpha_{\perp}\). We do not take into account the slow decay of the thermal signal due to cooling of the micelle to its surroundings [112]. For this approximation to be valid, we performed experiments on highly diluted samples of HDO in D\(_2\)O (H\(_2\)O:D\(_2\)O=1:40). In this case the heating of the micelles is very limited and the subsequent cooling very slow, making the thermal signal effectively constant.
Table 4.1. O–H stretch vibrational lifetimes (in ps), fractions, and reorientational time-constants (in ps) of core and interfacial water.

<table>
<thead>
<tr>
<th>( w_0 )</th>
<th>( n_{\text{water}} )</th>
<th>( T_{1,\text{core}} )</th>
<th>( T_{1,\text{interf.}} )</th>
<th>( f_{\text{core}} )</th>
<th>( f_{\text{interf.}} )</th>
<th>( \tau_{\text{core}} )</th>
<th>( \tau_{\text{interf.}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>50</td>
<td>1.0±0.2</td>
<td>2.8±0.2</td>
<td>0.39</td>
<td>0.61</td>
<td>3±1</td>
<td>&gt;20</td>
</tr>
<tr>
<td>4</td>
<td>150</td>
<td>0.9±0.2</td>
<td>2.8±0.2</td>
<td>0.50</td>
<td>0.50</td>
<td>3±1</td>
<td>&gt;15</td>
</tr>
<tr>
<td>7</td>
<td>425</td>
<td>0.9±0.2</td>
<td>2.8±0.2</td>
<td>0.63</td>
<td>0.37</td>
<td>3±1</td>
<td>&gt;15</td>
</tr>
<tr>
<td>12</td>
<td>2150</td>
<td>0.9±0.1</td>
<td>2.8±0.2</td>
<td>0.74</td>
<td>0.26</td>
<td>3±1</td>
<td>&gt;15</td>
</tr>
<tr>
<td>17</td>
<td>6200</td>
<td>0.9±0.1</td>
<td>2.8±0.2</td>
<td>0.80</td>
<td>0.20</td>
<td>3±1</td>
<td>&gt;15</td>
</tr>
<tr>
<td>20</td>
<td>10,000</td>
<td>0.8±0.1</td>
<td>2.8±0.2</td>
<td>0.83</td>
<td>0.17</td>
<td>3±1</td>
<td>&gt;15</td>
</tr>
<tr>
<td>40</td>
<td>80,000</td>
<td>0.8±0.1</td>
<td>2.8±0.2</td>
<td>0.91</td>
<td>0.09</td>
<td>3±1</td>
<td>&gt;15</td>
</tr>
<tr>
<td>bulk</td>
<td>∞</td>
<td>0.7±0.1</td>
<td>-</td>
<td>1</td>
<td>0</td>
<td>3±0.5</td>
<td>-</td>
</tr>
</tbody>
</table>

The vibrational lifetime of the interfacial water was a global fit parameter. The bulk vibration relaxation and reorientation time constant for HDO in D\(_2\)O were taken from reference [106].

over the time-window considered; subtracting the thermal signal at 15 times the average vibrational relaxation time instead of 10 did not lead to any significant change of the fit parameters. Note that the parallel and perpendicular signals experience the same thermal effect since rapid heat diffusion makes heating highly isotropic.

In the fit, the relative amplitudes \( \sigma_{\text{PP,core}} \) and \( \sigma_{\text{PP,interface}} \) may vary both with probe absorption frequency and size of the reverse micelle. Fig. 4.5 shows the obtained spectral amplitudes for all considered sizes of micelles. Table 4.1 lists the obtained time constants.

The orientational relaxation can be well described by assuming different anisotropy decays for the previously determined core and interfacial water fractions. By use of Eq. 4.1 we can write for the anisotropy parameter (analogous to Eq. 1.11):

\[
R(\omega, t) = f_{\text{core}}(\omega, t)R_{\text{core}}(t) + f_{\text{interface}}(\omega, t)R_{\text{interface}}(t),
\]

\[
f_{\text{core}}(\omega, t) = \frac{\Delta\alpha_{\text{RF,core}}(\omega, t)}{\Delta\alpha_{\text{RF}}(\omega, t)}, \quad f_{\text{interface}}(\omega, t) = \frac{\Delta\alpha_{\text{RF,interface}}(\omega, t)}{\Delta\alpha_{\text{RF}}(\omega, t)}.
\]

The time-dependent fractions \( f_{\text{core}} \) and \( f_{\text{interface}} \) are obtained from the fit to the rotation free signal. \( R_{\text{core}}(t) \) and \( R_{\text{interface}}(t) \) are the anisotropy parameters for the core and interfacial water sub-ensembles, which we assume to show an exponential decay. These two reorientational time constants are obtained from a global fit to the anisotropy curves at all spectral frequencies for each micelle size. The core water is found to reorient on a timescale of 2-4 ps, similar to bulk water. The reorientational time constant of the interfacial water is >15 ps. Fig. 4.6 shows the orientational relaxation for six different sizes of nanodroplets at two probe absorption frequencies each.
Figure 4.5. Spectral amplitudes of the core (fast) and interfacial (slow) components in the vibrational relaxation for all studied sizes of reverse micelles, obtained from a global fit to the vibrational relaxation curves, obtained by measuring the rotation free pump-probe signal $\Delta \alpha_{RF}$. The bottom right panel shows the relative core and interfacial fractions, which are obtained by spectrally integrating the positive (bleaching) part of the spectrum for each of the two components (see Table 4.1).
Figure 4.6. Orientational relaxation of the O–H stretch vibration of water in different sizes of reverse micelles. For six samples of different \(w_0\) we compare the anisotropy decay at 3550 and 3390 cm\(^{-1}\).