Supporting Information

Effect of Surface Charge on the Vibrational Dynamics of Interfacial Water

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1. Experimental:

a) Sample Preparation:

The IR fused silica prism (ISP optics) and Teflon sample holder were cleaned by piranha solution (3:1(v/v), concentrated sulfuric acid and 30 % hydrogen peroxide) prior to experiments. Buffer pH solutions were prepared using HCl (Fisher, ACS Certified), NaOH (Fisher, ACS certified) and distilled Millipore water (>18.2 MΩ.cm resistivity).

b) Optical set up:

A femtosecond regenerative amplifier (Quantronix, Integra-E; central wavelength 810 nm, repetition rate 1 kHz, pulsewidth ~110 fs FWHM, pulse energy ~3 mJ) pumps an optical parametric amplifier (Light Conversion, TOPAS) which generates tunable IR radiation (1180 – 2640 nm). Mid-infrared pulses, ~170 cm^{-1} FWHM, were obtained by difference frequency generation in an $AgGaS_2$ crystal. The IR pump, IR probe and visible beams with energies of ~8, 2 and 2 µJ/pulse, incident at the surface with angles of 72 $^{\circ}$, 58 $^{\circ}$ and 65°, were focused to beam waists of 250, 200 and 200 µm, respectively. The SFG signal was separated from the reflected visible light by short pass filters (Melles Griot) and detected by a CCD detector (Princeton Instruments) coupled with a spectrograph (300i, Acton Research Corp.).
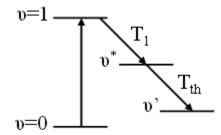
c) Pump-Probe set up:

IR pump-SFG probe measurements were conducted in one color scheme where the polarization and frequency of the IR pump and probe kept same. The third-order cross-correlation between IR pump, IR probe and visible was used to maximize the SFG signal and to define the position of t=0. The time delay between the IR probe and the visible was fixed and the time delay between the IR pump and the IR probe (and visible) was scanned for tr-SFG and third-order cross-correlation measurements. The SFG was recorded in 50 fs time steps using LABVIEW 8 software.

2. Data Analysis:

a) Four level system:

A four level system which has been extensively used in the interpretation of the vibrational dynamics of bulk [1] and, more recently, surface water [2,3], was employed to analyze the dynamics. As shown in scheme S1, the energy of the excited state of the OH stretch is first transferred to an intermediate state (υ^*) with relaxation time of T_1 attributed to the vibrational lifetime. This intermediate state involves hydrogen bond stretch or the overtone of bending mode [4,5]. The energy of the intermediate state is then transferred to the so called hot ground state $(\upsilon^')$ with a time constant T_{th} (thermalization time constant). The thermalization process may involve hydrogen bond breaking and re-formation and other structural dynamics [6].

Scheme S1. The four-level system for the

analyzing the vibrational dynamics.

Similar to previous analyses of dynamics at the silica water interface [3], the recovery of

the SFG signal was fit to the following expression:

$$S(t) = 1 - (1 - S_0)\, e^{-(t-t_0)/T_1} + \Delta S\, (1 - e^{-(t-t_0)/T_{th}})$$

(S1)

where S_0 is the SFG signal at $t=t_0$ and $|\Delta S|$ is the SFG signal offset at long delay times

(equilibrium). The value of t_0 which corresponds to the minimum of the SFG signal was

>0 (~100 fs) in the observed dynamics, indicating that the coherent artifact resulting from
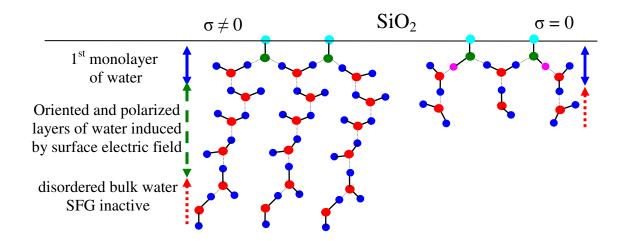
overlap of pump and probe is negligible [2].

b) Simultaneous fit:

For a given pH, the dynamics at 3200 and 3450 cm^{-1} were fit simultaneously to get a

common set of T_1 and T_{th} values. For a given pH and IR excitation wavelength we

acquired at least two data sets from independent experiments performed on different

days. For each set of data at 3200 and 3450 cm^{-1} at a given pH a simultaneous fit was

performed. The pump-probe data shown in Figure 1 is one of these data sets and the fit is

the simultaneous fit to that data. As can be seen the simultaneous fit describes the data

very well, suggesting a similar T_1 and T_{th} at 3200 and 3450 cm^{-1}, i.e. very rapid spectral diffusion. The T_1 and T_{th} time constants reported in the paper are the calculated average for all of these fits at a given pH and the error is the standard deviation.

3. Structure of water at neutral and charged silica surface:

As discussed in the text, at high pH, the surface electric field resulting from the deprotonation of the silanol groups, polarizes and orients several layers of water molecules into the initially disordered bulk water.   Consequently, the depth through which the water molecules contribute to the SFG differ at neutral and charged surface. Cartoon (S1) illustrates the different interfacial and bulk regions as well as the surface specificity of the SFG at neutral and charged surface.

Cartoon S1: structure of water at neutral (σ =0) and charged ($\sigma \neq$0) surface of SiO$_2$. The solid blue arrows, in both neutral and charged surface, show the first layer of water that is in contact with the silica surface. At the charged surface there are several layers of water that are oriented and/or polarized by the surface electric field and therefore contribute to

the SFG. The dashed green arrow shows these water molecules, which are absent at the neutral surface. Disordered bulk water lies just below the first layer monolayer of water (in the case of neutral surface) or oriented/polarized water (in the case of charged surface). These water molecules, spanning the region indicated by red dotted arrows in both neutral and charged surface, do not contribute to the SFG.

References:

(1)   Lock, A. J.; Woutersen, S.; Bakker, H. J. *Journal of Physical Chemistry A* **2001**, *105*, 1238-1243.
(2)   Smits, M.; Ghosh, A.; Sterrer, M.; Muller, M.; Bonn, M. *Physical Review Letters* **2007**, *98*, 098302.
(3)   McGuire, J. A.; Shen, Y. R. *Science* **2006**, *313*, 1945-1948.
(4)   Lawrence, C. P.; Skinner, J. L. *Journal of Chemical Physics* **2003**, *119*, 3840-3848.
(5)   Nibbering, E. T. J.; Elsaesser, T. *Chemical Reviews* **2004**, *104*, 1887-1914.
(6)   Rey, R.; Moller, K. B.; Hynes, J. T. *Chemical Reviews* **2004**, *104*, 1915-1928.