

## Communications to the Editor

## IR–Visible SFG Investigations of Interfacial Water Structure upon Polyelectrolyte Adsorption at the Solid/Liquid Interface

Joonyeong Kim and Paul S. Cremer\*

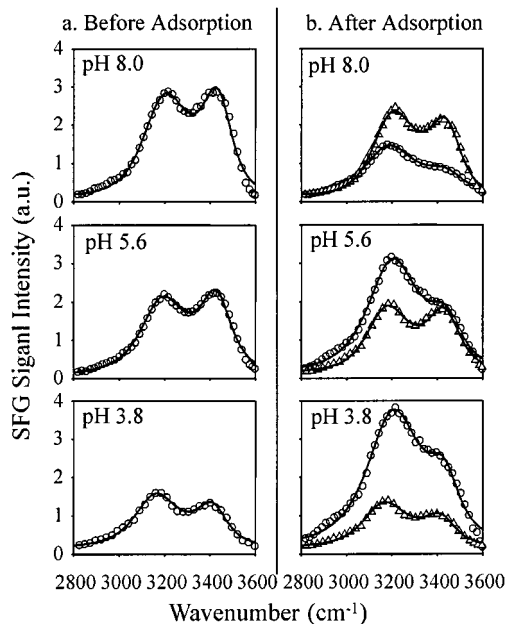
Department of Chemistry, Texas A&M University  
P.O. Box 30012, College Station, Texas 77842-3012

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The structure and bonding of interfacial water molecules at charged surfaces have attracted considerable attention due to their scientific and technological importance. Examples include reactions at electrode surfaces, colloidal stabilization, and interactions at biomembranes.<sup>1</sup> Unlike bulk water, interfacial water structure usually exhibits spatial orientation with respect to an underlying charged surface and thereby lacks inversion symmetry. This fact makes optical second harmonic generation (SHG) and infrared–visible sum frequency generation (SFG) ideal tools for the investigation of these buried aqueous interfaces.<sup>2</sup>

Previous SFG and SHG studies of interfacial water structure at the quartz/water interface have shown that molecular ordering is mainly governed by the surface charge density of titratable silanol groups, which are in turn regulated by the bulk pH.<sup>2c–d</sup> The water structure becomes increasingly aligned as the aqueous phase is made more basic. Herein, we report results that are quite different. Namely, upon deposition of a positively charged polyelectrolyte containing no titratable groups, the interfacial water structure shows better alignment at low pH and poorer alignment at high pH. This result is significant because adsorption of such polymers onto oppositely charged solid substrates is the key step in multilayer film growth via layer-by-layer deposition.<sup>3</sup>

In the experiments presented here, infrared–visible SFG was employed to obtain spectroscopic information in the OH stretch region of the vibrational spectrum upon polymer adsorption at the quartz/water interface at several pH values. The theory and experimental setup of SFG have been described in detail elsewhere.<sup>4</sup> We have chosen to investigate two linear polyelectrolytes, a positively charged species, polydiallyldimethylammonium chloride (PDDA), and the negatively charged sodium salt of polystyrene sulfonic acid (PSS). Figure 1 shows the SFG spectra of the quartz/water interface with and without polyelectrolyte at pH 8.0, 5.6, and 3.8 and with a total ionic strength of 32 mM. All spectra contained two major features. The first peak,



**Figure 1.** SFG spectra of the quartz/water interface in the OH stretch region at pH 8.0, 5.6, and 3.8: (a) bare quartz/water interface (b) after adsorption of PDDA (circle, ○) and subsequent deposition of PSS (triangle, △). Both the circles and triangles denote collected data. The solid lines are calculated fits to the data using a Voigt function from which peak positions, widths, and oscillator strengths can be obtained. The beam polarizations employed were s (sum frequency), s (visible), and p (infrared).

located near 3200  $\text{cm}^{-1}$ , is assigned to the OH symmetric stretch of tetrahedrally coordinated water molecules or “ice-like” molecular structure.<sup>5a–d</sup> The second peak around 3400  $\text{cm}^{-1}$  is from water molecules with more disordered hydrogen bonding or “water-like” structure.<sup>5a,e</sup> In Figure 1a, the ice-like and water-like peak intensities from the bare quartz/water system increased as the pH was raised, in agreement with previous results.<sup>2d</sup> This corresponds to increasing interfacial water structure as the aqueous solution was made more basic in this pH range.

Figure 1b shows SFG spectra after the deposition of PDDA from a 1.0 mg/mL stock solution at pH 8.0, 5.6, and 3.8 (circles). The intensities of the spectroscopic features in Figure 1b are quite dependent on the bulk pH, but the ice-like peaks show the opposite trend with respect to the bare surface. Namely, high intensity is observed at low pH, while this peak is attenuated at higher pH. Curve-fitting the results confirmed that the adsorption of PDDA suppressed the oscillator strength of the ice-like and water-like modes at pH 8.0 with respect to the bare surface. By contrast, the ice-like mode was actually increased at pH 5.6, while the water-like mode decreased. This trend continued at pH 3.8 where the ice-like oscillator strength was dramatically increased and the water-like mode attenuated slightly.

The SFG spectra after deposition of a PSS layer at the respective pH values onto the quartz/PDDA/water system are also

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\* To whom correspondence should be addressed. Telephone: 979-862-1200. Fax: 979-845-7561. E-mail: cremer@mail.chem.tamu.edu.

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shown in Figure 1b (triangles). The ice-like and water-like oscillator strengths in the SFG spectrum at pH 8.0 were enhanced by the formation of the PSS layer, and the overall intensity nearly reverted to the shape and intensity of the original spectrum for the bare solid/liquid interface (Figure 1a). The trend toward reverting to spectra reminiscent of the bare quartz/water interface extended to pH 5.6 and 3.8 as well.

Differences in the spectral intensities with and without the polyelectrolyte layer(s) can be explained in terms of changes in the surface charge density. The PDDA and PSS chains have fixed charges over the pH range probed here; however, both the charge density on the underlying surface of the fused quartz as well as the amount of polyelectrolyte adsorbed are subject to change as the pH is varied.<sup>6</sup> Previous studies have shown that polyelectrolyte adsorption overcompensates for the initial surface charge, leaving a residual charge of opposite sign.<sup>7</sup> The amount of excess charge is substantially greater at low pH than at high pH.<sup>6c,8</sup> Furthermore, the charge density at the PDDA-covered interface is more sensitive than the bare surface to changes in pH for the range explored here. Indeed, the results at pH 3.8 on the PDDA-covered surface are similar to those seen on the bare surface only well above pH 8.0.<sup>2d</sup> Namely, there is a large increase in the 3200  $\text{cm}^{-1}$  feature with a concomitant attenuation of the 3400  $\text{cm}^{-1}$  peak.

In a second set of experiments, PDDA was deposited onto a bare quartz/water interface at pH 5.6, the pH was then lowered to 3.8 (Figure 2a, squares), and subsequently raised to 8.0 (Figure 2b, squares). This was done to investigate the effect of pH cycling on the interfacial water structure. A reference spectrum for directly depositing the polymer at each pH (circles) is also shown in the figures for comparison.

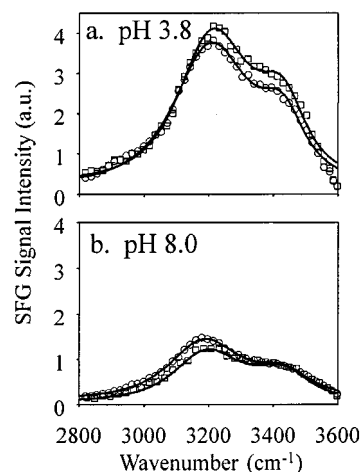
In Figure 2a, the SFG spectra obtained by pH cycling and direct deposition at pH 3.8 are strikingly similar; however, the former gives rise to slightly higher intensity. Furthermore, the spectrum obtained by cycling to pH 8.0 is similar to the directly deposited film, albeit of slightly lower intensity (Figure 2b). It has been previously shown that some portion of PDDA deposited at high pH is removed by rinsing at lower pH, due to the decreased electrostatic attraction.<sup>9</sup> Despite this, the amount of PDDA adsorbed by deposition at pH 5.6 and switching to 3.8 is still greater than that from direct adsorption at pH 3.8 because the adsorption process is not completely reversible. This could explain the slight intensity difference between the two spectra. On the other hand, no PDDA is eluted upon rinsing at pH 8.0. In fact, the amount of polymer on the surface is undoubtedly well short of that present when deposition occurs directly at pH 8.0.<sup>9</sup>

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**Figure 2.** SFG spectra in the OH stretch region of the quartz/PDDA/water system at (a) pH 3.8 and (b) pH 8.0. Squares (□) denote data for films that were formed at pH 5.6 and subsequently cycled to 3.8 and 8.0. Circles (○) represent data collected from direct deposition of PDDA at the given pH in Figure 1b for comparison. Solid lines are fitted data.

Nevertheless, the signal is only slightly reduced compared with the latter case. This observation is in agreement with the fact that increased polymer adsorption at a given pH leads to more deprotonation of surface silanols.<sup>6,10</sup> This implies that it is not necessary to form a complete polymer layer to achieve essentially constant charge density and water structure alignment at the interface at a fixed pH. Indeed, the titratable surface silanols seem to act like a buffer to adjust the surface charge density to a nearly set value under the prevailing pH conditions.

In summary, dramatic changes in SFG intensity were observed upon the adsorption of PDDA and PSS at the quartz/water interface that can be explained by changes in surface charge density at the corresponding pH. Water molecules were better aligned as the pH was lowered after adsorption of PDDA, but this trend was reversed by the subsequent adsorption of PSS. SFG is, therefore, a promising technique for studying the water structure during layer-by-layer growth of polymer films. Currently, further investigations of interfacial water structure upon polyelectrolyte adsorption are underway as a function of molecular weight, ionic strength of the bulk solution, and the nature of the counterions.

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**Supporting Information Available:** Details of laser system, data collection procedures, and Table S1 of curve-fit results for Figure 1 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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