

Anomalous Slowing Down of the Vibrational Relaxation of Liquid Water upon Nanoscale Confinement

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We study the vibrational dynamics of nanodroplets of liquid water with femtosecond two-color midinfrared 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 3 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.

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An excellent model system to study the properties of nanoconfined water is formed by so-called reverse micelles: small droplets of water covered by a surfactant and contained in an apolar solvent matrix. The water molecules close to the surfactant layer were found to be much more structured and much less mobile than the molecules in bulk liquid water [1]. The water in the core, i.e., a few molecular layers away from the interface, is much more similar to bulk liquid water [2], although in infrared spectroscopic studies it was shown that even for very large micelles with a diameter >6 nm, the hydrogen bonds between the water molecules are still weaker than in bulk liquid water [3,4].

In a study of the vibrational dynamics of pseudohalide ions (N_3^- , NCO^- , and NCS^-) in aqueous solution [5,6], it was found that the vibrational lifetime time increases when the size of the micelle is decreased. In this Letter, we present a systematic study of the effect of nanoconfinement on the vibrational dynamics of water itself. We find that the confinement to the nanometer 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.

The investigated samples were mixtures of the surfactant AOT (sodium di-2-ethylhexylsulfosuccinate, Aldrich, 99%), n octane (Aldrich, anhydrous grade 99 + %), and water H_2O (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 $\sim 10,000$ water molecules. The radius R in nm of the micelle can be approximated from $R = 0.15 \times w_0$, with $w_0 = [\text{H}_2\text{O}]/[\text{AOT}]$ [7].

In the pump-probe experiments, an intense femtosecond midinfrared pulse (pump) is used to excite a fraction of the water molecules to the first excited vibrational state of the O-H stretch vibration. The time-dependent absorption changes that result from this excitation are probed with a second, much weaker pulse (probe) with a polarization at the magic angle (54.7°) with respect to the polarization of the pump. The transmitted probe beams are dispersed in a monochromator, and detected by a 3×32 MCT (mercury-

cadmium-telluride) array detector. The frequency resolution is 16 cm^{-1} per pixel of the array. The midinfrared pump and probe pulses are independently tunable between 2.6 and $3.3 \mu\text{m}$ ($= 3000\text{--}3800 \text{ cm}^{-1}$), have pulse durations of 150 fs, and energies of 10 and $0.1 \mu\text{J}$, respectively [8].

Figure 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. Figure 2 displays transient spectra for a reverse micelle with $w_0 = 4$. At early delays the transient spectra reveal a bleaching at the $\nu = 0 \rightarrow 1$ transition around 3500 cm^{-1} and an induced absorption at the $\nu = 1 \rightarrow 2$ 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

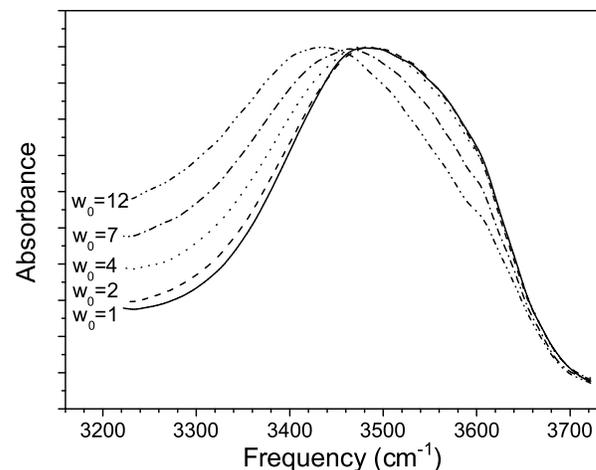


FIG. 1. Linear infrared absorption spectra of the O-H stretch vibrations of water in AOT/water/octane reverse micelles of various sizes: $w_0 = 1, 2, 4, 7,$ and 12 . The spectra are normalized for comparison. The absorption at the low-frequency side contains a strong contribution of the high-frequency wing of the absorption of the C-H stretch vibrations of AOT and n octane.

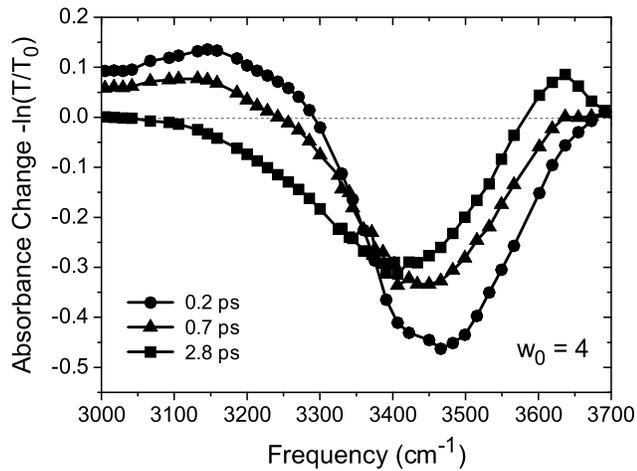


FIG. 2. Transient spectra measured for reverse micelles with $w_0 = 4$ at three different delays. The spectra are measured with a pump frequency of 3480 cm^{-1} .

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 Figs. 3(a) and 3(b) show an induced absorption corresponding to the $\nu = 1 \rightarrow 2$ 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 $\nu = 1$ 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 Figs. 3(a) and 3(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 Figs. 3(a) and 3(b) show an initial transmission

increase due to the bleaching of the fundamental $\nu = 0 \rightarrow 1$ transition of the O-H stretch vibration. In the lower curve of Fig. 3(b) it is clearly seen that the thermalization is delayed with respect to the vibrational relaxation. This implies that the relaxation of the $\nu = 1$ state of the O-H stretch vibration first leads to population of a nonthermal intermediate state. Only after the subsequent relaxation of this intermediate state, the energy becomes thermalized 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 our 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 [9]. For micelles with $w_0 = 4, 7, 12$, the population $n_1(t)$ of the excited $\nu = 1$ state first relaxes to a nonthermal combination of accepting modes 0^* with time constant T_1 . The relaxation of 0^* with time constant τ_{eq} leads to an equilibration of the energy over the full water pool of the reverse micelle. The resulting equilibrated state is denoted by 0^{**} , and its population by $n_{0^{**}}(t)$. The absorption cross section $\sigma_{01}(\omega)^{**}$ of the O-H stretch vibrations starting from this equilibrated state corresponds to the absorption spectrum of a strongly heated micelle. For the smallest micelles with $w_0 = 1$ and $w_0 = 2$ we did not observe a nonthermal intermediate state. Hence, in the modeling of these micelles the population n_1 is directly transferred to $n_{0^{**}}$ with time constant T_1 .

The equilibrated state 0^{**} decays due to cooling of the micelle. This cooling is a thermal diffusion process, which implies that its dynamics is nonexponential [7]. In this Letter 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

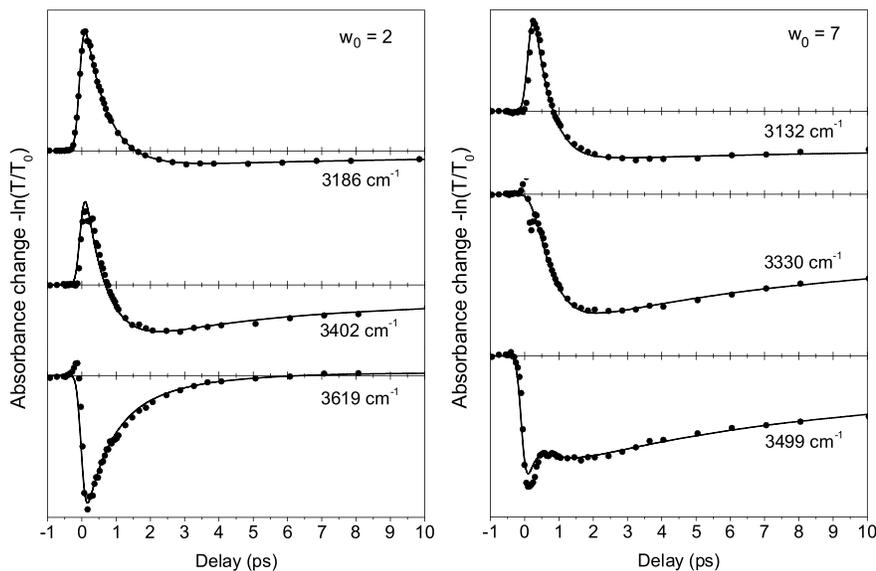


FIG. 3. Delay time scans measured at three different probe frequencies for reverse micelles with $w_0 = 2$ (a) and $w_0 = 7$ (b). The solid curves are obtained from a fit to the kinetic model described in the text.

the cooling up to a delay of 10 ps. For all micelles the cooling time constants are much longer than T_1 and τ_{eq} .

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

$$\Delta\alpha(\omega, t) = [\sigma_{12}(\omega) - 2\sigma_{01}(\omega)]n_1(t) + [\sigma_{01}^{**}(\omega) - \sigma_{01}(\omega)]n_{0^{**}}(t) + \Delta\alpha_T(\omega, t), \quad (1)$$

where $n_1(t)$ and $n_{0^{**}}(t)$ are obtained from solving the appropriate differential equations, and $\Delta\alpha_T(\omega, t)$ represents the absorption change that results after cooling of the micelles. 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, at which the coherent coupling effects have become negligibly small.

For each micelle size all (~ 50) recorded time traces are simultaneously fitted, yielding T_1 , τ_{eq} , $[\sigma_{12}(\omega) - 2\sigma_{01}(\omega)]$, and $[\sigma_{01}^{**}(\omega) - \sigma_{01}(\omega)]$. The values of T_1 are shown as a function of w_0 in Fig. 4. The value of τ_{eq} (for micelles with $w_0 = 4, 7, 12$) equals 0.3 ± 0.1 ps. The resulting cross section differences $[\sigma_{12}(\omega) - 2\sigma_{01}(\omega)]$ are very similar to the pump-probe spectra at 0.2 ps shown in Fig. 2. These spectra are dominated by the bleaching of the $\nu = 0 \rightarrow 1$ transition and the induced absorption of $\nu = 1 \rightarrow 2$ transition. The cross section differences $[\sigma_{01}^{**}(\omega) - \sigma_{01}(\omega)]$ and the absorption changes $\Delta\alpha_T(\omega, t)$ are all very similar in shape to the pump-probe spectrum measured at 2.8 ps shown in Fig. 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 behavior 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 our experiment. In liquid water an excitation of the O-H stretch 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) [9,10]. As a result, the observed relaxation is not a multicomponent 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 [11].

Figure 4 shows that the vibrational lifetime of the O-H stretch vibrations of water strongly increases with decreasing

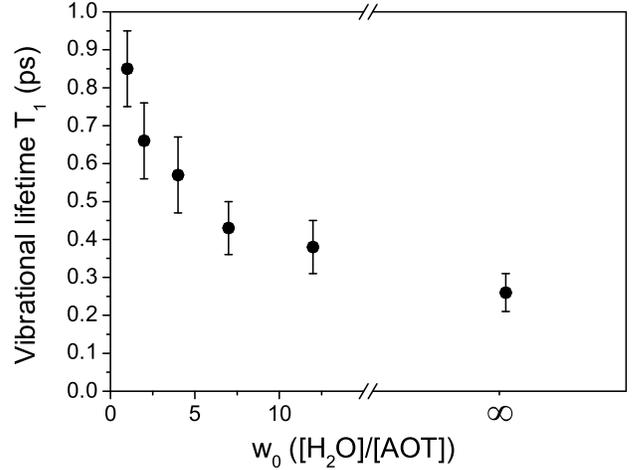


FIG. 4. Vibrational lifetime T_1 of the O-H stretch vibrations as a function of the value of w_0 of the reverse micelle. Also shown is the value of T_1 measured for bulk liquid water [8].

ing size of the reverse micelles. With decreasing micelle size the fraction of interface water also 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 amount of interfacial water is $\sim 10\%$ for the largest micelle with $w_0 = 12$. 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 $\sim 50\%$. This means that 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 [3,4].

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 ω_{OH} by [12]:

$$T_1(\omega) = a(\omega_{\text{OH}} - \omega_{\text{OH,g}})^{-1.8}, \quad (2)$$

with a a constant and $\omega_{\text{OH,g}}$ the vibrational frequency of the O-H group in the gas phase. Using $\omega_{\text{OH,g}} = 3706 \text{ cm}^{-1}$ (average of the symmetric and asymmetric O-H stretch vibrations), $\omega_{\text{OH,hb}} = 3420 \text{ cm}^{-1}$ for bulk liquid water, and $\omega_{\text{OH,hb}} = 3480 \text{ cm}^{-1}$ for a micelle with $w_0 = 1$; the value of T_1 is expected to increase from ~ 260 fs [8] to ~ 400 fs, going from bulk to $w_0 = 1$. The latter value of T_1 is more than 2 times shorter than the measured value of 0.85 ± 0.1 ps, which is surprising since for bulk HDO:D₂O, Eq. (2) is closely followed when the frequency of the O-H stretch vibration is varied by changing the temperature [13].

A striking observation is that the nanoconfinement leads to a 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 nonthermal intermediate state, whereas for micelles with $w_0 = 1$ and $w_0 = 2$ such a state is not observed. The nonthermal intermediate state that can no longer be reached for small micelles is probably formed by the overtone of the H-O-H bending mode, which is in resonance with the red wing of the O-H stretch absorption band of bulk liquid water. The truncation 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. 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 redshift 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 nonthermal 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 [14], but not for $w_0 = 2$ micelles [15]. The relaxation time constant τ_{eq} therefore probably 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 ~ 0.2 ps [16], which agrees quite well with the value of τ_{eq} of 0.3 ± 0.1 ps. The bending mode itself can only relax to the intermolecular modes of which the librations have the highest frequencies ($\sim 800 \text{ cm}^{-1}$). The librational frequencies show a decrease of $\sim 25\%$ when liquid water is confined in a micelle with $w_0 = 1$ [3], which probably will affect τ_{eq} . Unfortunately, we could determine τ_{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 liquid H_2O . For most other systems, including HDO and alcohols, the overtone of the bending mode is far out of resonance with the stretch vibration. This explains why the value of T_1 of bulk liquid H_2O is ~ 3 times shorter than that of bulk liquid HDO: D_2O [13]. 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_2O at the same frequency of the

O-H stretch vibration [13] (attained at an elevated temperature), and to that of ethanol clusters at the same frequency [17]. We conclude that the confinement of liquid water to the nanometer 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 Eq. (2).

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- [1] R.E. Riter, D.M. Willard, and N.E. Levinger, *J. Phys. Chem. B* **102**, 2705 (1998).
 - [2] J. Faeder and B.M. Ladanyi, *J. Phys. Chem. B* **104**, 1033 (2000).
 - [3] D.S. Venables, K. Huang, and C.A. Schmuttenmaer, *J. Phys. Chem. B* **105**, 9132 (2001).
 - [4] D. Fioretto, M. Freda, S. Mannaioli, G. Onori, and A. Santucci, *J. Phys. Chem. B* **103**, 2631 (1999).
 - [5] Q. Zhong, A.P. Baronavski, and J.C. Owrutsky, *J. Chem. Phys.* **118**, 7074 (2003).
 - [6] Q. Zhong, A.P. Baronavski, and J.C. Owrutsky, *J. Chem. Phys.* **119**, 9171 (2003).
 - [7] G. Seifert, T. Patzlaff, and H. Graener, *Phys. Rev. Lett.* **88**, 147402 (2002).
 - [8] A.J. Lock and H.J. Bakker, *J. Chem. Phys.* **117**, 1708 (2002).
 - [9] S. Woutersen and H.J. Bakker, *Nature (London)* **402**, 507 (1999).
 - [10] M.L. Cowan, B.D. Bruner, N. Huse, J.R. Dwyer, B. Chugh, E.T.J. Nibbering, T. Elsaesser, and R.J.D. Miller, *Nature (London)* **434**, 199 (2005).
 - [11] T. Patzlaff, M. Janich, G. Seifert, and H. Graener, *Chem. Phys.* **261**, 381 (2000).
 - [12] R.E. Miller, *Science* **240**, 447 (1988).
 - [13] S. Woutersen, U. Emmerichs, H.K. Nienhuys, and H.J. Bakker, *Phys. Rev. Lett.* **81**, 1106 (1998).
 - [14] J.C. Deak, S. Rhea, L. Iwaki, and D.D. Dlott, *J. Phys. Chem. A* **104**, 4866 (2000).
 - [15] J.C. Deak, Y. Pang, T.D. Sechler, Z. Wang, and D.D. Dlott, *Science* **306**, 473 (2004).
 - [16] N. Huse, S. Ashihara, E.T.J. Nibbering, and T. Elsaesser, *Chem. Phys. Lett.* **404**, 389 (2005).
 - [17] S. Woutersen, U. Emmerichs, and H.J. Bakker, *J. Chem. Phys.* **107**, 1483 (1997).