Chapter 6

Vibrational relaxation of confined neat water

We study the vibrational dynamics of nanodroplets of neat liquid water (H$_2$O) with femtosecond two-color mid-infrared pump-probe spectroscopy. For the smallest nanodroplet, containing 10-15 water molecules, the lifetime $T_1$ of the O–H stretch vibrations is equal to 0.85±0.1 ps, which is more than three times as long as in bulk liquid water. We find that the truncation of the hydrogen-bond network of water leads to a dramatic change of the relaxation mechanism.

6.1 Introduction

In a study of the vibrational dynamics of pseudohalide ions (N$_3^−$, NCO$^−$ and NCS$^−$) in aqueous solution [135,136], it was found that the vibrational lifetime changes when such ions are confined in reverse micelles. The vibrational lifetime was found to increase when the size of the micelle was decreased. Here we present a systematic study of the effect of nanoconfinement on the vibrational dynamics of neat water itself. We find that the confinement to the nanometre scale leads to an increase of the lifetime of the O–H stretch vibrations of the water molecules that is much stronger than can be expected from the change in vibrational frequency.

6.2 Experimental

The investigated samples were mixtures of the surfactant AOT (sodium di-2-ethylhexylsulfosuccinate, Aldrich, 99%), n-octane (Aldrich, anhydrous grade 99+%), and water H$_2$O (Aldrich, HPLC grade). The molar water-to-AOT ratio $w_0$ was set to 1, 2, 4, 7 and 12 respectively, creating reverse micelles containing a water pool consisting of ~10 to ~10,000 water molecules. The radius $R$ in nm
Figure 6.1. Linear infrared absorption spectra of the O–H stretch vibrations of water in AOT/water/octane reverse micelles of various sizes: \( w_0 = 1, 2, 4, 7 \) and 12. The spectra are normalised for comparison. The absorption at the low-frequency side contains a strong contribution of the high-frequency wing of the absorption of the C–H stretch vibrations of AOT and \( n \)-octane.

of the micelle can be approximated from \( R = 0.15 \times w_0 \), with \( w_0 = [\text{H}_2\text{O}]/[\text{AOT}] \) [112].

In the pump-probe experiment we monitor the time-dependent absorption changes that result from the pump excitation by a probe pulse with a polarisation at the magic angle (54.7°) with respect to the polarisation of the pump. At this polarisation angle all absorption changes related to molecular reorientation are averaged out, and we only record the isotropic absorbance change \( (\Delta \alpha(\omega, t) = \Delta \alpha_{RF}(\omega, t)) \).

6.3 Results and Discussion

Fig. 6.1 shows the linear absorption spectrum of the OH-stretching band of water confined in reverse micelles of various sizes. The amplitude of the low-frequency part of the OH absorption band strongly decreases as the water content is reduced. Fig. 6.2 displays transient spectra for a reverse micelle with \( w_0 = 4 \). At early delays the transient spectra reveal a bleaching at the \( v = 0 \rightarrow 1 \) transition around 3500 cm\(^{-1}\) and an induced absorption at the \( v = 1 \rightarrow 2 \) transition extending from 3300 cm\(^{-1}\) to below 3000 cm\(^{-1}\). The measurable spectral range was limited on the low-frequency side by the strong C–H absorption of AOT and the octane solvent. At longer delays the transient spectrum takes the form of a thermal difference spectrum: upon heating the OH-stretch band shifts slightly to the blue and its area is reduced.
The delay curves in the top of Fig. 6.3a,b show an induced absorption corresponding to the $v = 1 \rightarrow 2$ transition of the O–H stretch vibration. The comparison of the decay rates measured for micelles with $w_0 = 2$ and $w_0 = 7$ shows that the lifetime of the $v = 1$ state increases when the micelle becomes smaller. The vibrational relaxation leads eventually to heating of the micelle, leading to an increase of the transmission at the red side of the O–H absorption band. This heating effect is also clearly present in the middle traces of Fig. 6.3a,b. The heating of the micelles is followed by a cooling process in which energy is transferred to the surrounding solvent. The lower traces of Fig. 6.3a,b show an initial transmission increase due to the bleaching of the fundamental $v = 0 \rightarrow 1$ transition of the O–H stretch vibration. In the lower curve of Fig. 6.3b it is clearly seen that the thermalisation is delayed with respect to the vibrational relaxation. This implies that the relaxation of the $v = 1$ state of the O–H stretch vibration first leads to population of a non-thermal intermediate state. Only after the subsequent relaxation of this intermediate state, the energy becomes thermalised over the micelle. This relaxation mechanism is only observed for micelles with $w_0 \geq 4$.

We use a simple kinetic model to extract the vibrational relaxation time constants from the data. We do not observe any effect of spectral hole burning in the experiments which shows that the spectral diffusion in the O–H stretch vibrational band is much faster than the vibrational relaxation, in agreement with previous results obtained for bulk liquid water [131]. For micelles with $w_0 = 4, 7, 12$, the population $N_1(t)$ of the excited $v = 1$ state first relaxes to a non-thermal combination of accepting modes $0^*$ with time constant $T_1$. The relaxation of $0^*$ with time constant $\tau_{eq}$ leads to an equilibration of the energy
Figure 6.3. Delay time scans measured at three different probe frequencies for reverse micelles with \( w_0 = 2 \) (Fig. a) and \( w_0 = 7 \) (Fig. b). The solid curves are obtained from a fit to the kinetic model described in the text.

over the full water pool of the reverse micelle, which brings the micelle at an elevated temperature. As a result of this higher temperature the absorption spectrum of the water molecules changes, which leads to a thermal absorbance change \( \Delta \alpha_T(\omega,t) \) observed in the pump probe experiment. For the smallest micelles with \( w_0 = 1 \) and \( w_0 = 2 \) we did not observe a non-thermal intermediate state \( 0^* \). Hence, in the modelling of these micelles the population \( N_1 \) is directly thermalised with time constant \( T_1 \).

The heating effect \( \Delta \alpha_T(\omega,t) \) decays due to cooling of the micelle. This cooling is a thermal diffusion process, which implies that its dynamics are non-exponential [112]. We do not pursue to investigate the cooling process in detail, and we describe this process with a single or bi-exponential function. This gives an accurate description of the cooling up to a delay of 10 ps. For all micelles the cooling time constants are much longer than \( T_1 \) and \( \tau_{\text{eq}} \).

The time-dependent absorption change \( \Delta \alpha(\omega,t) \) resulting from the relaxation dynamics is given by:

\[
\Delta \alpha(\omega,t) = \sigma_{\text{PP}}(\omega)N_1(t) + \Delta \alpha_T(\omega,t),
\]

(6.1)

where

\[
\sigma_{\text{PP}}(\omega) = [\sigma_{12}(\omega) - 2\sigma_{01}(\omega)].
\]

(6.2)
The population $N_1(t)$ and the time evolution of the heating effect are obtained from solving the appropriate differential equations, fully analogous to the treatment in the appendix of chapter 5.

The delay-dependent absorption change $\Delta \alpha (\omega, \tau)$ is obtained by convoluting $\Delta \alpha (\omega, t)$ with a gaussian function representing the cross-correlation trace of the pump and probe pulses. In fitting $\Delta \alpha (\omega, \tau)$ to the data, we only considered delays $>0.2$ ps, when coherent coupling effects have become negligibly small.

For each micelle size all ($\sim 50$) recorded time traces are simultaneously fitted, yielding $T_1$, $\tau_{eq}$, $\sigma_{PP}(\omega)$, and the spectrum of the heating effect $\Delta \alpha_T(\omega)$. The values of $T_1$ are shown as a function of $w_0$ in Fig. 6.4. The value of $\tau_{eq}$ (for micelles with $w_0 = 4, 7, 12$) equals $0.3 \pm 0.1$ ps. The resulting cross-section difference spectrum $\sigma_{PP}(\omega)$ is very similar to the pump-probe spectrum at 0.2 ps shown in Fig. 6.2. These spectra are dominated by the bleaching of the $v = 0 \rightarrow 1$ transition and the induced absorption of $v = 1 \rightarrow 2$ transition. The cross-section spectrum of the heating effect $\Delta \alpha_T(\omega)$ is very similar in shape to the pump-probe spectrum measured at 2.8 ps shown in Fig. 6.2. This spectrum represents the difference of the spectrum of the micelle at an elevated temperature with that at room temperature.

For all micelle sizes, we observe that the vibrational relaxation is not completely single exponential. This behaviour hints at the presence of inhomogeneity in the studied samples. It should be noted here that the inhomogeneity of the water in the micelles, although most certainly present, cannot be observed in this experiment. In liquid water an excitation of the O–H stretch vibrations as a function of the value of $w_0$ of the reverse micelle. Also shown is the value of $T_1$ measured for bulk liquid water [83].

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure6.4}
\caption{Vibrational lifetime $T_1$ of the O–H stretch vibrations as a function of the value of $w_0$ of the reverse micelle. Also shown is the value of $T_1$ measured for bulk liquid water [83].}
\end{figure}
vibration rapidly hops from one molecule to another, which implies that the excitation samples all different types of local O–H oscillators on a very short time scale (<100 fs) [29,131]. As a result, the observed relaxation is not a multi-component process containing for instance a component of interfacial water and components of core water, but instead a single component with a time constant that is a weighted average of the $T_1$ values of all O–H oscillators within the micelle. Hence, the slight deviation from single-exponential character that we observe in our experiment most likely results from the variation in the size of the micelles. The size of the reverse micelles has a polydispersity with a width that ranges from $\sim$30% for small $w_0$ to $\sim$15% for large $w_0$ [97].

Fig. 6.4 shows that the vibrational lifetime of the O–H stretch vibrations of water strongly increases with decreasing size of the reverse micelles. With decreasing micelle size also the fraction of interface water increases, for which $T_1$ can differ from that of the water in the core. However, the increase of the experimentally observed average value of $T_1$ cannot be just explained from an increased contribution of interfacial water. The relative amount of the interfacial water increases from $\sim$10% for the largest micelle with $w_0 = 12$, to near 100% for a micelle with $w_0 = 1$. Hence, if the increase of $T_1$ of a micelle with $w_0 = 12$ with respect to bulk water would only result from an increased contribution of interfacial water, the observed $T_1$ would increase by only a few percent in comparison to bulk liquid water. Instead, $T_1$ increases by $\sim$50%. Hence, the confinement affects the vibrational relaxation rate of all water molecules in the micelle. This notion agrees with the observation that even for micelles with $w_0 > 20$ the vibrational spectrum differs from that of bulk liquid water [49,125].

The increase of $T_1$ is much stronger than is usually observed for hydrogen-bonded systems. For many hydrogen-bonded systems $T_1$ is related to the O–H stretch frequency $\omega_{OH}$ by [89]:

$$T_1(\omega) = a(\omega_{OH} - \omega_{OH,g})^{-1.8},$$  

(6.3)

with $a$ a constant and $\omega_{OH,g}$ the vibrational frequency of the O–H group in the gas phase. Using $\omega_{OH,g} = 3706$ cm$^{-1}$ (average of the symmetric and asymmetric O–H stretch vibrations), $\omega_{OH,lb} = 3420$ cm$^{-1}$ for bulk liquid water, and $\omega_{OH,lb} = 3480$ cm$^{-1}$ for a micelle with $w_0 = 1$, the value of $T_1$ is expected to increase from $\sim$260 fs [83] to $\sim$400 fs, going from bulk to $w_0 = 1$. The latter value of $T_1$ is more than two times shorter than the measured value of 0.85±0.1 ps, which is surprising since for bulk HDO:D$_2$O equation (6.3) is closely followed when the frequency of the O–H stretch vibration is varied by changing the temperature [133].

A striking observation is that the nanoconfinement leads to a drastic change of the relaxation mechanism. For micelles with $w_0 \geq 4$, the relaxation of the O–H stretch vibration leads to population of a non-thermal intermediate state, whereas for micelles with $w_0 = 1$ and $w_0 = 2$ such a state is not observed. The non-thermal intermediate state that can no longer be reached for small micelles is likely formed by the overtone of the H–O–H bending mode. This overtone has a frequency of $\sim$3300 cm$^{-1}$, and is thus in resonance with the red wing of the O–H stretch absorption band of bulk liquid water. The truncation
6.3 Neat water in anionic micelles

of the hydrogen-bonded network leads to a weakening of the hydrogen-bond interactions between the water molecules. As a result, the red wing of the absorption spectrum of the O–H stretch vibrations vanishes (Fig. 6.1), which implies that the overlap with the overtone of the H–O–H bending mode strongly decreases. The nanoconfinement also leads to a small red shift of a few cm$^{-1}$ of the H–O–H bending mode, thus contributing to the loss of overlap with the O–H stretch vibration.

The assignment of the non-thermal intermediate state to the overtone of the bending mode is supported by the observation that the relaxation of the O–H stretch vibrations leads to excitation of the bending mode for bulk liquid water [33], but not for $w_0 = 2$ micelles [34]. The relaxation time constant $\tau_{\text{eq}}$ thus likely represents the vibrational lifetime of the first and/or second excited state of the H–O–H bending mode. Recently, the lifetime of the first excited state of the bending mode was measured to be $\sim 0.2$ ps [59], which agrees quite well with the value of $\tau_{\text{eq}}$ of $0.3 \pm 0.1$ ps. The bending mode itself can only relax to intermolecular modes of which the librations have the highest frequencies ($\sim 800$ cm$^{-1}$). The librational frequencies show a decrease of $\sim 25\%$ when liquid water is confined in a micelle with $w_0 = 1$ [125], which probably will affect $\tau_{\text{eq}}$. Unfortunately, we could determine $\tau_{\text{eq}}$ only in the interval from $w_0 = 12$ to $w_0 = 4$, and we did not find a statistically significant change.

The Fermi resonance of the O–H stretch vibrations with the overtone of the H–O–H bending mode is a special property of H$_2$O water. For most other systems, including HDO and alcohols, the overtone of the bending mode is far out of resonance with the stretch vibration. This difference in resonance explains why the value of $T_1$ of bulk liquid H$_2$O is $\sim 3$ times shorter than that of bulk liquid HDO:D$_2$O [133]. Nanoconfinement of water leads to a vanishing of the low-frequency O–H stretch vibrations, and thus to a closing of the relaxation channel to the overtone of the H–O–H bending mode. As a result, for small micelles with $w_0 = 1$, the value of $T_1$ is similar to that of HDO:D$_2$O at the same frequency of the O–H stretch vibration [133] (attained at an elevated temperature), and to that of ethanol clusters at the same frequency [132]. We conclude that the confinement of liquid water to the nanometre scale leads to a loss of its special vibrational relaxation properties, thus making this liquid much more similar to other hydrogen-bonded liquids. This effect of nanoconfinement explains why the increase of $T_1$ with decreasing micelle size is anomalously strong, and cannot be described with equation (6.3).