Vibrational Spectra of Water Molecules at Quartz/Water Interfaces

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Optical sum-frequency generation was used to study OH stretch vibrations of water molecules at fused quartz/water interfaces. The results indicate that orientations and bond ordering of interfacial water molecules are strongly affected by electrostatic interaction and hydrogen bonding of the molecules with the quartz surface.

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Buried water interfaces play an important role in many surface science phenomena. Examples range from electrochemistry [1] and micelle formation [2] to biological processes such as membrane stability [2] and protein activity [3]. Over the past decades a great deal of insight on interfacial water molecules has been gained from theoretical studies, especially those with numerical simulations [4]. Experimental research on the topic, however, has been limited. Measurements of forces between two surfaces immersed in aqueous solution but separated at molecular distances seem to indicate that water molecules at the surfaces have both translational and orientational order [5]. Nuclear magnetic resonance studies also show some evidence that water molecules at surfaces behave differently than the bulk [6]. Optical second harmonic generation (SHG) and sum-frequency generation (SFG) have recently been proven to be ideal tools for investigation of liquid interfaces [7–9]. They can be readily adopted to probe water/solid interfaces. A SHG study has indeed been carried out to illustrate that water molecules near a charged surface are strongly oriented [8]. Unfortunately, little detail could be deduced because of a lack of spectroscopic information. In this paper, we present our work on vibrational spectra of water molecules, obtained by infrared-visible SFG, at fused quartz/water interfaces under various conditions. The results indicate that water molecules can interact with a quartz surface via two opposing forces: hydrogen bonding with silanol groups on the quartz surface and electrostatic interaction with surface charges resulting from ionization of the surface silanol (SiOH) groups. By varying the degree of surface ionization through adjustment of the pH value in the bulk water, it is possible to alter the relative strength of the two opposing forces, and induce a flip in the orientation of the surface water molecules. It appears that the orientations of the interfacial water molecules are closely related to the hydration force and heterogeneous ice nucleation at interfaces. Although our study is carried out only on quartz/water interfaces, we expect that the general behavior can be found for other water interfaces.

SFG as a technique for surface vibrational spectroscopy has been described in earlier publications [7]. Within the electric dipole approximation the process is forbidden in a centrosymmetric bulk medium like water, but allowed at the surface where the inversion symmetry is broken. It has been established in a previous paper [9] that the quadrupolar bulk contribution from water is not appreciable and the SFG is mainly from the dipolar contribution of water molecules with preferred orientation at the surface. The reflected SFG signal is proportional to the square of the surface nonlinear susceptibility $\chi_s^{(2)}(\omega_{\mathrm{out}}=\omega_{\mathrm{vis}}+\omega_{\mathrm{ir}})$, which can be decomposed into a resonant and a nonresonant part,

$$\chi_s^{(2)}=\chi_s^{(2)\mathrm{R}}+\chi_s^{(2)\mathrm{NR}}\,, \tag{1}$$

with ω_{ir} near resonance and ω_{vis} off resonance. The resonant $\chi_s^{(2)\mathrm{R}}$ can be related to the second order molecular polarizability $\alpha_{lmn}^{(2)}$ through a coordinate transformation averaged over the molecular distribution, denoted below by the angular brackets,

$$\chi_{s,ijk}^{(2)\mathrm{R}}=N_s\sum_{l,m,n}\langle(\hat{\mathbf{i}}\cdot\hat{\mathbf{l}})(\hat{\mathbf{j}}\cdot\hat{\mathbf{m}})(\hat{\mathbf{k}}\cdot\hat{\mathbf{n}})\rangle\alpha_{lmn}^{(2)}\,, \tag{2}$$

$$\alpha_{lmn}^{(2)}=\sum_q\frac{A_q}{(\omega_q-\omega_{\mathrm{ir}}-i\Gamma_q)}\,, \tag{3}$$

where N_s is the number of molecules per unit area contributing to the orientational average, while A_q, ω_q, and Γ_q are the strength, resonant frequency, and damping constants of the qth vibrational mode of the molecules. In the case of more than one monolayer of molecules having preferred polar orientation, N_s is proportional to the number of oriented layers. The SFG spectrum is obtained by tuning ω_{ir} over vibrational resonances. In our experiment on quartz/water interfaces, the fused quartz plate may also contribute to $\chi_s^{(2)}$. However, the contribution is small and nonresonant, and can be simply absorbed into $\chi_s^{(2)\mathrm{NR}}$. We also did not find spectral features due to the silanol groups at the quartz surface. Their contribution is expected to be small because the density of the surface silanol groups is known to be about $5/(\mathrm{nm})^2$ [10], smaller than the surface density of OH groups of $20/(\mathrm{nm})^2$ from water molecules at the surface. Furthermore, the bond angle between Si-O and O-H is about 120°; with the Si-O bond perpendicular to the surface the O-H bond is tilted at 60° from the surface nor-

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mal, making it weak for SFG detection.

The experimental setup for our SFG measurement has also been described elsewhere [7]. Briefly, a picosecond passive-active mode-locked laser system produced 0.5 mJ visible pulses at 0.532 μm and 0.2 mJ infrared pulses tunable from 2700 cm^{-1} to 3900 cm^{-1}. Both pulses were incident at angles around 47° from the quartz side and overlapped at a quartz/water interface formed by a fused quartz window in contact with ultrapure water (resistivity higher than 18 $\mathrm{M}\Omega/\mathrm{cm}$, obtained from Millipore filtration system) in a Teflon cell. Careful cleaning of the window and the cell was necessary to avoid any contamination. To vary the *p*H value of the bulk water, Fisher standard HCl and NaOH solutions were used. Adding NaCl to the solution allowed us to control the electrolyte concentration. All SFG spectra were normalized to the SFG signal reflected from a quartz crystal in order to reduce the effects of laser fluctuation, change of beam overlap, and ir absorption ($\sim 10\%$) of the fused quartz window.

Figure 1 presents the SFG spectra obtained from fused quartz/water interfaces for different *p*H values in the bulk water. A spectrum of the quartz/ice interface is also included for comparison. The output/input polarization combination for the spectra is *s* output, *s* visible input, and *p* infrared input, respectively. It is chosen to be discussed here because the resonant surface nonlinear susceptibility component $\chi_{yyz}^{(2)R}$ (with $\hat{z}$ along the surface normal) that can be deduced from the spectra is proportional to the Raman polarizability $\alpha_{yy}^{\mathrm{Raman}}$ of which the bulk water spectra have been discussed extensively in the literature. Indeed, our spectra resemble those of the isotropic Raman component of liquid water [11] except that peaks in our spectra are narrower, presumably due to restricted motion of water molecules at the surface. Two characteristic peaks appear at about 3200 and 3450 cm^{-1}, respectively, with another hardly visible one at 3600 cm^{-1}. The peak at 3200 cm^{-1} is generally attributed to the coupled symmetric OH stretch mode of tetrahedrally coordinated water molecules [11(b)]. This peak dominates in the ice spectra and therefore its strength is an indication of bond ordering in the water molecular arrangement. The assignment of the peak at 3450 cm^{-1} is still controversial. Some researchers assign it to be the symmetric stretch mode of asymmetrically bonded water molecules [11(b)] (molecules with one H strongly hydrogen bonded and the other H weakly bonded to neighboring molecules). Others assign it to molecules with bifurcated hydrogen bonds [11(c)]. In any case the strength of this peak is an indication of bond disordering of water molecular arrangement. The peak at 3600 cm^{-1} is believed to be due to the antisymmetric OH stretch of asymmetrically bonded water molecules. Its extreme weakness presumably results from a certain degree of forbiddance in the corresponding Raman scattering. This then suggests by inference that the antisymmetric OH stretch of the tetrahedrally coordinated water molecules is also not easily detectable, as it seems to be missing in our spectra.

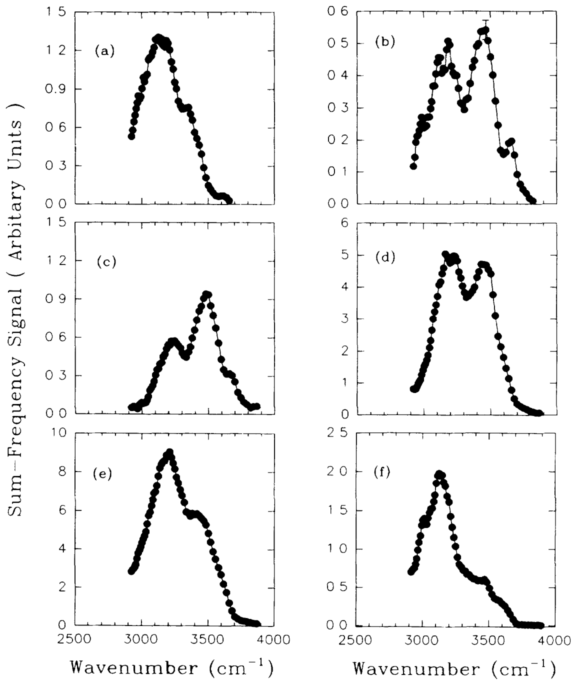

FIG. 1. SFG spectra from the quartz/water interfaces with different *p*H values in the bulk water: (a) *p*H = 1.5; (b) *p*H = 3.8; (c) *p*H = 5.6; (d) *p*H = 8.0; and (e) *p*H = 12.3. (f) SFG spectrum from the quartz/ice interface. The lines are guides for the eyes; a typical error bar for the measurement is shown in (b).

The spectra in Fig. 1 show how the two peaks at 3200 and 3450 cm^{-1} vary with the *p*H value in water. At *p*H = 1.5, the spectrum in Fig. 1(a) resembles that of the quartz/ice interface in Fig. 1(f), indicating that most of the interfacial water molecules are orderly arranged with tetrahedral coordination. As the *p*H values increase [Figs. 1(b)-1(e)], the relative strength of the two peaks varies. The 3200 cm^{-1} peak first decreases while the 3450 cm^{-1} one increases. Then with *p*H > 5.6, both peaks get strengthened, with the former increasing more rapidly. Finally, at *p*H ~ 12.3, the spectrum of Fig. 1(e) again resembles that of the quartz/ice interface, but the peak strength is significantly larger than in the latter case as well as in Fig. 1(a). The results can be understood from possible surface-induced ordering or disordering of interfacial water molecules.

The surface chemistry of silica has been well studied [12]. A normally cleaned quartz surface is terminated by OH groups (silanol groups) which can be negatively charged by deprotonation in water with a sufficiently low proton concentration (high *p*H values). It is neutral for *p*H ≤ 2 and fully ionized for *p*H ≥ 10 [13]. With the surface silanol groups all ionized, the negative surface charges should produce a strong electric field of $\sim 10^7$ V/cm close to the surface, taking dielectric saturation into account [14]. This field can orient several monolayers of interfacial water molecules with their dipole moments pointing into the solid. The similarity between the spectrum of quartz/water (pH ~ 12) and quartz/ice interfaces, Figs. 1(e) and 1(f), suggests that the interfacial structure of water at an electrified surface is icelike. This is consistent with the general notion that electric field can nucleate ice [15], but contrary to some molecular dynamics simulations which indicate that water molecules close to a charged surface may not be hydrogen bonded as well as ice [16].

If the quartz surface is neutral (e.g., at $p\mathrm{H} = 1.5$), then interfacial water molecules tend to form hydrogen bonds with their oxygen facing the quartz surface [17], opposite to the orientation expected for the high pH case. The spectrum of Fig. 1(a) shows that it is also icelike. However, compared to the high pH case, the signal strength is much smaller (by a factor of ~7). With hydrogen bonding to the surface providing the orienting force, one would expect only 1 or 2 monolayers of water molecules being oriented. This supports the argument that for the high pH case, the surface field can align up to 3 to 5 layers of interfacial water molecules, consistent with the known semi-long-range nature of the hydration force at ionic surfaces, and the well accepted view that oriented water molecules are the origin of the repulsive hydration force between surfaces [5(b)].

For an intermediate pH value [Fig. 1(b) or 1(c)], the spectrum is weaker and the two peaks at 3200 and 3450 cm^{-1} appear equally pronounced, indicating a reduction of the ordering of the interfacial water molecular arrangement. This is also manifested by the appearance of the weak shoulder at about 3600 cm^{-1}. The relative strength of the two major peaks varies significantly with the pH value [Figs. 1(b)-1(d)], suggesting that disordering of molecular arrangement can be readily perturbed by the degree of surface ionization. We understand the results as follows. When the surface is partially ionized, the opposite aligning forces on interfacial molecules from the surface field and from hydrogen bonding with the surface silanol groups compete with each other and yield a less ordered interfacial water structure. Because the surface field has an orienting effect over several more molecular layers, the spectral intensity increases when the surface field dominates [Fig. 1(d)]. This then suggests that the repulsive hydration force from strong ionic surfaces extends over a longer range than that from surfaces terminated by polar groups only [18].

To see whether the water molecules at the quartz/water interfaces indeed have opposite orientations at low and high pH values, we have measured the phases of $\chi_{yyz}^{(2)R}$ for the 3200 cm^{-1} peak at low and high pH values. This was accomplished using the technique described in Ref. [19]. If the molecular orientations are reversed, the phase of $\chi_{yyz}^{(2)R}$ should change by 180°. This was actually found in our experiment.

To further confirm the picture, we have studied the effect of electrolytes on the SFG spectra of quartz/water interfaces by dissolving NaCl in the aqueous solution. Representative results are shown in Fig. 2. For the low pH case [Fig. 2(a)] with the quartz surface being neutral, the salt ions (even at $0.5M$ NaCl) have no effect on the spectrum since they are not expected to disturb the interfacial system appreciably. For the high pH case, the addition of NaCl reduces the spectral intensity because of screening of the surface field by the positive Na^+ ions. It is, however, interesting to note that the spectrum actually indicates an increase in molecular ordering. This is because ions now participate in the formation of a thinner double layer, leading to an enhancement of the double-layer surface field. For the pure water case [Fig. 2(b)], the effect of the electrolyte is much more pronounced because the balance of the two competing forces at the interface is easily upset by the presence of Na^+ ions; the spectrum now resembles that of the low pH case.

A discussion of SFG spectra for quartz/ice interfaces is in order. The interfaces were prepared by gradually cooling the fused quartz window with cold nitrogen gas to around −10 °C over several hours before freezing suddenly set in. Comparison between the quartz/ice and quartz/water interfaces spectra, Figs. 1(f) and 1(a), shows that the two have roughly the same strength, both arising from approximately 1 monolayer of surface water molecules. The stronger dominance of the 3200 cm^{-1} peak in the quartz/ice interface spectrum indicates a better bond ordering of the ice surface as expected. Spectra of quartz/ice interfaces frozen from bulk water with different pH values do not show an appreciable difference in their spectral features and overall strengths. Measurement of the phase of the 3200 cm^{-1} peak led to the conclusion that during freezing, the interfacial water mole-

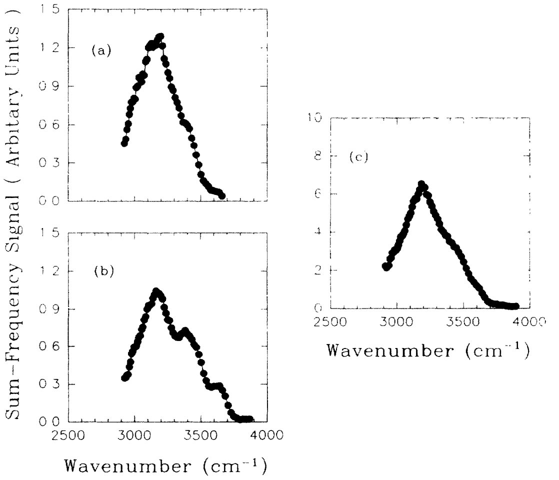

FIG. 2. SFG spectra from quartz/water interfaces with (a) $p\mathrm{H} = 1.5$, $0.5M$ NaCl; (b) $p\mathrm{H} = 5.6$, $0.1M$ NaCl; and (c) $p\mathrm{H} = 12.3$, $0.5M$ NaCl, in bulk water.

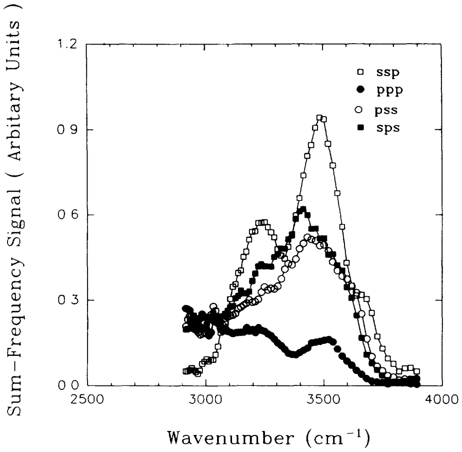

FIG. 3. SFG spectra with different polarization combinations from a quartz/water interface with the bulk water at *p*H = 5.6.

cules contributing to the spectrum do not flip in their orientation. In the high *p*H case, the sudden decrease of the signal strength upon freezing must be due to a reversing of the inner field-oriented layers of interfacial water molecules to nonpolar structure.

We have also obtained the SFG spectra of quartz/water interfaces with different input/output polarization combinations. Figure 3 depicts the case with water at *p*H = 5.6. Unlike the case of vapor/water interfaces reported in Ref. [9], the spectra here for all polarization combinations are clearly visible, suggesting that interfacial water molecules are not as well oriented as in the former. For the (*pss*) and (*sps*) polarization combinations, which yield $\chi_{zyy}^{(2)}$ and $\chi_{yzy}^{(2)}$, respectively, the spectra seem to be less sensitive to bond ordering than the (*ssp*) spectrum. As the *p*H varies, the 3450 cm^{-1} peak remains at least as prominent as the 3600 cm^{-1} peak. Their relative strengths also correlate well with disordering in the interfacial water structure. The spectra in Fig. 3 can in principal allow us to deduce some quantitative information about the average OH bond orientation, assuming that the peak assignment is definite. Such analysis is presently under way.

In summary, we have used infrared-visible SFG to study OH stretch vibrations of water molecules at fused quartz/water interfaces with different bulk *p*H values and found that the interfacial orientation and bonding structure of water are strongly influenced by the electrostatic interaction and hydrogen bonding of molecules with the surface. The outcome depends sensitively on the balance between them. Such behavior has long been postulated in electrochemistry at metal electrodes [1]. More specifically, we have found for our system that the interfacial water structure can undergo an order-disorder-order change accompanied by a flip of the molecular orientation when the bulk *p*H is varied. Several monolayers of interfacial water molecules can be polar ordered if the surface is highly ionized at high *p*H values. These results are generally important to many surface phenomena involving the solvent structure of water.

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