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Hydrogen Bonds

Finite Size Effects on Hydrogen Bonds in Confined Water**

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Bulk water has unique properties deriving from its ability to form a labile hydrogen-bond network.[1,2] However, water is often not present in its bulk form but rather trapped in small cavities (e.g., water in concrete, clays, zeolites, and nanochannels). Consequently, many efforts have been devoted to describing the confinement effects on the structure and dynamics of water.[3–7] The present understanding is that nanoconfinement induces a freezing of the molecular motions near the confining surface on a layer with a thickness of 0.4–0.8 nm.[8–11] Herein we clearly demonstrate that even large pores (up to 50 nm diameter), in which interfacial effects are negligible, can alter the properties of water. The hydrogen-bond network properties in confined media have been traced in real time by transient absorption infrared spectroscopy of the OH vibration.

We performed IR pump–probe experiments on nanoconfined water in fully hydrated controlled-pore glasses (CPG) of 1, 13, and 50 nm pore diameters, on surface water in low-hydration CPG (1 nm), and on bulk water.[12] We decided to work with dilute HOD in D_2O to suppress energy transfer between neighboring OH vibrators and to tune the optical density of the sample.

Figure 1 shows the time dependence of the transient absorption anisotropy that is directly connected to the rotational diffusion of the water molecules.[13,14] The characteristic rotational diffusion time increases when the pore size decreases. Such an evolution was to be expected as quasielastic neutron scattering[15,16] studies have shown slower diffusive motions in small pores. For a pore size of 50 nm, the rotational time (2.8 ps) is almost identical to that measured in bulk water (2.5 ps).[14] Water trapped in 1 nm pores compares well with surface water, for which the anisotropy, which remains high at long delay times, demonstrates hindered rotational motions. Similar behavior has been recently observed for water adsorbed both on soft[17] and hard[18,19] surfaces.

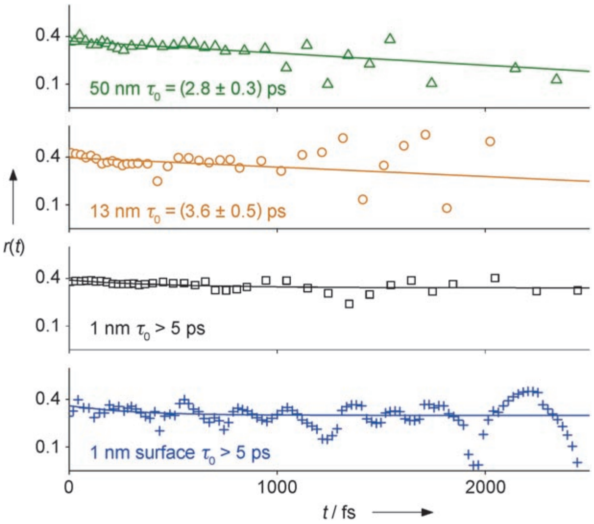

Figure 1. Anisotropy ($r(t)$ on a logarithmic scale) decay of surface water in a low-hydration 1 nm porous glass (+) and water confined in fully hydrated 50 nm (△), 13 nm (○), and 1 nm (□) porous glasses (lines correspond to a single-exponential fit).

All other transient absorption data (Figures 2B and 3) seem to contradict this apparent smooth dependence of the behavior of water on pore size. The transient spectra (Figure 2B) and the excited-state lifetime (Figure 3) show a discontinuous evolution when going from bulk to nanoconfined water and from nanoconfined to surface water.

The transient spectra of water are equivalent (Figure 2B) in all CPGs, but differ from both bulk and surface water: with respect to surface water, the shape and the bandwidth of the transient absorption are different; yet, contrary to bulk water no excited-state absorption is observed. The latter observation is even more surprising considering that there is no difference between the steady-state absorption spectra of bulk and nanoconfined water (Figure 2A).

To translate the data presented in Figure 2A and B into fundamental hydrogen-bond properties, we computed the OH frequency using a modified Lippincott–Schroeder (LS) potential function[20,21] for the O–H···O interactions. The absorption bands (static and transient) were calculated according to the procedure of Bakker et al.[21] These calculations rationalize the observed differences in Figure 2B as an approximately 100 cm^{-1} red shift of the excited-state absorption band of confined water with respect to bulk water (Figure S6 in the Supporting Information). Therefore, one has to invoke a substantial confinement-induced enhancement of the anharmonic character of the OH vibrator.

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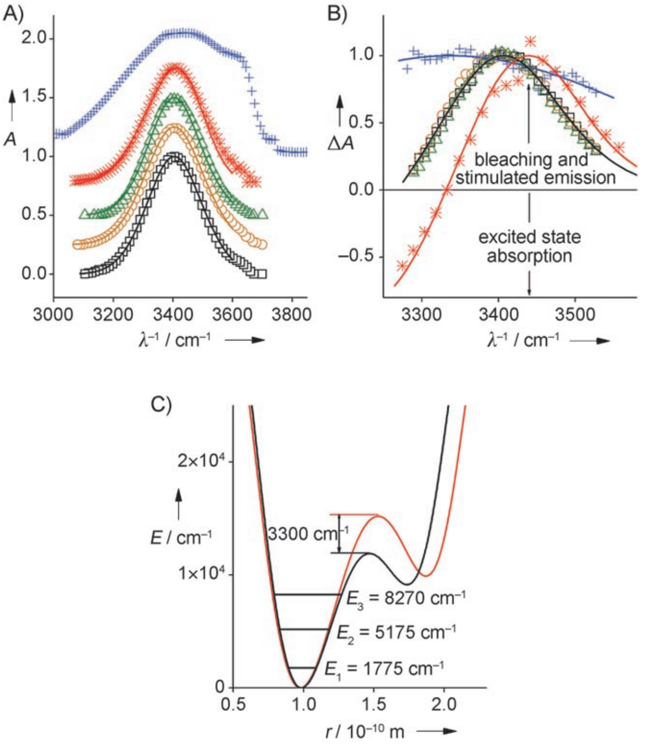

Figure 2. A) Normalized IR absorption spectra of surface water in a 1 nm sample in a low hydration state (+), confined water in fully hydrated 50 nm (△), 13 nm (○), and 1 nm (□) samples, and bulk water (*) in the OH stretching region. For clarity, the normalized spectra are offset by 0.2 absorbance units with respect to each other. The solid lines for water and nanoconfined water are obtained from a modified Lippincott–Schroeder[21,22] model. B) Normalized initial transient spectra of bulk, confined, and surface water; symbols as in (A). The solid lines for water (in red) and nanoconfined water (in black) are obtained from the same Lippincott–Schroeder model as for (A). The line for surface water is drawn to guide the eye. C) Potential (*E*) of a O–H···O system as described by the modified Lippincott–Schroeder model used in (A) and (B) for bulk (red) and confined (black) water. *r* is the O–H distance; the other parameters of the model are given in Table S4 in the Supporting Information, and the energy levels are given for nanoconfined water.

The LS potentials that fit both static and transient spectra of bulk and confined water are represented in Figure 2C for the most probable oxygen–oxygen distance: 0.288 nm for bulk water and 0.276 nm for confined water. Recent neutron-scattering experiments indeed indicate a contraction of the oxygen–oxygen distances in 4 nm porous glasses.[22] Another relevant result from Figure 2C is the drastic lowering (by 3300 cm^{-1}) of the proton-transfer potential barrier. Such a modification of water properties was invoked only for nearby interfaces.[23,24] Our capability to identify this change of the acid character of water far from the surface relies on probing vibrational excited states that are energetically close to the barrier for proton transfer.

One observes three different frequency dependencies for the OH relaxation time (Figure 3),[12] corresponding to surface, confined, and bulk water. Several models predict the dependency of relaxation times with respect to HO vibrational frequency.[25–28] However, there is a general agreement that the relaxation process depends on both structural factors (the O···O distance distribution,[25] the overlap of the stretching with the bending overtone,[26,27] and the average number of hydrogen bonds[28]) and dynamical ones (the time evolution of these structural factors before the relaxation process occurs; that is, the spectral diffusion).

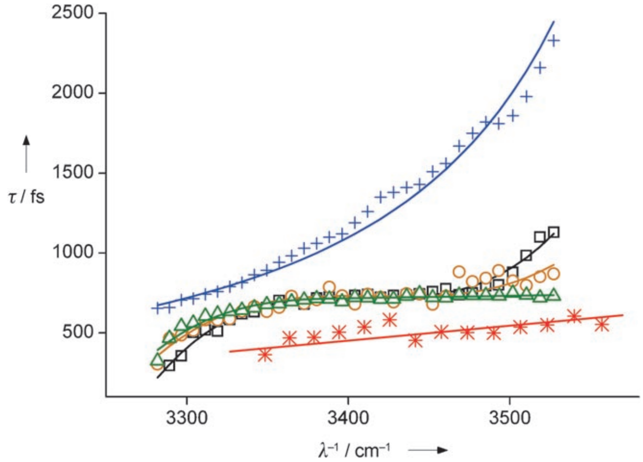

Figure 3. OH vibrator excited-state lifetime (τ) as a function of wavenumber (λ^{-1}) for surface water in a low hydration 1 nm porous glass (+), confined water in fully hydrated 50 nm (△), 13 nm (○), and 1 nm (□) samples, and bulk water (*). The line for surface water is a fit following the law proposed by Staib and Hynes.[25,29] The other lines are drawn to guide the eye.

For surface OH groups, the relaxation time τ_{OH} exhibits a strong frequency dependence that follows directly the relation $\tau_{OH} = \text{constant}/(\delta\omega_{OH})^{1.8}$ proposed by Staib and Hynes[25,29] for relaxation occurring through coupling of the OH stretch with the accepting O···O mode. Our capability to measure precisely such a dependency demonstrates that the spectral diffusion is limited at the interface, as already observed for alumina.[19]

For bulk water we observe a weak linear frequency dependence centered at 500 fs, which agrees with the measurements of Gale et al.[26] The calculations of Lawrence and Skinner reproduce this dependency by evaluating the coupling of the OH stretch with the HOD bending mode.[27]

The relaxation behavior of nanoconfined water is unique both in its average value and in its frequency dependence. We will not discuss the lifetime decrease below 3400 cm^{-1}, as we can not exclude an effect of the excited-state absorption in this region (see Figure S6 in the Supporting Information). On the blue side of the spectrum we measure a marginal increase of the lifetime when the pore size decreases, which may be the signature of increased spectral diffusion for large pores and must be connected to the slower rotational dynamics with a higher confinement (Figure 1). However, this pore-size dependence is too small (see Section VII in the Supporting Information) to interpret the data with a frozen component at the interface and a core component with the characteristics of bulk water, as proposed for reverse micelles.[8,9,13] The fact that the average transient optical density lifetime value of 730 ± 20 fs (Section VII in the Supporting Information) is quasi independent on the pore size and significantly larger than that in bulk water (570 ± 20 fs[12]) confirms that there is a global change of the relaxation behavior by confinement effects. According to Schwarzer et al.,[28] such an increase of lifetime can be associated with a decrease of the mean number of hydrogen bonds. Indeed, neutron-scattering studies in Vycor glasses have suggested that the number of hydrogen bonds decreases in nanoconfined samples relative to bulk water.[22]

Our study confirms that the confinement effect influences the molecular motions and proton delocalization, but, up to now, such effects have been observed only for water in the immediate vicinity of interfaces;[5,23] therefore, no confinement effects were expected for large pores (> 5–8 nm). The present study demonstrates that even very large pores induce specific modifications of the hydrogen-bond properties, both with respect to surface water and to bulk water.

The changes of the hydrogen bond properties are not dependent on the surface/volume ratio, which proves that they are not surface-induced but rather finite size effects. These observations differ significantly from that of Dokter et al.[13] because that study involved reverse micelles that are flexible and in equilibrium with the surrounding oil, whereas this study addresses rigid materials. The results differ also from simulations of water in small model pores which predict a two-layer system.[11,30] However, as stated by Brovchenko and Oleinikova,[30] the wetting behavior of water may change with the pore radius, but very large pore simulations are required to confirm such a hypothesis.

Thus, the present findings lead us to assume that the microscopic properties of water are globally modified by nanoconfinement; that is, the microscopic properties of water are influenced by the space it occupies.

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[1] F. H. Stillinger, *Science* **1980**, *209*, 451 – 457.
[2] E. Nibbering, T. Elsaesser, *Chem. Rev.* **2004**, *104*, 1887 – 1914.
[3] U. Raviv, P. Laurat, J. Klein, *Nature* **2001**, *413*, 51 – 54.
[4] M. C. Bellissent-Funel, *J. Mol. Liq.* **1998**, *78*, 19 – 28.
[5] A. M. Dokter, S. Woutersen, H. J. Bakker, *Phys. Rev. Lett.* **2005**, *94*, 178301.
[6] H. S. Tan, I. R. Piletic, R. E. Riter, N. E. Levinger, M. D. Fayer, *Phys. Rev. Lett.* **2005**, *94*, 057405.
[7] D. E. Moilanen, N. E. Levinger, D. B. Spry, M. D. Fayer, *J. Am. Chem. Soc.* **2007**, *129*, 14311 – 14318.
[8] I. R. Piletic, D. E. Moilanen, D. B. Spry, N. E. Levinger, M. D. Fayer, *J. Phys. Chem. A* **2006**, *110*, 4985 – 4999.
[9] D. Cringus, A. Bakulin, J. Lindner, P. Vohringer, M. S. Pshenichnikov, D. A. Wiersma, *J. Phys. Chem. B* **2007**, *111*, 14193 – 14207.
[10] M. Rovere, M. A. Ricci, D. Vellati, F. Bruni, *J. Chem. Phys.* **1998**, *108*, 9859 – 9867.
[11] P. Gallo, M. A. Ricci, M. Rovere, *J. Chem. Phys.* **2002**, *116*, 342 – 346.
[12] Nonlinear infrared experiments are sensitive to the pump–probe setup. An example of such sensitivity is presented in the Supporting Information for transient absorption (see Section VI). This point was also discussed by Laubereau and coworkers (R. Laenen, K. Simeonidis, A. Laubereau, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 925 – 932) for the vibrational relaxation time. Therefore, even though quite similar experiments were already conducted on bulk water, we revisited it along with surface and confined water to get data sets that would be fully comparable.
[13] A. M. Dokter, S. Woutersen, H. J. Bakker, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15355 – 15358.
[14] G. Gallot, S. Bratos, S. Pommeret, N. Lascoux, J. C. Leicknam, M. Kozinski, W. Amir, G. M. Gale, *J. Chem. Phys.* **2002**, *117*, 11301 – 11309.
[15] M. C. Bellissent-Funel, *J. Phys. Condens. Matter* **2001**, *13*, 9165 – 9177.
[16] A. Faraone, L. Liu, C. Y. Mou, P. C. Shih, J. R. D. Copley, S. H. Chen, *J. Chem. Phys.* **2003**, *119*, 3963 – 3971.
[17] A. Ghosh, M. Smits, J. Bredenbeck, M. Bonn, *J. Am. Chem. Soc.* **2007**, *129*, 9608 – 9609.
[18] J. A. McGuire, Y. R. Shen, *Science* **2006**, *313*, 1945 – 1948.
[19] S. Le Caer, D. J. Palmer, M. Lima, J. P. Renault, G. Vigneron, R. Righini, S. Pommeret, *J. Am. Chem. Soc.* **2007**, *129*, 11721 – 11729.
[20] E. R. Lippincott, R. Schroeder, *J. Chem. Phys.* **1955**, *23*, 1099 – 1106.
[21] H. J. Bakker, H. K. Nienhuys, G. Gallot, N. Lascoux, G. M. Gale, J. C. Leicknam, S. Bratos, *J. Chem. Phys.* **2002**, *116*, 2592 – 2598.
[22] H. Thompson, A. K. Soper, M. A. Ricci, F. Bruni, N. T. Skipper, *J. Phys. Chem. B* **2007**, *111*, 5610 – 5620.
[23] V. Garbuio, C. Andreani, S. Imberti, A. Pietropaolo, G. F. Reiter, R. Senesi, M. A. Ricci, *J. Chem. Phys.* **2007**, *127*, 154501.
[24] R. Senesi, A. Pietropaolo, A. Bocedi, S. E. Pagnotta, F. Bruni, *Phys. Rev. Lett.* **2007**, *98*, 138102.
[25] A. Staib, J. T. Hynes, *Chem. Phys. Lett.* **1993**, *204*, 197 – 205.
[26] G. Gale, G. Gallot, N. Lascoux, *Chem. Phys. Lett.* **1999**, *311*, 123 – 125.
[27] C. P. Lawrence, J. L. Skinner, *J. Chem. Phys.* **2003**, *119*, 3840 – 3848.
[28] D. Schwarzer, J. Lindner, P. Vohringer, *J. Phys. Chem. A* **2006**, *110*, 2858 – 2867.
[29] R. Rey, K. B. Moller, J. T. Hynes, *Chem. Rev.* **2004**, *104*, 1915 – 1928, and references therein.
[30] I. Brovchenko, A. Oleinikova, *J. Phys. Chem. C* **2007**, *111*, 15716 – 15725.