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# Effect of Surface Charge on the Vibrational Dynamics of Interfacial Water

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Hydrogen bonds are responsible for many properties of water.[1] Fast molecular rearrangements of this dynamic network, resulting from the breaking and reforming of hydrogen bonds on the ultrafast time scale, dictate many fundamental phenomena in aqueous media.[2] The rate at which water molecules accept energy dissipated during the course of chemical reactions in aqueous media affects the reaction dynamics. Energy transfer within and between water molecules ultimately governs many biological and chemical processes.[3] This has motivated the search for detailed knowledge of the structure and the dynamics of hydrogen bonded networks of water.[3−8] It is known that the vibrational lifetime of the O−H stretch in bulk $H_2O$ is ~200 fs.[9] Population relaxation is believed to proceed via coupling to the overtone of the bending mode and a combination of the bending mode and low frequency hydrogen bond modes.[4,10]

Until recently, the study of surface water vibrational dynamics has been a challenge.[11−13] The vibrational relaxation and thermalization in the hydrogen bonded network of interfacial water at the silica surface at neutral pH (~5.7) were determined to proceed with time constants of 300 and 700 fs, respectively.[11] The dynamics of hydrogen bonded OH species at the air/water interface were reported to involve fast (100 fs) and slower (~500 fs) time constants, assigned to vibrational lifetime and thermalization, respectively.[12] The similarity of the time constants of vibrational dynamics at surfaces and in the bulk led to the general conclusion that, despite the difference in ordering of interfacial and bulk water, the ultrafast dynamics are the same.[11,12]

The vibrational dynamics of membrane water was, however, shown to be significantly different from that of the air/water interface.[14] The vibrational lifetime is long (~500 fs) at the blue side (~3500 $cm^{-1}$) and reaches the values of bulk or air/water interface (<200 fs) at the red side (3200 $cm^{-1}$) of the hydrogen bond spectral region.[14] The frequency dependent vibrational lifetime was assigned to the decoupling of interfacial water from the bulk.[14] The dynamics of membrane bound water is complicated by the numerous different water species, e.g., those which strongly interact with the surface headgroup, water molecules inside the alkyl chains and the interfacial water molecules that interact with the bulk water. It is interesting to eliminate such complexity and to probe the vibrational dynamics of interfacial water terminating the bulk.

The water/silica interface is an ideal model to explore the effect of ordering of water on vibrational dynamics. In this system the surface charge, interfacial electric field, and interfacial water structure can conveniently be changed via bulk pH. The surface charge density at the silica/water interface is known to be close to zero at a pH range of 2−5 and starts increasing from pH ≈ 6.[15,16] At pH > 10 most of the surface silanols are deprotonated leading to a strong interfacial electric field.[15,16] Second harmonic generation measurements reveal that the surface electric field polarizes and orients several layers of water molecules into the bulk phase, so that the near interface region also contributes to the nonlinear optical response.[17] Vibrational sum frequency generation (VSFG) has also been used to study the structure of water near the silica surface, and two prominent peaks at ~3200 and ~3450 $cm^{-1}$ were observed.[18−21] Regardless of the peak assignments, which are still under debate,[22−24,28] it is known that the electric field resulting from the deprotonation of the silica surface at high pH leads to the enhancement of the VSFG signal.[18−20] It is reasonable to expect that the vibrational dynamics of O−H stretching in the hydrogen bond region of the water/fused silica interface should change as the interfacial charge, and hence the solvent ordering, is altered.

Here for the first time we report the effect of surface charge, the associated surface electric field, and the resulting ordering of interfacial water on the vibrational dynamics of O−H stretching of interfacial water at the $H_2O$/fused silica interface. Our results suggest that the vibrational lifetime of hydrogen-bonded OH at the water/fused silica interface becomes dramatically longer at neutral surface charge (low pH), in the absence of the surface electric field.

The vibrational dynamics was measured using IR pump-SFG probe (see Supporting Information (SI)). The magnitude of the decrease in the VSFG signal (bleach) after IR pump excitation of the red (3200 $cm^{-1}$) or blue (3450 $cm^{-1}$) side of the hydrogen bonded OH region of the $H_2O$/fused silica interface is approximately the same at pH = 2 and 12 (Figure 1). However, the recovery of the bleach to equilibrium values shows significantly different behavior for pH = 2 and 12.

A four level system (SI), extensively used in the interpretation of the vibrational dynamics of bulk[9] and, more recently, surface water,[11,12] was employed to analyze the data and extract the vibrational lifetimes ($T_1$) and thermalization ($T_{th}$) time constants. For a given pH, the data at 3200 and 3450 $cm^{-1}$ were simultaneously fit using a global fit (see SI). The biexponential fit (SI) reveals that the value of $T_1$ at pH = 2 (570 ± 70 fs) is more than two times longer than that at pH = 12 (255 ± 25 fs). $T_{th}$ is longer than $T_1$ and occurs with a similar time constant for pH = 2 (700 ± 50 fs) and pH = 12 (800 ± 30 fs).

The change in the vibrational lifetime of hydrogen bonded OH should in principle be related to the structural change of interfacial water observed in the SHG and VSFG spectra of the water/silica interface.[17−20] The electric field, resulting from the deprotonation of the silica surface with increasing pH, penetrates into the bulk water and extends the anisotropic interfacial regions into the initially centrosymmetric bulk phase resulting in the contribution of the third-order nonlinear susceptibility ($\chi^{(3)}$) to the VSFG, in addition to the second-order term ($\chi^{(2)}$).[17] At high pH, therefore, the SFG probes water molecules that may in principle be as far as the Debye length from the interface, resulting in dynamics that is similar to that of bulk water.

At low pH, the surface is neutral and therefore no charge induced electric field is present at the surface. In this situation VSFG probes only the dynamics of the few noncentrosymmetric layers of water molecules at the silica surface. According to the four level system (SI), the rate of vibrational energy transfer depends on the availability of inter- and intramolecular modes (intermediate state)

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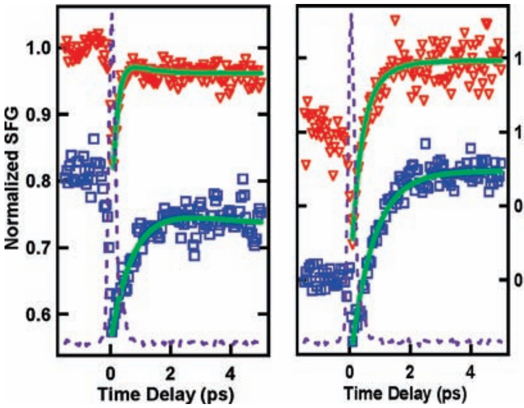

***Figure 1.*** IR pump-SFG probe trace of O−H stretching of water/IRFS for $\nu_{\text{probe}} = \nu_{\text{pump}} = 3200$ cm$^{-1}$ (left) and $\nu_{\text{probe}} = \nu_{\text{pump}} = 3450$ cm$^{-1}$ (right) at pH = 2 (blue square) and pH = 12 (red triangle). The green solid lines are the biexponential fit (see SI). The third-order cross-correlation between IR pump, IR probe and visible is shown by the dashed line. The polarization combination for SFG, visible and IR is S,S,P.

to dissipate the vibrational energy. Compared to the bulk, water molecules at the interface have lost part of their solvation shell (SI) which leads to a decrease in the number of accepting modes for the vibrational energy, less efficient inter- and intramolecular coupling, and ultimately the lengthening of the vibrational lifetime.

While the major step in $T_1$ relaxation is the transfer of energy to a single accepting mode through an intramolecular process, the density of states of intermolecular modes plays a role too.[29] The density of intermolecular states accessible to the molecules probed at high pH is greater because under those conditions most of the water molecules detected by VSFG are completely solvated, whereas at low pH interfacial water molecules are incompletely solvated and experience a reduced density of low frequency hydrogen bond and libration modes. After the initial vibrational relaxation ($T_1$), additional relaxation channels (e.g., thermalization), for both high and low pH, proceed with similar time constants (700−800 fs) as in the bulk.

The slowing down of the vibrational dynamics at low pH observed here is analogous with the vibrational dynamics of water confined in reversed micelles where water molecules in the vicinity of the surfactant have longer vibrational dynamics than water molecules in the core shell (bulk water).[25,26] Similarly, simulations of the vibrational dynamics of neutral solutes at aqueous interfaces predict a lengthening of the vibrational lifetime, rationalized by the reduced effective solvation at the interface, compared to the bulk.[27]

The vibrational lifetime reported for the water/silica interface at near neutral pH (∼5.7), ∼300 fs,[11] is consistent with our results; i.e., it lies between the vibrational lifetimes at pH = 2 and 12 reported here. At pH (∼5.7) the silica surface has acquired some charge, although less than at pH = 12. The resulting electric field polarizes water molecules to some extent into the bulk water (SI) which leads to the conclusion that the dynamics are similar to that of the bulk.

Our results demonstrate that there is a fundamental difference between the vibrational dynamics of bulk and surface water in the absence of surface charge. The primary reason for the longer vibrational lifetime of O−H at the $H_2O$/silica interface at the neutral surface is attributed to the decrease in the density of states of the low frequency modes (intermolecular forces) due to incomplete solvation of the first layer of interfacial water molecules, resulting from the decreased number of neighboring water molecules, probed by VSFG.

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**Supporting Information Available:** Description of the setup, sample preparation, and data analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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## References

(1) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997.
(2) Hochstrasser, R. M.; Hofacker, G. L.; Trommsdorff, H. P.; Chandler, D. *Chem. Phys.* **2000**, *262*, VI–VI.
(3) Woutersen, S.; Bakker, H. J. *Nature* **1999**, *402*, 507–509.
(4) Wang, Z. H.; Pakoulev, A.; Pang, Y.; Dlott, D. D. *J. Phys. Chem. A* **2004**, *108*, 9054–9063.
(5) Steinel, T.; Asbury, J. B.; Zheng, J. R.; Fayer, M. D. *J. Phys. Chem. A* **2004**, *108*, 10957–10964.
(6) Fecko, C. J.; Eaves, J. D.; Loparo, J. J.; Tokmakoff, A.; Geissler, P. L. *Science* **2003**, *301*, 1698–1702.
(7) Cowan, M. L.; Bruner, B. D.; Huse, N.; Dwyer, J. R.; Chugh, B.; Nibbering, E. T. J.; Elsaesser, T.; Miller, R. J. D. *Nature* **2005**, *434*, 199–202.
(8) Rey, R.; Moller, K. B.; Hynes, J. T. *Chem. Rev.* **2004**, *104*, 1915–1928.
(9) Lock, A. J.; Woutersen, S.; Bakker, H. J. *J. Phys. Chem. A* **2001**, *105*, 1238–1243.
(10) Nibbering, E. T. J.; Elsaesser, T. *Chem. Rev.* **2004**, *104*, 1887–1914.
(11) McGuire, J. A.; Shen, Y. R. *Science* **2006**, *313*, 1945–1948.
(12) Smits, M.; Ghosh, A.; Sterrer, M.; Muller, M.; Bonn, M. *Phys. Rev. Lett.* **2007**, *98*, 098302.
(13) Bordenyuk, A. N.; Benderskii, A. V. *J. Chem. Phys.* **2005**, *122*, 134713–134724.
(14) Ghosh, A.; Smits, M.; Bredenbeck, J.; Bonn, M. *J. Am. Chem. Soc.* **2007**, *129*, 9608–9609.
(15) Bolt, G. H. *J. Phys. Chem.* **1957**, *61*, 1166–1169.
(16) Dove, P. M.; Craven, C. M. *Geochim. Cosmochim. Acta* **2005**, *69*, 4963–4970.
(17) Ong, S. W.; Zhao, X. L.; Eisenthal, K. B. *Chem. Phys. Lett.* **1992**, *191*, 327–335.
(18) Du, Q.; Freysz, E.; Shen, Y. R. *Phys. Rev. Lett.* **1994**, *72*, 238–241.
(19) Kim, J.; Kim, G.; Cremer, P. S. *J. Am. Chem. Soc.* **2002**, *124*, 8751–8756.
(20) Nihonyanagi, S.; Ye, S.; Uosaki, K. *Electrochim. Acta* **2001**, *46*, 3057–3061.
(21) Ostroverkhov, V.; Waychunas, G. A.; Shen, Y. R. *Chem. Phys. Lett.* **2004**, *386*, 144–148.
(22) Tian, C. S.; Shen, Y. R. *Phys. Rev. Lett.* **2008**, *101*, 139401.
(23) Sovago, M.; Campen, R. K.; Wurpel, G. W. H.; Muller, M.; Bakker, H. J.; Bonn, M. *Phys. Rev. Lett.* **2008**, *101*, 139402.
(24) Tian, C.; Shen, Y. R. *J. Am. Chem. Soc.* **2009**, *131*, 2790–2791.
(25) Park, S.; Moilanen, D. E.; Fayer, M. D. *J. Phys. Chem. B* **2008**, *112*, 5279–5290.
(26) Cringus, D.; Lindner, J.; Milder, M. T. W.; Pshenichnikov, M. S.; Vohringer, P.; Wiersma, D. A. *Chem. Phys. Lett.* **2005**, *408*, 162–168.
(27) Benjamin, I. *Chem. Phys. Lett.* **2009**, *469*, 229–241.
(28) Sovago, M.; Campen, R. K.; Wurpel, G. W. H.; Muller, M.; Bakker, H. J.; Bonn, M. *Phys. Rev. Lett.* **2008**, *100*, 173901.
(29) Kropman, M. F.; Nienhuys, H. K.; Woutersen, S.; Bakker, H. J. *J. Phys. Chem. A* **2001**, *105*, 4622–4626.

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