Vibrational Spectroscopy of Water at Liquid/Solid Interfaces: Crossing the Isoelectric Point of a Solid Surface

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We have used IR-visible sum-frequency generation (SFG) spectroscopy to demonstrate that water dipoles at a liquid/solid interface flip by 180° when the *p*H of the aqueous solution crosses the isoelectric point of the surface (IEPS). We have also shown, for the first time, that the SFG signal intensity and thus the nonlinear polarizability of a water/solid interface depends strongly on the hydroxyl number density of the solid surface. A new methodology for the determination of the IEPS of a nonconductive, low-surface area material was introduced.

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Many physical and chemical properties of water/solid oxide interfaces are linked to the isoelectric point of solid surfaces (IEPS) [1]. When the *p*H of an aqueous solution crosses the isoelectric point of an oxide surface, the interfacial charge changes sign. This crossing affects many important interfacial phenomena such as the orientation of water dipoles, competitive adsorption, near interface interaction-distribution of ions and surface hydration. Despite the critical importance of these fundamental phenomena in a wide variety of practical treatment operations and processes, a complete microscopic understanding of their chemistry and physics affected by crossing the IEPS is still not available. This is due, in part, to the limitation of the number of sensitive probes suitable for direct inspection of buried interfaces.

IR-visible sum-frequency generation (SFG) and second-harmonic generation (SHG) spectroscopy techniques have been shown to be unique tools for characterization of buried interfaces [2–8]. Water/SiO_2 interfaces have been studied intensively using SFG and SHG probes [3,8]. Since the IEPS of SiO_2 is ~2 (i.e., total interface charge of water/SiO_2 is zero when the *p*H of the aqueous solution is ~2) for the range of *p*H covering most applications of interest the water/SiO_2 interface is either neutral or negatively charged. Therefore, the water/SiO_2 system does not provide the opportunity to evaluate the interfacial phenomena that can occur when the *p*H of the aqueous solution crosses the IEPS of a system.

However, the IEPS of sapphire (Al_2O_3) is ~8, thus both a positively (when the *p*H of the solution is <8) and a negatively (when the *p*H of the solution is >8) charged aqueous/solid interface can be achieved in this system. We have used SFG spectroscopy to monitor the structure of water molecules at water/Al_2O_3 interfaces. In this Letter we are reporting that the water dipole flips as the *p*H of the solution crosses the IEPS. This reorientation of water molecules was predicted by many researchers [9], but to our knowledge, was never directly observed. We have also shown, for the first time, that the SFG interfacial water signal intensities depend strongly on the total hydroxyl number density of the solid surface. This dependence provides a new method to investigate the mechanism governing the hydration and dehydration of oxide surfaces [10]. In addition, we have demonstrated that the effect of the interfacial charge density on the water SFG signal can be used to determine the IEPS of a nonconductive, low-surface area material.

In our experiments, the vibrational modes of water were excited using a tunable infrared laser beam with photon energy of 3000 to 3800 cm^{-1}. These excitations were combined with optical transitions, caused by a visible laser beam, to produce SFG resonance signals. The infrared light was generated by stimulated Raman scattering of a doubled Nd:YAG pumped dye laser in a multipass H_2 cell [11]. A portion of the output of the doubled Nd:YAG laser was used as the visible light source. The incident light pulse had a duration of ~7 nsec and an intensity of ~25 mJ/cm^2 for both the visible and IR beams. The visible, IR and SFG beams were set and detected in a P-polarization configuration where all electric fields are in the plane of incidence. Using this configuration, the sensitivity of the SFG signal intensities to ordering-disordering of interfacial water molecules was enhanced [12].

Our solid substrates consisted of equilateral Al_2O_3 (sapphire) and SiO_2 (quartz) prisms. A liquid cell was fabricated by clamping the sample prism against a Teflon backing machined with a hollow recess to hold the liquid sample. The SFG signals were generated at the interface of the solid prism and the liquid in a total-internal-reflection geometry at room temperature. Prior to each measurement the cell was disassembled and the prism was cleaned using a low-pressure RF plasma. H_2O was distilled and deionized using a milli-*Q* system (18M) and the *p*H of the aqueous solutions was varied to the desired value using NaOH or CH_3COOH.

To investigate the interaction between water and solid surfaces and to relate our investigation to previous work conducted on water/SiO_2 systems, we start our discussion by studying the SFG spectrum of a water/quartz interface. The SFG spectrum of the water/quartz interface, depicted in Fig. 1, exhibits two broad resonance features at ~3200 and ~3450 cm^{-1}. These features were identified earlier as the OH vibrational modes of H_2O from the Raman spectrum of bulk liquid water [13]. To further investigate the origin of these resonances and their dependence on molecular structure we measured the SFG spectrum of a H_2O-D_2O(1:1)/quartz interface. With this system we reduced the effective number density of water (H_2O) at the liquid/solid interface by *at least* a factor of 2. It should be noted that the isotopic H-D exchange and higher dipole moment of D_2O produce an even lower number density of H_2O at the interface. If we assign the resonance structures in Fig. 1*A* to isolated H_2O molecules, irrespective of their interfacial structures, then we would observe a SFG spectrum of the H_2O-D_2O(1:1)/quartz system that is qualitatively identical to the H_2O/quartz SFG spectrum, but *at least 4* times less intense. This is reproduced in Fig. 1*C* where we have divided data of Fig. 1*A* by a factor of 4. Comparing this to the SFG spectrum measured at the interface of the H_2O-D_2O(1:1)/quartz system (Fig. 1*B*), we see it is markedly different. This illustrates that the resonance signals generated at ~3200 and ~3450 cm^{-1} are not solely generated by isolated water molecules, but rather strongly depend on the structure of water at the liquid/solid interface.

Schere and co-workers [13] have shown that the feature at ~3200 cm^{-1} is an indication of a strong intermolecular coupling using both isotropic and anisotropic Raman spectra of bulk water at various temperatures. The resonance signal at ~3450 cm^{-1} was related to structurally disordered water molecules. These resonances were assigned to the ν_1 mode (OH stretching) and the Fermi resonance between ν_1 and the binary overtone of ν_2 (HOH deformation) mode [13,14]. A direct comparison between the SFG spectrum of water at a liquid/vapor interface and the infrared adsorption spectrum of ice has shown that water possesses a highly ordered structure at its liquid/vapor interface [15]. A similar interface induced ordering was also observed at water/solid interfaces and was linked to the interfacial electric field [8].

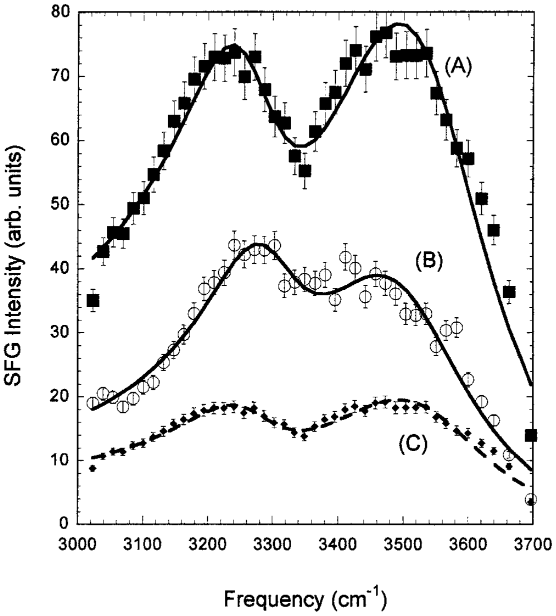

FIG. 1. SFG spectra of quartz/H_2O (*A*) and quartz/H_2O-D_2O(1:1) (*B*) interfaces. The spectrum, labeled *C*, was produced by dividing the SFG spectrum of quartz/H_2O (*A*) interface by a factor of 4.

The existence of a strong electric field at aqueous/oxide interfaces has been known for many years [9]. The interfacial electric field is produced by the oxide surface charge and can be as strong as 10^7 V/cm. This intense field interacts with the dipole moment of water and induces ordering of up to several layers at the interface [16]. The strength and the direction of the electric field at an aqueous/oxide interface are a function of the solution *p*H and the IEPS of the substrate. The isoelectric point of the surface (IEPS) is the *p*H of the aqueous solution where the total surface charge density is zero. The surface of the substrate is negatively (positively) charged if the *p*H of the solution is greater (less) than the IEPS of the substrate. This results from the following chemical reaction at the interface [17,18]:

$$\begin{aligned} \mathrm{SO^-}(p\mathrm{H} > \mathrm{IEPS}) &\overset{\mathrm{H^+}}{\longleftrightarrow} -\mathrm{SOH}(p\mathrm{H} = \mathrm{IEPS}) \\ &\overset{\mathrm{H^+}}{\longleftrightarrow} -\mathrm{SOH_2^+}(p\mathrm{H} < \mathrm{IEPS}) \quad (1) \end{aligned}$$

where *S* represents the substrate, and in our case is aluminum or silicon. The chemical equilibrium [1] suggests that the surface with the highest hydroxyl number density generates the strongest electric field at the interface. Motivated by this fact, we have obtained SFG spectra of the interface between water and two different Al_2O_3 surfaces, mainly a hydrated and a dehydrated surface. The surface of the first sample (sample *A*) was dehydrated using a 36 h/750 °C heat treatment. The surface of the second substrate (sample *B*) was hydrated using a 1 h boiling water treatment. As a result of these treatments, the number density of surface hydroxyl groups for sample *B* became much greater than that of sample *A* [19]. In Fig. 2 the interfacial SFG spectrum of water (pH = 3.0)/hydrated Al_2O_3 is compared to the SFG spectrum of water (pH = 3.0)/dehydrated Al_2O_3 interface. The strong SFG signal intensity produced by the hydrated substrate is due to a high surface density of hydroxyl groups which becomes positively charged in the presence of an acidic solution. This experiment convincingly demonstrates the dependence of the SFG signal strength on the interfacial charge density and more importantly on the total number density of surface hydroxyl.

Now that the strong effect of the interfacial electric field on the SFG spectrum of water is established, this phenomenon can be used to determine the IEPS of the substrate. There are several well-established experimental methodologies for the measurement of the IEPS of high

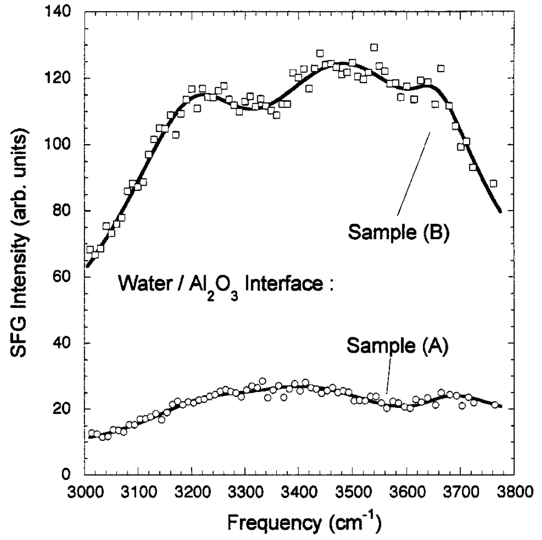

FIG. 2. SFG spectra of water (pH = 3.0)/dehydrated Al_2O_3 (sample A) and water/hydrated Al_2O_3 (sample B) interfaces. The strong SFG signal intensity produced by the hydrated substrate (sample B) was related to a high density number of surface hydroxyl group which became positively charged in the present of an acidic solution.

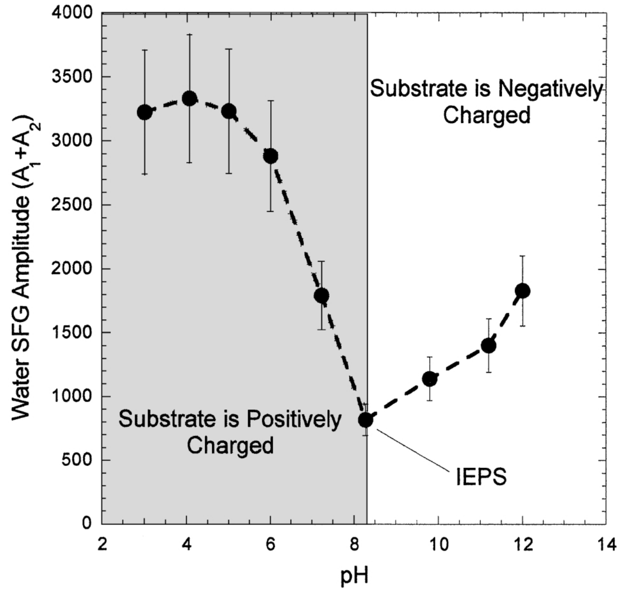

FIG. 3. The variation in total water SFG signal with the pH of the solution. The marked minimum in the signal strengths indicates that the IEPS of our sapphire surface is ~8.

surface area materials [20]. However, prior to our work, there was not a direct, nondestructive method to measure the IEPS of a low-surface area, nonconductive material. Our work was based on the observation that the amount of water detected by SFG probes (i.e., structurally ordered and disordered water) depends on the interfacial charge density and thus the electric field. Hence, the water SFG signal intensities are minimized at a pH equal to the IEPS where the total charge density is zero at the interface. In our experiments we have measured the SFG spectra of water/Al_2O_3 over a range of pH. To eliminate any possible variation caused by the frequency dependence of the IR source, each SFG spectrum was normalized to the IR power spectrum. To obtain quantitative results, the normalized SFG spectra were fitted to the following standard Lorentzian model [2],

$$I_{\mathrm{SFG}} = \left| A_{\mathrm{NR}} + \sum_{\alpha=1}^{3} \frac{A_\alpha e^{i\phi_\alpha}}{\omega - \omega_\alpha + i\Gamma_\alpha} \right|^2,$$

where A_α, Γ_α, and ω_α are the strength, damping constant, and angular frequency of a single resonant vibration, respectively. A_{NR} and ϕ_α are the nonresonant amplitude and the relative phase between the nonresonant and the resonant signals, respectively. In our analysis, we have used three resonance features with angular frequencies of ~3200, ~3450, and ~3700 cm^{-1} [21]. The result of the analysis is shown in Fig. 3 where we have plotted the sum of vibrational strengths at ~3200 and ~3450 cm^{-1} (i.e., $A_1 + A_2$). The marked minimum in the water signal strengths at pH of ~8 is assigned to a surface charge density of zero. This result indicates that the IEPS of our surface is ~8. This value is in agreement with previous results obtained with high surface area α alumina using electrophoresis [22] (IEPS = 8.4) and adsorption isotherms of potential-determining ions [18] (IEPS = 9.1).

Reaction [1] also suggests that the direction of the interfacial electric field changes with the pH of the aqueous solution. Based on the data presented above and reaction [1], the interfacial electric fields are in the opposite direction at the water (pH = 3)/Al_2O_3 and water (pH = 12)/Al_2O_3 interfaces. These fields align water molecules in opposite directions which results in different SFG spectra. For fix A_{NR} sign, when the dipole moment of a molecule rotates by 180° the relative phase between the resonant and nonresonant part of the signal changes by π. Using the interference spectra produced with SFG signals of SiO_2/stearic acid and D_2O/Al_2O_3 interfaces in the range of 2800 to 3000 cm^{-1}, we have determined that the A_{NR} sign does not vary with the solution pH. In Fig. 4 we have plotted the SFG spectra of water (pH = 3)/Al_2O_3 and water (pH = 12)/Al_2O_3 interfaces with their fitted curves. The results of our analysis indicate that the difference between the relative phase of these two spectra at ~3200 and ~3450 cm^{-1} are $(0.99 \pm 0.09)\pi$ and $(0.97 \pm 0.04)\pi$, respectively. This clearly demonstrates that when the pH of an aqueous solution crosses the isoelectric point of the surface (IEPS), the orientation of water dipoles flips by 180°. The effect of these orientation differences on the adsorption of organic materials from an aqueous solution onto solid surfaces is currently under investigation at our laboratory and will be reported shortly.

In conclusion, the molecular structure of water at liquid/solid interfaces was studied using SFG spectroscopy. To access both negatively and positively charged interfaces, an Al_2O_3 substrate was used as a model system. This

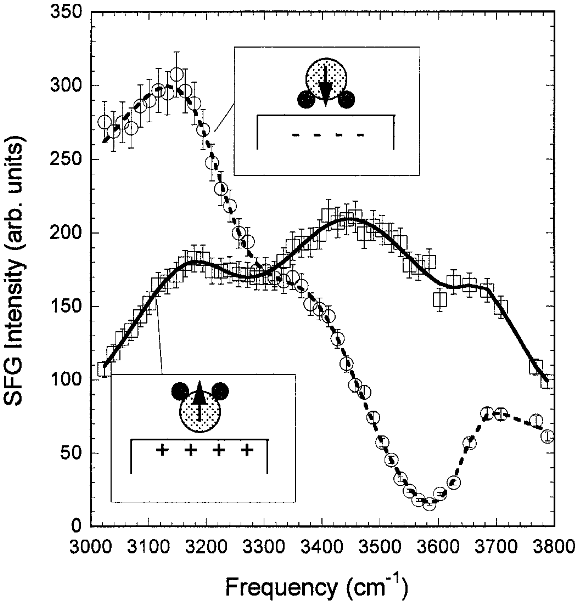

FIG. 4. SFG spectra of water ($p\mathrm{H} = 3$)/Al_2O_3 and water ($p\mathrm{H} = 12$)/Al_2O_3 interfaces with their fitted curves. The difference between the relative phase of these two spectra at ~3200 and ~3450 cm^{-1} demonstrates that when the pH of an aqueous solution crosses the IEPS the orientation of water dipoles flips by 180°.

system was essential for studying the effect of changing interfacial charge, achieved by crossing the IEPS of the substrate, on the structure of interfacial water molecules. We have demonstrated, for the first time, that the interfacial water SFG signal intensities depend strongly on the total hydroxyl number density at the interface and convincingly showed that the water dipole flips by 180° when the pH of the solution crosses the IEPS of the substrate. The dependence of the SFG signal intensities on total charge density was used to determine the IEPS of nonconductive, low-surface area materials.

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[1] T. W. Healy and D. W. Fuersteau, J. Colloid Sci. **20**, 376 (1965); C. Tanford, *The Hydrophobic Effect* (Wiley Interscience, New York, 1973).

[2] P. B. Miranda, V. Pflumio, H. Saijo, and Y. R. Shen, Chem Phys. Lett. **264**, 387 (1997); P. Guyot-Sionnest, J. H. Hunt, and Y. R. Shen, Phys. Rev. Lett. **59**, 1597 (1987).

[3] S. Ong, X. Zhao, and K. B. Eisenthal, Chem. Phys. Lett. **191**, 327 (1992).

[4] R. N. Ward, D. C. Duffy, P. B. Davies, and C. D. Bain, J. Phys. Chem. **98**, 8536 (1994).

[5] D. E. Gragson and G. L. Richmond, Langmuir **13**, 4804 (1997); D. E. Gragson and G. L. Richmond, J. Am. Chem. Soc. **120**, 366 (1998).

[6] S. R. Hatch, R. S. Polizzotti, S. D. Dougal, and P. Rabinowitz, J. Vac. Sci. Technol. A **11**, 2232 (1993).

[7] M. S. Yeganeh, J. Qi, A. G. Yodh, and M. C. Tamargo, Phys. Rev. Lett. **68**, 3761 (1992).

[8] Q. Du, E. Freysz, and Y. R. Shen, Phys. Rev. Lett. **72**, 238 (1994); **70**, 2313 (1993).

[9] See, for example, J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry* (Plenum, New York, 1973), Vol. 2, Ch. 7, and references therein.

[10] The dependence of SFG signal intensities on total hydroxyl number density has been utilized to study the hydration of SiO_2 surface *in situ.* D. Zhang, S. M. Dougal, and M. S. Yeganeh (to be published).

[11] P. Rabinowitz, B. N. Perry, and N. Levinos, Quantum Electron. **22**, 797 (1986).

[12] The second order susceptibility tensor elements of water acting in ppp, as opposed to sps and ssp, polarization are proportional to $\Pi_{i=1,3} f_i(\theta)$, where θ is the angle between the molecular axis and the direction normal to the interface and $f_i(\theta)$ represents $\sin(\theta)$ and/or $\cos(\theta)$ functions. M. S. Yeganeh, Bull. Am. Phys. Soc. **42**, 805 (1997).

[13] J. R. Schere, in *Advances in Infrared and Raman Spectroscopy,* edited by R. J. H. Clark and R. E. Hester (Heyden, Philadelphia, 1978), Chap. 3, p. 5.

[14] Some researchers assigned the resonance at ~3450 cm^{-1} to bifurcated hydrogen bonded water; see, for example, P. A. Giguere, J. Raman Spectrosc. **15**, 354 (1984).

[15] Q. Du, R. Superfine, E. Freysz, and Y. R. Shen, Phys. Rev. Lett. **70**, 2313 (1993).

[16] M. F. Toney *et al.,* Nature (London) **368**, 444 (1994); A. E. Russell, A. S. Lin, and W. E O'Grady, J. Chem. Soc. Faraday Trans. **89**, 195 (1993).

[17] J. C. Bolger, *Adhesion Aspects of Polymeric Coatings*, edited by K. L. Mittal (Plenum Press, New York, 1983); K. F. Hayes, G. Redden, W. Ela, and J. O. Lecie, J. Colloid Interface Sci. **142**, 48 (1991); S. M. Ahmed, Can. J. Chem. **44**, 1663 (1966); J. A. Davis, R. O. James, and J. O. Leckie, J. Colloid Interface Sci. **63**, 480 (1978).

[18] J. A. Yopps and D. W. Fuerstenau, J. Colloid Sci. **19**, 61 (1964).

[19] C. Morterra, G. Ghiotti, E. Garrone, and F. Boccuzzi, J. Chem. Soc. Faraday Trans. 1 **72**, 2722 (1976); G. D. Gatta, B. Fubini, and G. Venturello, Conf. Int. Thermodyn. Chim. **7**, 72 (1975).

[20] See, for example, A. W. Adamson, *Physical Chemistry of Surface* (John Wiley and Sons, New York, 1982).

[21] Since the free OH of the water molecules at an air/water interface generates resonance SFG signals at ~3700 cm^{-1} [8], we intuitively assign the ~3700 cm^{-1} resonance structure observed at a solid/water interface to the interfacial free OH. The intensity of this resonance signal varies with solid substrates. It is relatively strong at the Al_2O_3/water interface and undetectably small at both hydrated (hydrophilic) and dehydrated (hydrophobic) quartz/water interfaces. The exact spatial origin of the free hydroxyl group is under investigation in our laboratory.

[22] P. G. Johansen and A. S. Buchanan, Aust. J. Chem. **10**, 398 (1957).