

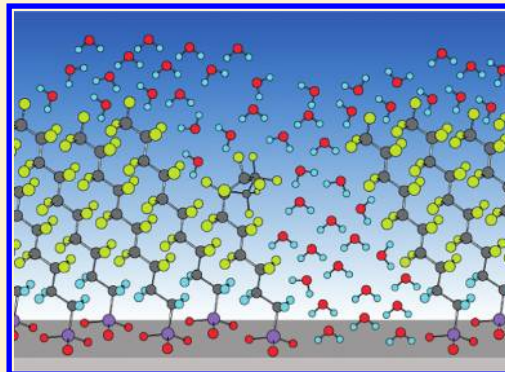
# SAMs under Water: The Impact of Ions on the Behavior of Water at Soft Hydrophobic Surfaces

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**S** Supporting Information

**ABSTRACT:** Understanding the behavior of water at hydrophobic surfaces has been a topic of much interest for many decades. In most areas of biological, environmental, or technological relevance, the aqueous phase is not pure water, but comprises a host of ions including those associated with the acidity or basicity of the solution. The notion that ions, including hydroxide and/or hydronium, accrue at hydrophobic interfaces is increasingly invoked as a possible explanation for the behavior of water adjacent to soft hydrophobic interfaces such as liquids and monolayers. The focus of this study is on exploring the behavior of aqueous solutions of salts, acids and bases in contact with hydrocarbon and fluorocarbon self-assembled monolayers (SAMs) using vibrational sum frequency spectroscopy (VSFS). The studies take a systematic approach to understanding how each component of the SAMs' interfaces contribute to the overall observed behavior of ions and water in the overall boundary region. To achieve this, the spectroscopy of the SAM/water interface in the presence and absence of aqueous phase ions, acids and bases is compared with similar measurements taken at the substrate (SiO<sub>2</sub>)/water interface and the hydrophobic liquid/water interface. The results show that the behavior of water and ions at the SAM/aqueous interface is significantly influenced by the substrate surface for both hydrocarbon and fluorocarbon SAM systems. Conditions where water and ions near a SAM interface mimic that of a liquid hydrophobic surface are identified.



## INTRODUCTION

Since hydrophobic surfaces are by definition “water hating”, one might assume from a simplistic perspective that solvated ions in the water would avoid a hydrophobic surface. While this might be true for idealized solid hydrophobic surfaces,<sup>1–3</sup> it is certainly not the case for solvated ions near more complex biological assemblies where ions not only approach but also transport across these boundary layers. Unraveling the various factors that influence ion behavior in these complex biological systems relative to their idealized solid systems is not an easy task. For example, what roles do the polar groups of a biological assembly play, or that the more fluid nature of the hydrophobic boundary layer plays? At the air/water and solid/liquid interfaces, the polarity of adsorbates such as proteins and macromolecules alters the structure of interfacial water and affects ion adsorption behavior.<sup>4–6</sup> Recent studies of aqueous ionic solutions near simple hydrophobic liquids are shedding light on the effect of ions on water at an extended hydrophobic fluid interface.<sup>7–11</sup> From these spectroscopic<sup>7,8</sup> and computational studies<sup>9–11</sup> it is clear that inorganic ions do penetrate into the aqueous/hydrophobic liquid interface. Experimental support for these conclusions comes from spectroscopically observed changes of the molecular orientation and hydrogen bonding of interfacial water molecules when ions are present at the liquid/liquid interface. These studies show that the weak interactions between water and the hydrophobic liquid assist in the formation of an interfacial potential that creates an environment that can draw ions into

the interfacial region. The behavior is found to be quite distinct from what has been observed for interfacial water in similar experimental<sup>12–19</sup> and computational studies conducted at the air/water interface.<sup>17,20–30</sup> Comparison of the experimental results obtained at the air/water and CCl<sub>4</sub>/water interface using similar ions and techniques show that there is a greater tendency for the ions to go to the organic liquid/water interface than the air/water interface. The case has recently been made that other ions, such as OH<sup>−</sup>, are also attracted to hydrophobic liquid interfaces because of the stabilization afforded by the approach of the OH<sup>−</sup> ions, which reduces the dielectric constant at the interface and the dipole fluctuations.<sup>31,32</sup> These ions are estimated to have a density maximum some 6–7 Å from the Gibbs dividing surface at the liquid/liquid and air/water interfaces.<sup>31,32</sup>

Recently, there has been an increased interest in using hydrophobic self-assembled monolayers (SAMs) chemically attached to a silica substrate as model systems for understanding water and ion behavior at more complex soft hydrophobic surfaces.<sup>33</sup> If the behavior of water molecules at the SAM/water junction is largely determined by the nature of the water/hydrophobic interactions at the terminus of the monolayer, then one can use such SAM/water systems as a model for exploring a

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variety of ionic and molecular adsorption processes at more complex hydrophobic interfaces of biological and technological importance. One caveat to this premise is that these SAM systems are themselves complex with regards to water and ion adsorption. For example, defects in the monolayers could lead to water and ions penetrating to the SiO<sub>2</sub> substrate, potentially altering the overall interfacial electrostatics and subsequent behavior of ions and water molecules at the terminus of the monolayer.

The focus of this study is on exploring the behavior of aqueous solutions of salts and acids in contact with hydrocarbon and fluorocarbon SAMs using vibrational sum-frequency spectroscopy (VSFS). The studies take a systematic approach to understanding how each component of the SAM/water interface contributes to the overall observed behavior of ions and water in the boundary region. Spectroscopic comparison of hydrocarbon- and fluorocarbon-terminated SAMs exploits the sensitivity of VSFS to differences in the molecular interactions of water with these two chemical functionalities at the interface. We are able to distinguish between the behavior of water at the terminus of these two monolayer systems from that of H<sub>2</sub>O in other regions of the interface, such as those closer to the substrate or deeper into the bulk liquid. Contributions from the substrate are determined by examining and comparing the VSFS response from SiO<sub>2</sub> in contact with various ion and acid solutions. Further insights into the influence of the substrate and monolayers on interfacial water and electrolytes are obtained from both new studies of acids and bases at the CCl<sub>4</sub>/H<sub>2</sub>O interface and previous studies<sup>7,8,34–36</sup> of water and aqueous solutions of ions in contact with various hydrophobic organic liquids where a substrate is not a factor.

## ■ VSFS BACKGROUND

VSFS is uniquely suited for these studies because of its inherent sensitivity to the orientation and dynamics of water molecules in the interfacial region of monolayers and other hydrophobic surfaces.<sup>37–45</sup> Detailed explanations of VSFS can be found in the literature;<sup>46–52</sup> thus, a concise description will be given here. The VSFS experiments within utilize a fixed frequency visible beam ( $\omega_{\text{vis}}$ ) that is overlapped spatially and temporally with a tunable infrared (IR) beam ( $\omega_{\text{IR}}$ ) at the interface, which generates a beam at the sum of the two incident frequencies ( $\omega_{\text{SF}}$ ). Using the electric dipole approximation, this beam is generated only by molecules in a non-centrosymmetric environment such as that at the solid/liquid interface. No contribution to the VSFS beam originates from molecules in the bulk liquid or solid environments, and thus, the signal is limited to the few molecular layers experiencing net orientation at the interface.

The intensity of  $\omega_{\text{SF}}$  is given by eq 1:

$$I(\omega_{\text{SF}}) \propto |\chi_{\text{eff}}^{(2)}|^2 I(\omega_{\text{IR}}) I(\omega_{\text{vis}}) \propto \sum_{i=0}^n |\chi_{v_i}^{(2)} + \chi_{\text{NR}}^{(2)}|^2 \quad (1)$$

where  $I(\omega_{\text{IR}})$  is the intensity of the IR beam and  $I(\omega_{\text{vis}})$  is the intensity of the visible beam.  $\chi_{\text{eff}}^{(2)}$  is the effective macroscopic nonlinear susceptibility and is composed of a sum of resonant terms,  $\chi_{v_i}^{(2)}$ , and a nonresonant term,  $\chi_{\text{NR}}^{(2)}$ .  $\chi_{\text{NR}}^{(2)}$  was found to be small in the experiments within. Each resonant term can be described by a discrete resonance of the form shown in eq 2.

$$\chi_{v_i}^{(2)} \propto \frac{NA_{v_i}}{\omega_{v_i} - \omega_{\text{IR}} - i\Gamma_{v_i}} \quad (2)$$

In eq 2,  $N$  is the number density of molecules, and  $A_{v_i}$  is the product of the Raman and IR transition moments.  $\omega_{v_i}$  is the frequency of the IR transition,  $\omega_{\text{IR}}$  is the frequency of the tunable

IR, and  $\Gamma_{v_i}$  is the line width of the transition. These quantities that are normally complex result in terms with both amplitude and phase that can interfere with other vibrational terms. The resonant macroscopic susceptibility,  $\chi_{v_i}^{(2)}$ , is related to the molecular hyperpolarizability ( $\beta$ ) by eq 3,

$$\chi_{v_i}^{(2)} = \frac{N}{\epsilon_0 \langle \beta \rangle} \quad (3)$$

in which  $\epsilon_0$  is the permittivity of free space and the angle brackets denote an ensemble average over the different molecular orientations. Choosing different polarizations of the visible, IR, and VSF spectra allows different elements of  $\chi_{v_i}^{(2)}$  to be investigated. The spectra within have all been collected in the SSP polarization scheme (S-VSF, S-vis, P-IR), which probes transition dipole moment components normal to the interfacial plane.

The spectra have been analyzed using a nonlinear global curve-fitting routine in IgorPro (Wavemetrics, Beaverton, OR) which accounts for spectral interferences and the deviations from ideal transition line shape by convoluting the expressions for Gaussian and Lorentzian curves as initially developed by Bain and co-workers.<sup>53,54</sup> The global fit allows all spectra within a series to be analyzed simultaneously. Each resonant mode in eq 1 is fitted to eq 4:

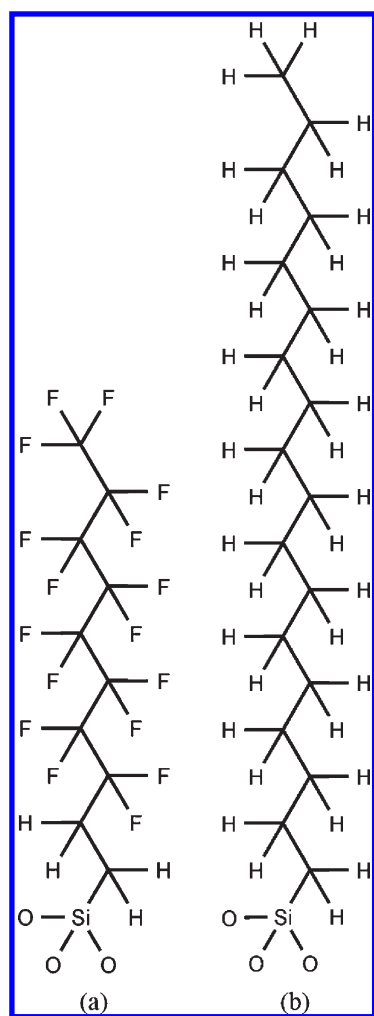
$$\chi_{v_i}^{(2)} = A_i \exp(i\phi_i) \int_0^\infty \frac{1}{\omega_{v_i} - \omega_{\text{IR}} + i\Gamma_{v_i}} \exp\left(-\frac{\omega_{v_i} - \omega_{\text{IR}}}{\Gamma_{v_i}}\right) \quad (4)$$

where  $A_i$ ,  $\phi_i$ ,  $\omega_{v_i}$ ,  $\Gamma_{v_i}$ , and  $\Gamma_{v_i}$  are fittable parameters for the amplitude, phase, resonant frequency, Lorentzian line width, and Gaussian line width of the  $i$ th mode. To reduce the number of fittable parameters, Lorentzian line widths were fixed at 2 cm<sup>-1</sup> for CH modes and 5 cm<sup>-1</sup> for OH modes, and the resonant phases were only allowed values of 0 or  $\pi$ .

## ■ EXPERIMENTAL SECTION

**Liquid/Liquid Experiments.** The CCl<sub>4</sub>/H<sub>2</sub>O experiments presented here were performed using a commercially available VSFS system from Ekspla (Vilnius, Lithuania) and sample cell that has been previously described.<sup>7,34</sup> For the VSFS experiments, a 532 nm visible beam from the frequency doubled output of picosecond Nd:YAG laser is overlapped spatially and temporally with the output of an IR generator pumped by the same source. The IR is tunable from 1000 to 4300 cm<sup>-1</sup>. The beam energies used were 80  $\mu$ J and  $\sim$ 200–250  $\mu$ J for the visible and IR beams, respectively. The beam angles were chosen to maintain a total internal reflection geometry for the visible beam for all concentrations examined: 69.5° and 75° for the visible and IR beams, respectively. Multiple spectra of each interface were taken and averaged to achieve an acceptable signal-to-noise level. Each spectrum was normalized for the IR and 532 nm output as well as the absorption of the prism.

The VSFS spectra are extremely sensitive to chemical impurities, so great care was taken to eliminate any effects from these. CCl<sub>4</sub> ( $\geq$ 99.9% +, Chromosolv HPLC grade) was purchased from Sigma-Aldrich and twice distilled before use. The HCl and NaOH were both purchased from Sigma-Aldrich. The HCl was ACS reagent grade, 37%, and was used from the bottle for making acidic solutions. NaOH pellets, 99.998% metals basis purity, were used for the basic experiments. Although of high-grade purity, using the NaOH pellets as purchased yielded inconsistent results



**Figure 1.** Hydrophobic coatings studied in this report are (a) 1H,1H,2H,2H-perfluorodecylsilane (FDS) and (b) octadecylsilane (ODS).

and often gave spectra similar to those containing small concentrations of surfactants. To overcome this, the NaOH pellets were baked in an oven at 220 °C for ~12 h prior to use. Fresh solutions were prepared each day, and the pH was tested prior to use with indicator strips. The sample cell and all glassware were cleaned in NoChromix (Godax Laboratories) dissolved in concentrated sulfuric acid, then rinsed copiously with water from a Nanopure II system.

**Solid/Liquid Experiments.** VSFS experiments at solid/liquid interfaces were performed using a custom-built IR generation system. The master oscillator is a Spectra-Physics Lab 110 Nd:YAG laser (10 Hz, 600 mJ, 6.5 ns, 1064 nm) the output of which is split to pump a potassium titanyl phosphate (KTP) frequency doubler and an optical parametric oscillator (OPA). The frequency doubled output of 60 mJ is used to pump a double-pass KTP optical parametric oscillator (OPO). The remainder of the 532 nm doubled output is then attenuated and polarization selected before being sent toward the interface. Typically, 1.5 mJ of 532 nm was used at the sample area. OPO output is mixed with ~120 mJ of the 1064 nm fundamental in a two-stage (four-crystal) potassium titanyl arsenate OPA. The tunable OPA output ranges from 2600  $\text{cm}^{-1}$  to 4000  $\text{cm}^{-1}$  (1–4 mJ) with a 2  $\text{cm}^{-1}$  bandwidth.

Samples were compression fitted onto a Kel-F sample cell with a Kalrez O-ring. IR and visible beams were directed at the sample through a 23.1 °, triangular IR grade fused silica prism with a 1 in.<sup>2</sup> top surface (ISP Optics). Beam angles relative to the optical bench surface were 17 ° and 23.1 ° for the IR and 532 nm, respectively. Samples were mated to the prism via a drop of microscope immersion oil (Cargille, custom code 43421). The spectra were normalized for IR adsorption of the prism and sample plate.

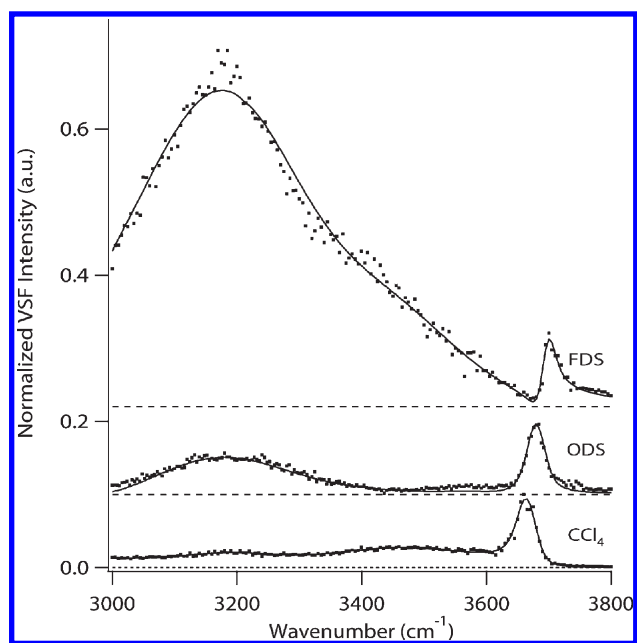
The two types of coatings used in this paper are FDS and ODS and are shown in Figure 1. FDS monolayers were deposited using 1H,1H,2H,2H-perfluorodecyltriethoxysilane (FDES) (Gelest, Tullytown, PA) precursors via Langmuir–Blodgett (LB) deposition on a KSV Minitrough. After verifying the trough cleanliness by measuring the surface tension of water ( $72.4 \pm 0.2$  mN/m), the trough was filled with 0.01 M hydrochloric acid to catalyze the cleavage of the ethoxy groups. After immersing a substrate in the dipping well, a 1–3  $\mu\text{M}$  solution of FDES precursors in  $\text{CHCl}_3$ , the exact concentration determined by mass, was spread on the surface of the liquid layer to a starting density of 1 molecule per 45  $\text{Å}^2$ . This surface layer was then equilibrated for 30 min. The barriers were then compressed to a surface pressure of 15 mN/m (27  $\text{Å}^2$  mean molecular area) at which point the substrate was withdrawn from the trough at a rate of 5 mm/min.

ODS monolayers were prepared using a solution phase deposition technique similar to methods previously published.<sup>55</sup> First, a freshly cleaned  $\text{SiO}_2$  substrate was humidified for 30 min over a saturated solution of  $\text{Ca}(\text{NO}_3)_2$ . The substrate was then soaked in a 4:1 (vol:vol) solution of hexadecane/ $\text{CCl}_4$  with a 1 mM concentration of octadecyltrichlorosilane (Gelest) for 6 h. The ODS sample was then rinsed with hexadecane, chloroform, acetone, and methanol and sonicated for 1 min in  $\text{CHCl}_3$ , followed by rinsing with acetone and methanol. Lastly the SAMs were blown dry with argon. Both FDS and ODS monolayers were cured at 110 °C for 1 h. All samples were stored in a vacuum desiccator until used.

FDS samples were prepared using the LB technique to eliminate the problem of spontaneous polymerization in solution of the trichlorosilane functionality. Any small amount of water resulted in very rapid reaction kinetics that were not controllable in our laboratory. The LB method was found to produce the best coatings using the FDES precursor. Solution polymerization of ODS was minimized by the use of fresh, dry solvents and careful choice of reaction time.

Phosphoric acid buffers of pH 2, 7, and 11 were prepared from phosphoric acid and its sodium salts with an ionic strength of 0.01 M. Ionic strength effects were examined using NaCl solutions at pH  $\approx 5.8$ . Solutions were made by serial dilution of a 1 M NaCl(aq) solution to  $1 \times 10^{-4}$  M. To ensure the consistency of our spectra, both in terms of ionic strength and pH, fresh solutions were made each day. All water used in the solid/liquid experiments was generated by a Barnstead Nanopure II or E-Pure water purification system fed by deionized water.

Contact angle data was collected on a home-built goniometer and captured using a remotely triggered Olympus C-3030 camera in grayscale mode at a resolution of 1024  $\times$  768 pixels. Data analysis was performed using the LB-ADSA plugin for ImageJ developed by Stalder et al.<sup>56</sup> All reported contact angles are averages of 10 individual measurements. The FDS samples, because of deposition size restrictions, were blown off with argon after five measurements before new images were collected. AFM data was collected on a Digital Instruments Nanoscope IIIa in



**Figure 2.** SSP polarized VSFS spectra of the neat water interfaces (pH  $\approx$  5.8) with  $\text{CCl}_4$ , ODS, and FDS SAMs. The solid lines are fits to the data, which have been scaled such that the free-OH peaks have equal amplitude. Data are truncated at  $3000\text{ cm}^{-1}$  for clarity.

intermittent contact mode using Nanosensors PPP-NCST tips. AFM data were analyzed in Gwyddion 2.12. More detailed sample analysis is included in the Supporting Information and shows that the samples have nearly ideal chain structure and density.

## RESULTS AND DISCUSSION

**Neat Hydrophobic Interfaces.** Over the past several years VSFS and computational studies have examined water structure and bonding at the interface between water and a variety of hydrophobic media.<sup>7,8,34,35,57–61</sup> From a molecular perspective, the simplest systems are those comprising water and small nonpolar organic molecules such as  $\text{CCl}_4$ . The bottom trace in Figure 2 is representative VSFS data for the  $\text{CCl}_4/\text{H}_2\text{O}$  system where the OH stretching modes of water have been measured in the SSP polarization. The distinct spectral features convey information about the structure and interactions at the boundary between the two phases and have been well described in the literature.<sup>7,57</sup> The relatively sharp spectral feature near  $3665\text{ cm}^{-1}$  corresponds to the energetically uncoupled OH stretch modes of straddling interfacial water molecules. This OH oscillator, referred to as the “free-OH”, points directly into the  $\text{CCl}_4$  phase. The frequency of this mode is red-shifted from the free-OH at the air/water interface, which is located at  $3706\text{ cm}^{-1}$ ,<sup>62</sup> indicating a weak binding interaction between water and  $\text{CCl}_4$  at the interface. These water molecules are in direct contact with the organic phase and physically reside in the topmost layer closest to the dividing surface. Due to the geometry of water molecules, the companion OH oscillators on the straddling water molecules are oriented toward the aqueous phase where they can hydrogen bond with other water molecules. These have been referred to as “donor OH” modes and are energetically similar to other more weakly hydrogen bonded species in the interface and appear in the  $3400\text{--}3550\text{ cm}^{-1}$  spectral region in Figure 2.<sup>27,35,63</sup> In fact, the spectrum is dominated by these

**Table 1.** Frequencies of the Free-OH Mode of Interfacial Water Molecules for Different Hydrophobic Phases

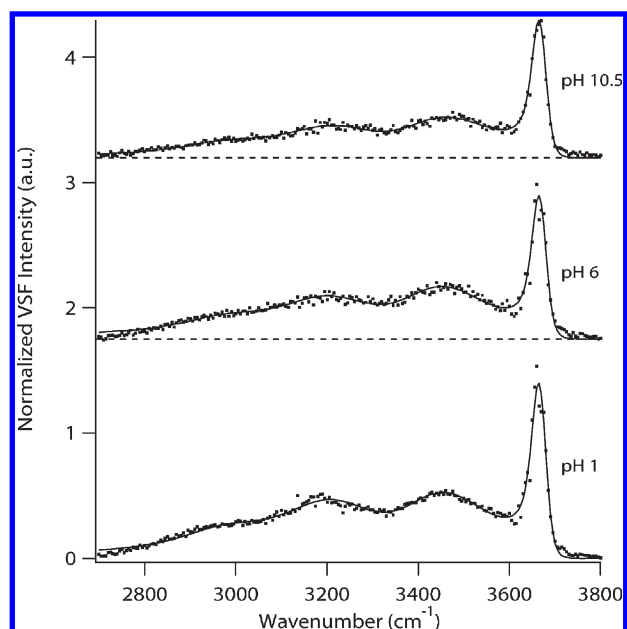
nonaqueous phase	free-OH location ( $\text{cm}^{-1}$ )
air <sup>62</sup>	$3706 \pm 5$
FDS	$3693 \pm 2$
ODS	$3673 \pm 2$
stearate/ $\text{CaF}_2$ <sup>39</sup>	$3674 \pm 5$
alkanes <sup>36</sup>	$3674 \pm 3$
$\text{CCl}_4$ <sup>34</sup>	$3669 \pm 2$
$\text{CHCl}_3$ <sup>34</sup>	$3645 \pm 2$
$\text{CHCl}_2 + \text{CCl}_4$ <sup>8</sup>	3642

weakly bonded and highly oriented water molecules. The  $\text{CCl}_4/\text{H}_2\text{O}$  interface also contains a small fraction of oriented water molecules with greater hydrogen bonding character. Their spectral contributions are primarily assigned to the lower frequency region of the spectrum centered around  $3200\text{ cm}^{-1}$  and they reside somewhat deeper in the interfacial region.<sup>27,35,63</sup>

Figure 2 compares the VSFS response from water at the  $\text{CCl}_4/\text{H}_2\text{O}$  interface to the response from water at the two monolayer films examined, ODS and FDS. As shown, both monolayer/water interfaces exhibit a free-OH mode corresponding to water molecules that straddle the water and the hydrophobic medium, just as in the liquid/liquid studies. The presence of this peak is indicative of a relatively sharp interface. For monolayers with significant structural defects as indicated by AFM analysis, the free-OH mode is greatly diminished or absent. The intensities of the free-OH modes shown for the three spectra have been used to normalize the results for discussion.

As shown in our previous studies,<sup>8,60,62</sup> the free-OH region is representative of water molecules that are in direct contact with the organic layer. The frequency of this mode is highly sensitive to the degree of interaction between water and the hydrophobic medium. The frequencies of several free-OH vibrations at different hydrophobic interfaces are compiled in Table 1. The FDS free-OH frequency of  $3693\text{ cm}^{-1}$  is higher than for the other hydrophobic surfaces, but lower than what is measured at the air/water interface. This frequency red-shift relative to the air/water interface is a clear indicator of a weak water–fluorocarbon interaction. The water/ODS free-OH frequency indicates a stronger interaction with water than its fluorocarbon counterpart, but its frequency is the same as that measured for other hydrocarbon monolayer and alkane systems. The polarizable nature of  $\text{CCl}_4$  gives it a stronger interaction with interfacial water, though still weaker than with the slightly polar  $\text{CHCl}_3$ . An interesting feature of the alkane systems that has relevance to later discussion of ODS is that the free-OH peak is found to be consistently broader than the free-OH at the  $\text{CCl}_4/\text{H}_2\text{O}$  interface. Using MD simulations, Brown et al. attributed this breadth and asymmetry to multiple types of water/alkane interactions.<sup>36</sup>

The free-OH frequency differences for the FDS and ODS monolayers are indicative of their different molecular characteristics when in contact with water. At the termini of both monolayers, water only experiences nonpolar interactions. The strengths of these interactions are driven by the ability of water to induce a dipole in the nonaqueous phase. The free-OH value of  $3669\text{ cm}^{-1}$  at the  $\text{CCl}_4/\text{H}_2\text{O}$  interface is lower than at the ODS or FDS surfaces because the large size of the Cl atoms makes it relatively easy to polarize. The C–F bond is not so readily polarized because of the strong affinity for electrons by fluorine.



**Figure 3.** SSP polarized VSFS spectra of the  $\text{CCl}_4/\text{H}_2\text{O}$  interface at pH 1, 6, and 10.5. Solid lines are fits to the data, and the dashed lines indicate zero signal.

This has the effect of making water unable to interact strongly with fluorocarbon groups. Hydrocarbons have nearly equal electron sharing between the carbon and hydrogen atoms; however, with no strong affinities for electrons, water is readily able to perturb this bond, resulting in the large frequency shift of the free-OH mode from the air/water value of  $3706\text{ cm}^{-1}$ . It is important to note that the effect of molecular size on hydrophobicity has been recently studied by Dalvi and Rosky<sup>64</sup> and cited as the reason for the enhanced hydrophobicity of fluorocarbons relative to hydrocarbons. However, size alone does not seem to sufficiently explain the free-OH frequency shifting trend seen here.

The most striking difference between the three spectra in Figure 2 is in the coordinated water region around  $3200\text{ cm}^{-1}$ . The dominant feature for FDS peaks near  $3200\text{ cm}^{-1}$  and continues to be strong up to the free-OH peak. The ODS/ $\text{H}_2\text{O}$  interface shows a much smaller peak near  $3200\text{ cm}^{-1}$  from these highly coordinated water molecules, as well as a small amount of signal near  $3600\text{ cm}^{-1}$ . In contrast, the  $\text{CCl}_4/\text{H}_2\text{O}$  system shows very little signal throughout this region, as is the case for all of the other organic liquids cited in Table 1 that have been studied to date. The striking difference in the water spectra at frequencies below  $\sim 3600\text{ cm}^{-1}$  at the SAM/ $\text{H}_2\text{O}$  interfaces leads us to conclude that these larger signals, relative to what is observed in the liquid/liquid systems, are due to the influence of the  $\text{SiO}_2$  substrate on interfacial water molecules. Water molecules contributing to this region of the spectrum are known to be highly sensitive to interfacial charge and polarity, which can influence the number and degree of orientation of water molecules in the double layer region adjacent to the substrate.<sup>65</sup> Further discussion of such effects follows in later sections.

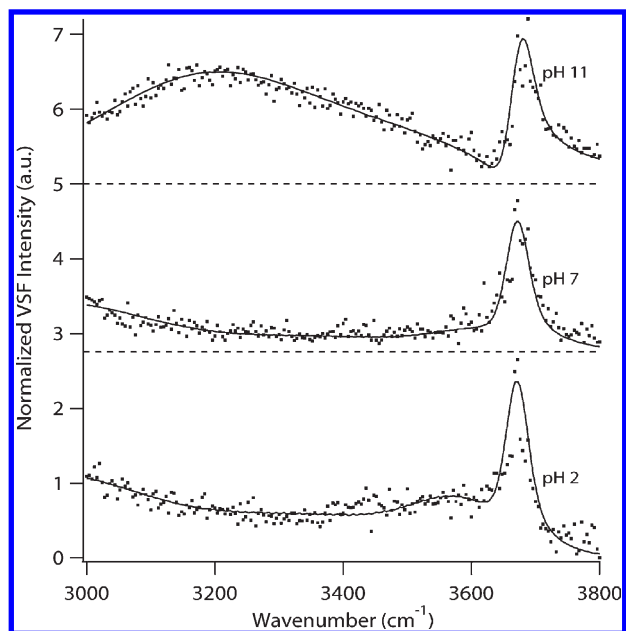
**pH Effects on Hydrophobic Interfaces.** The above studies suggest water orientation in the interfacial region is influenced by both the hydrophobic monolayer as well as the underlying substrate. To test this assumption further and also explore ion adsorption at these interfaces, similar studies of ODS and FDS interfaces upon variation of the pH have been conducted. The

pH effects at the  $\text{CCl}_4/\text{H}_2\text{O}$  interface have also been measured and are used both as a comparator and a starting point for discussion. As shown in Figure 3, the addition of acid or base to the aqueous phase of the  $\text{CCl}_4/\text{H}_2\text{O}$  system results in measurable changes in the interfacial water system, indicating that ions in the aqueous solutions migrate into the interfacial region and alter the behavior of interfacial water. At acidic pH, inspection and spectral fitting show increased intensity in the more strongly and weakly coordinated OH stretching regions near  $3200\text{ cm}^{-1}$  and  $3450\text{ cm}^{-1}$ , respectively, but minimal change in the free-OH. The addition of NaOH to the aqueous phase results in a measurable intensity decrease throughout the bonded region of the interfacial spectra. These trends continue at higher and lower pHs and are shown in the Supporting Information. The intensity and frequency of the free-OH mode is constant, regardless of pH.

Several factors contribute to the increase in VSFS intensity across the coordinated water stretching region ( $3000\text{--}3600\text{ cm}^{-1}$ ) at acidic pH for the  $\text{CCl}_4/\text{H}_2\text{O}$  system. These include changes to the number of contributing water molecules in their corresponding spectral region, reorientation of various water molecules relative to the surface normal and the presence of protonated water species in the interfacial region. It is most likely that all of these effects contribute. When acid is added to the aqueous phase of the interface, strong electrostatic interactions take place between  $\text{H}^+$  and the surrounding water molecules. Isotopic dilution studies at the air/water interface showed that solvated proton species residing at the topmost region of the interface increase the water intensity at higher frequencies between  $3400$  and  $3600\text{ cm}^{-1}$ , similar to what is observed here.<sup>14</sup> In the air/water studies<sup>14,18,66</sup> the intensity increase has been attributed to the solvation of protonated species, which is consistent with the prediction of Voth and co-workers.<sup>28</sup> Given the similar VSFS response, it is likely that the same fundamental interactions are taking place between water and  $\text{H}^+$  ions as those at the  $\text{CCl}_4/\text{H}_2\text{O}$  interface. However, the effect is much larger at the liquid/liquid interface than what was found at the air/water interface where measurable effects require much higher acidities.

The intensity increase observed at lower frequencies under acidification is also consistent with air/water studies<sup>14</sup> although, as previously noted, the effect is more pronounced in the liquid/liquid case. We credit the intensity increase in this region to water molecules affected by the presence of protonated species and to the protonated species themselves. IR spectra of bulk acid solutions attribute a peak at  $3300\text{ cm}^{-1}$  to Eigen protons in the Zundel adsorption continuum.<sup>15,67</sup> The presence of such species would result in an enhanced signal in this spectral region as well as contribute to enhanced water orientation in the deeper portion of the interface due to the presence of electrostatic fields. The lower-frequency region from  $3000$  to  $3400\text{ cm}^{-1}$  is known to be particularly sensitive to such effects.<sup>14</sup>

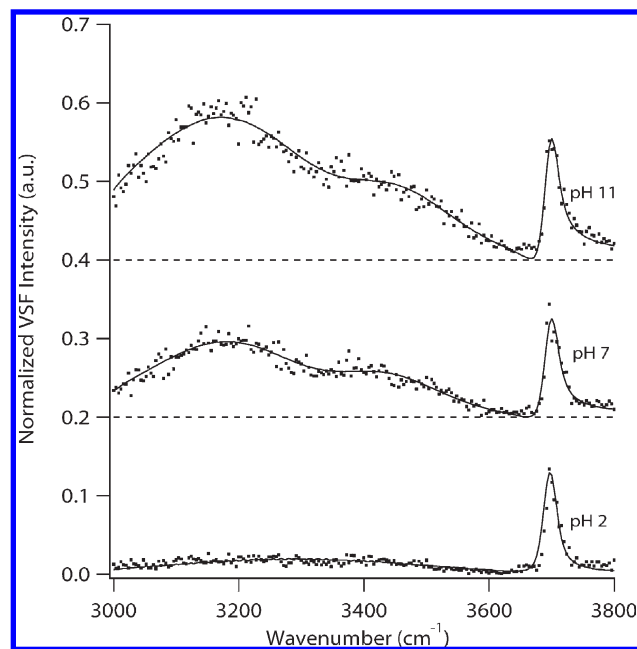
Spectra of basic solutions show a distinct decrease in intensity throughout the entire spectral region below  $\sim 3600\text{ cm}^{-1}$ , which is a clear indication of  $\text{OH}^-$  ions in the interfacial region. We attribute the decrease in intensity to a disruption of water ordering and a displacement of water molecules in the topmost water layers, which reduces the number of contributing water molecules and thus the VSFS intensity. Similar spectral changes have been reported for basic solutions at the air/water interface,<sup>14</sup> and again the observed effects are much smaller than at the liquid/liquid interface. In fact, it is not until nearly pH 14 that measurable effects can be observed at the air/water interface, whereas the  $\text{CCl}_4/\text{H}_2\text{O}$  interface exhibits changes near pH 10.



**Figure 4.** VSFS spectra of the ODS/H<sub>2</sub>O interface at 0.01 M ionic strength with bulk pHs 2, 7, and 11 in the SSP polarization scheme. These spectra are magnified 13.5 times the sensitivity of the spectra of the other solid/liquid interfaces shown. Solid lines are fits to the data, and the dashed lines indicate zero signal.

Compared to the CCl<sub>4</sub>/H<sub>2</sub>O system, water at an ODS-coated SiO<sub>2</sub> surface is much more sensitive to changes in bulk pH and exhibits very different trends, as is evident in Figure 4. The VSFS signal from the CH modes of the hydrocarbon chains of the ODS monolayer is much higher than that of the OH stretching modes and is not shown, but can be found in the Supporting Information. The CH modes indicate that the chains are in an all-trans configuration.

To understand the large spectral changes with solution pH, spectral fitting routines have been employed. The free-OH has constant frequency ( $3673 \pm 2 \text{ cm}^{-1}$ ), amplitude, and width ( $17 \pm 4$ ) at the ODS interface as the pH is varied, just as at the CCl<sub>4</sub>/H<sub>2</sub>O interface. Detailed analysis of the ODS/water spectra reveals an additional small peak near  $3600 \text{ cm}^{-1}$  that we attribute to water molecules in very weakly coordinated environments, such as partially trapped within the monolayer chains. Hydrocarbon SAMs are somewhat flexible, and this flexibility can lead to water molecules pushing aside the terminal methyl groups and interacting with CH<sub>2</sub> groups a couple of units down the chain. Such molecules are not able to engage in a full range of hydrogen bonding but act almost as water monomers. A similar spectral feature has been predicted by MD work at the alkane/water interface,<sup>36</sup> and recent simulations have found that water is able to perturb the top few units of a well-ordered ODS monolayer.<sup>68</sup> This feature is apparent in all the spectra, and it changes phase as the pH is decreased from 11 to 2. This sensitivity to bulk pH further supports the assignment to water trapped in the ODS chains. The phase of surface silanols, which are known to vibrate near  $3500 \text{ cm}^{-1}$ ,<sup>69</sup> a frequency much lower than what is observed here, should not be sensitive to bulk pH. Water solvating ions has been seen at solid/liquid<sup>45,70</sup> and liquid/liquid<sup>57,68</sup> interfaces near this same frequency. However, it is unlikely that this peak originates from ions at the interface because it is not present at the FDS/H<sub>2</sub>O interface, which has the same general response to



**Figure 5.** VSFS spectra of the FDS/H<sub>2</sub>O interface at 0.01 M ionic strength with bulk pH 2, 7, and 11. The spectra are SSP polarized. Solid lines are fits to the data, and the dashed lines indicate zero signal. The CH<sub>2</sub> stretching region has been excluded from the spectra.

bulk pH as ODS. We also note that phosphate salts were used in these buffered experiments; however, unbuffered pH work with NaOH and HCl revealed the same interfacial water structures, indicating that the effects seen here are not due to the presence of complex ions.

In contrast to the free-OH peak, the spectral region below  $3600 \text{ cm}^{-1}$  is strongly pH dependent. At neutral pH and 0.01 M ionic strength, the water signal is nearly zero in the  $3200 \text{ cm}^{-1}$  region, indicating that there is very little water with net orientation normal to the interface. At high pH, a large coordinated water signal appears that is centered around  $3200 \text{ cm}^{-1}$ . This signal is nearly zero at pH 7 and is slightly larger at pH 2. The higher signal level at  $3000 \text{ cm}^{-1}$  relative to that in the  $3200\text{--}3400 \text{ cm}^{-1}$  range is due to tailing of the CH stretching modes of the ODS SAMs. The simplest explanation for this behavior is that the interface is negatively charged at high pH, which results in the electrostatic orientation of water molecules. At pH 2, the number of electrostatically oriented interfacial water molecules increases slightly compared to neutral pH, as evidenced by the small intensity increase in this region. We attribute this increase to a reversal of the interfacial charge from negative to positive. This is confirmed by the phase change from 0 to  $\pi$  of the water modes at pH 2. This behavior matches well with studies of the  $\zeta$ -potential of ODS coatings on planar SiO<sub>2</sub>, which show the interfacial potential transitioning from large and negative to small and positive near pH 3.<sup>71,72</sup>

As shown in Figure 5, the changes to interfacial water as a function of pH on FDS-coated SiO<sub>2</sub> are dramatic, just as for ODS. The CH<sub>2</sub>(as) vibrations from the FDS monolayer are unaffected by changes in the bulk pH and are not shown as they are much more intense than the water signals.

The free-OH mode is located at  $3694 \pm 2 \text{ cm}^{-1}$  and is unaffected by changes in the bulk pH, just as for ODS and CCl<sub>4</sub>. It is important to note that the peak identified in ODS near

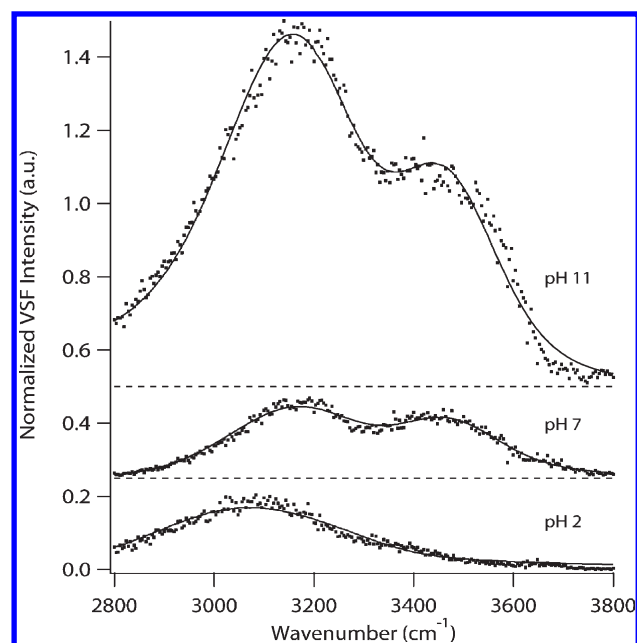
$3600\text{ cm}^{-1}$  as water in the ODS chains is not apparent at this interface. We ascribe this difference to the greater stiffness of the fluorocarbon chains, which are much larger in diameter than the ODS chains, making water less able to partially penetrate into the SAM.

The more coordinated water signal between  $3000$  and  $3500\text{ cm}^{-1}$  behaves similarly to that of ODS; the intensity in this spectral region is greatest at pH 11, and it decreases with decreasing pH. We attribute changes in the signal primarily to changes in the interfacial potential; the difference between the coordinated water signal in this spectral region on FDS and ODS is principally due to the shorter FDS chains. Measurements of the  $\zeta$ -potential of the aqueous FDS interface found that the potential decreases from  $\sim -60$  to  $-30\text{ mV}$  between pH 11 and pH 7, consistent with the intensity decrease near  $3200\text{ cm}^{-1}$  in Figure 5.<sup>71,72</sup> At pH 2, the VSFS signal is nearly flat in the coordinated water region; the spectrum can be well-fit using very broad water peaks with phases of either  $0$  or  $\pi$ . Thus, it is unclear from the fits whether the interfacial water molecules have reversed their orientation at this pH. However,  $\zeta$ -potential measurements have found the potential to be slightly positive at pH 3 for this interface, suggesting that the interfacial charge has switched from negative to positive by pH 2.<sup>71,72</sup>

While the two monolayer chains have different hydrophobicities, as is reflected in the frequency shifts of the free-OH mode, the similar spectral features of hydrogen-bonded interfacial water molecules as a function of pH at ODS, and FDS is indicative of similar orientation and bonding of the more strongly bonded interfacial water. This is in contrast to the very different observations for the  $\text{CCl}_4$  interface. These results are consistent with the conclusion in the previous section that a large amount of the water signal in the coordinated spectral region originates from some common feature of the SAMs, such as the influence of the substrate.

It has previously been suggested that ions can access the  $\text{SiO}_2$  substrate and generate an electrostatic field that orients water molecules above the chains.<sup>73</sup> The most likely means for this to occur is through defects in the SAM, which allow water molecules to penetrate through small gaps in the coverage and access the substrate. The procedure used to prepare the ODS surface has been shown to create high initial coverage that fills in over time,<sup>55</sup> but these same conditions lead to the deposition of occasional polymerized silanes on the surface, where water may find access. Similarly, the variations in surface pressure and transfer function during deposition of FDS lead to defects in FDS monolayers. Thus, a small number of  $\text{SiO}_2$  surface sites are available to react with acid or base and create a field to orient water. Substrate access is thus granted by pinhole defects in the SAMs, not through penetration of the monolayer chains themselves. Molecular dynamics simulations have shown that dense, well-ordered regions of ODS and FDS SAMs are not greatly disturbed by the presence of water.<sup>68,74</sup> If water penetrated to the substrate through the well-ordered regions of the SAMs, the coatings would degrade rapidly, which we do not see. However, small defects can fill with water and leave the remainder of the SAM relatively unaffected.<sup>68</sup> It is unlikely that water is able to access a large number of silanols given the high contact angle of the SAMs and the durability of these types of surfaces.

To determine how important these water–silanol interactions are for the SAM systems, we compare their behavior to that at the bare  $\text{SiO}_2/\text{H}_2\text{O}$  interface. The  $\text{SiO}_2/\text{H}_2\text{O}$  interface, which has been well-explored in the literature,<sup>40,75–77</sup> can be described via

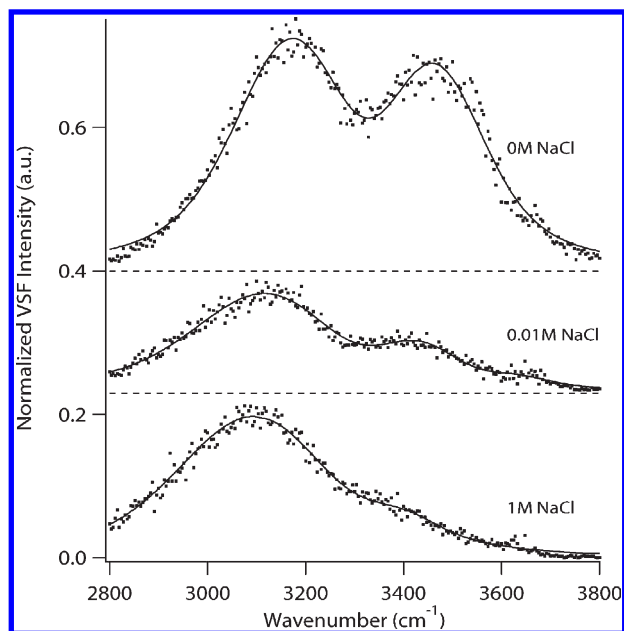


**Figure 6.** VSFS spectra in the SSP polarization scheme of the  $\text{SiO}_2/\text{H}_2\text{O}$  interface at different pH values with an ionic strength of  $0.01\text{ M}$ . Solid lines are fits to the data, and dashed lines represent zero signal.

the reaction of surface silanols with water.  $\text{SiO-H}$  groups on the surface react with water to set up an interfacial electrostatic potential that depends on the bulk pH. At high pH, the  $\text{SiO}_2/\text{H}_2\text{O}$  interface is highly negatively charged due to the deprotonation of  $\text{SiO-H}$  groups on the  $\text{SiO}_2$  substrate. This large negative charge generates an electrostatic field that orients water molecules with their OH bonds pointing toward the interface. Decreasing the pH reduces the number of deprotonated surface sites, reducing the interfacial electrostatic field until pH 2 when the surface is no longer charged—the point of zero charge (PZC).<sup>75</sup> At the PZC, second harmonic<sup>75</sup> and VSFS<sup>40,77</sup> studies measure signal that arises from water molecules that are inherently oriented by their interactions with  $\text{SiO}_2$  and not electrostatic interactions.

VSFS results for the  $\text{SiO}_2/\text{H}_2\text{O}$  interface at constant ionic strength, shown in Figure 6, confirm this picture. At pH 11 the VSFS signal is largely due to the electrostatic orientation of water molecules, and the spectrum consists of two broad peaks near  $3200$  and  $3450\text{ cm}^{-1}$ . The broad mode near  $3200\text{ cm}^{-1}$  corresponds to water molecules in a strongly coordinated hydrogen-bonding environment, while the intensity in the  $3450\text{ cm}^{-1}$  region is due to molecules that are more asymmetrically coordinated. At pH 7 the VSFS signal decreases due to a smaller electrostatic field and the hydrogen-bonding interactions of water with protonated silanols. At pH 2, the PZC of the  $\text{SiO}_2/\text{H}_2\text{O}$  interface, there is still significant signal from oriented water molecules, but the spectral shape has changed significantly. These spectra are at constant ionic strength; thus, the screening length is constant, and the pH 2 VSFS spectrum is attributed to species inherently oriented by their interactions with  $\text{SiO}_2$ .

The similarities in the pH-driven behavior of interfacial water at the SAM and  $\text{SiO}_2$  interfaces, namely increasing signal with increasing pH, provides further support for the conclusion that the substrate is influencing the overall orientation and bonding of interfacial water for these SAMs systems. At the SAM/water interface, water molecules are clearly able to access some percentage of

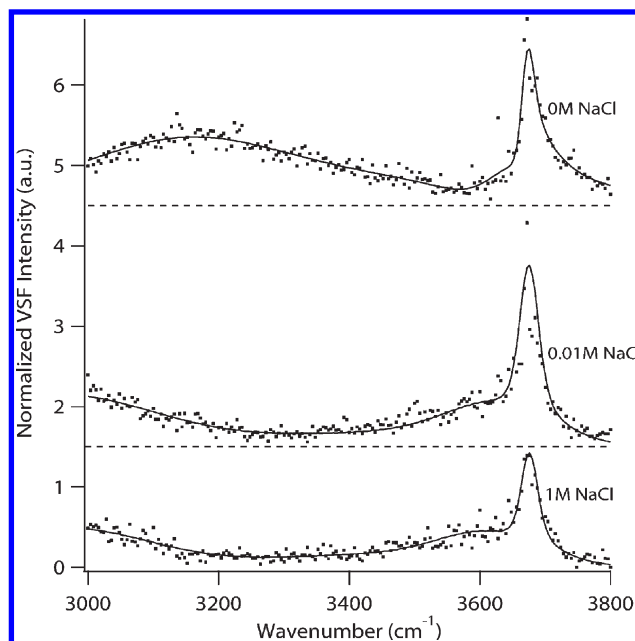


**Figure 7.** VSFS spectra in the SSP polarization scheme of the SiO<sub>2</sub>/H<sub>2</sub>O interface with pure water, 0.01 M NaCl and 1 M NaCl at pH 5.8. Solid lines are fits to the data, and dashed lines represent zero signal.

the SiO<sub>2</sub> substrate and engage in protonation/deprotonation reactions. The deviation from the exact behavior of SiO<sub>2</sub> is due to the small number of sites available for protonation/deprotonation reactions. There is no free-OH at the SiO<sub>2</sub>/H<sub>2</sub>O interface because the silanols are engaged in hydrogen bonding with the aqueous phase.

The free-OH amplitudes are unaffected by changes in bulk pH for all of the hydrophobic interfaces examined within, indicating that H<sup>+</sup> and OH<sup>-</sup> ions are neither displacing straddling water molecules nor is the hydrophobic interface becoming more disorganized, as this would reduce the intensity of the free-OH by increasing the angular distribution of the OH oscillators. This suggests that the direct interactions of H<sub>2</sub>O with FDS, ODS and CCl<sub>4</sub> are similar and that the topmost H<sub>2</sub>O layers are nearly identical. Differences observed between the two SAMs for the more coordinated water region is due to a combination of the differences in the electrostatic potential at the monolayer surfaces, arising primarily from the chain length and chemical composition differences of the two SAMs which mask the substrate charge and possibly have different affinities for OH<sup>-</sup> and H<sup>+</sup> ions at the two hydrophobic surfaces. The water molecules at the FDS interface may also be more highly oriented normal to the interface, resulting in a greater VSFS response based on the sharpness of the interface, which shows no signs of water molecules trapped within or disrupting the monolayer chains as is seen in ODS by the resonance near 3600 cm<sup>-1</sup>.

**Ionic Strength Effects on Hydrophobic Interfaces.** The pH experiments show the effects of changing interfacial charge on water structure at hydrophobic interfaces. However, the picture revealed is incomplete without complementary data that probes electrostatic field effects explicitly. As noted above, the stronger the field strength and subsequent depth, the larger the number of oriented water molecules that contribute to the VSFS signal. To reduce this effect, high concentrations of nonspecifically adsorbing ions, Na<sup>+</sup> and Cl<sup>-</sup> have been employed to screen the electrostatic field at the SiO<sub>2</sub> and SAM interfaces and then



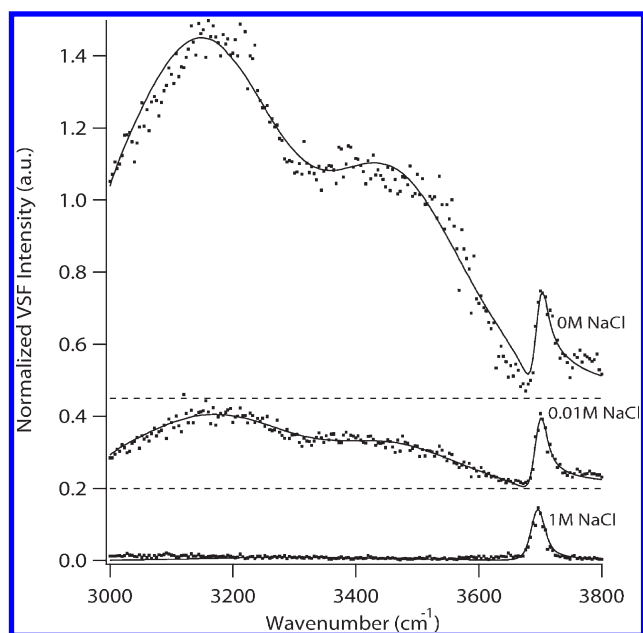
**Figure 8.** SSP polarized VSFS spectra of the ODS/H<sub>2</sub>O interface at pH 5.8 and with no added ions, 0.01 and 1 M NaCl. Solid lines are fits to the data. The spectra are offset for clarity.

compared with recent similar studies for CCl<sub>4</sub>. This method of electrostatic field screening has been used to reveal the structure of surface water layers at aqueous CaF<sub>2</sub><sup>45</sup> and SiO<sub>2</sub><sup>78</sup> interfaces.

Surface charge-induced orientation of water by SiO<sub>2</sub> can be verified by collecting VSFS at constant pH and varying the ionic strength, as shown in Figure 7. At pH 5.8, the SiO<sub>2</sub> surface has a negative charge, but the magnitude of this charge is much smaller than at pH 11. Under these pH conditions, the water spectrum is dominated by two peaks near 3200 and 3450 cm<sup>-1</sup>. Adding NaCl and increasing the ion content screens the field originating from the charged SiO<sub>2</sub> surface, reducing the number of electrostatically oriented water molecules. Compression of the field by ions results in significant changes in the spectral shape, and at 1 M NaCl the SiO<sub>2</sub>/H<sub>2</sub>O spectrum is nearly identical to that seen at pH 2 in Figure 6, where the surface field should be at a minimum. At this ionic strength, the double layer thickness under the Debye–Hückel approximation is 0.4 nm. A recent study of the SiO<sub>2</sub>/H<sub>2</sub>O interface performed similar ionic strength experiments using multiple polarization schemes to determine the orientation of the interfacial water molecules.<sup>78</sup> Their VSFS results are qualitatively similar to ours, and the differences between our spectra of this interface and others<sup>40,77,78</sup> can be attributed to the use of different SiO<sub>2</sub> surfaces.

VSFS spectra of the ODS/water interface at pH 5.8 with no added salt, 0.01 and 1 M NaCl concentrations are shown in Figure 8. The 0.01 M ionic strength is shown for comparison with the pH solutions of Figure 4 that were also at this ionic strength. For ODS, increasing the ionic strength of the pH 5.8 solution to 0.01 M results in a spectrum somewhere between the pH 2 and pH 7 results of Figure 4. Continuing to increase the ionic strength to 1 M results in almost no change to the VSFS spectrum as the interfacial electrostatic field is already well screened by the Na<sup>+</sup> and Cl<sup>-</sup> ions. The spectral decrease that occurs as the ionic strength is increased is mainly in the coordinated water region near 3200 cm<sup>-1</sup> where water signal is largely from water molecules deeper in the interfacial region.





**Figure 9.** VSFS spectra of the FDS/H<sub>2</sub>O interface at pH 5.8 and with no added ions, 0.01 and 1 M NaCl. The spectra are SSP polarized, and solid lines are fits to the data. The spectra are offset for clarity.

Additionally, as electrolyte concentration is increased, a shoulder becomes apparent near 3600 cm<sup>-1</sup> from water molecules within the ODS chains, just as seen at pH 2. The amplitude of the free-OH itself appears to change with increasing ionic strength, but this is due to changing spectral interferences. As the ionic strength is increased, the spectra resemble the alkane/water spectra where the substrate effects are absent.<sup>36</sup> The spectral intensity in the 3000–3200 cm<sup>-1</sup> region of the higher ionic strength spectra is due to the tailing of the CH stretching vibrations of the ODS chains and a small amount of strongly coordinated water.

The effects of a high concentration of NaCl on FDS/H<sub>2</sub>O spectra resemble those at ODS; spectra of FDS/water and FDS/NaCl(aq) are shown in Figure 9. The FDS/H<sub>2</sub>O spectrum at 0.01 M is nearly identical to that seen at pH 7 in Figure 5 also conducted at 0.01 M ionic strength with a large intensity comprised of two broad modes in the 3000–3500 cm<sup>-1</sup> region arising from the stretching vibrations of more and less strongly coordinated water molecules. The intensity of these modes decreases to nearly zero with the addition of NaCl, supporting the conclusion that the majority of the oriented water molecules for these monolayer systems arise from interfacial fields. There is a small amount of water signal in the 3000–3200 cm<sup>-1</sup> range, possibly from water molecules at the SiO<sub>2</sub> substrate in defect sites. The apparent amplitude of the free-OH peak appears to decrease when spectra are collected in NaCl solutions, just as with ODS. However, spectral fitting shows that this is due to the loss of constructive interference with the coordinated water modes and that the peak remains unaffected by the presence of Na<sup>+</sup> and Cl<sup>-</sup> ions in the interfacial region. In the case of both ODS and FDS, this indicates that ions do not displace or change the orientation of the straddling interfacial water molecules.

In the absence of added salt or acid, a larger signal in lower frequencies is present at the FDS/H<sub>2</sub>O interface than at the ODS interface. Dipoles such as those present between CF<sub>2</sub> and CH<sub>2</sub> groups can cause decreased water contact angle<sup>79</sup> and may cause

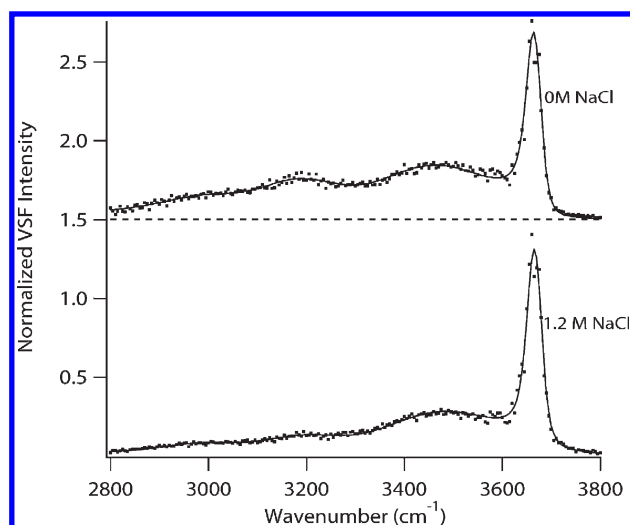
water orientation. However, the dipole effect on contact angle is nonexistent once the total fluorocarbon length is greater than four,<sup>80</sup> which is the case with FDS monolayers. Furthermore, the high degree of fluorination in the FDS monolayers is greater than that required for minimizing the surface free energy in semi-fluorinated alkane thiols. At eight fluorocarbons, the polar work of adhesion is near zero for semifluorinated alkane thiols<sup>80</sup> and the van der Waals surface energy is approximately 10 mJ/m<sup>2</sup>.<sup>81</sup> This is a further indication that the FDS layer itself should not induce significant orientation of water molecules and should interact with water molecules only very weakly, as seen by the free-OH frequency.

Nevertheless, the greater water signal suggests that the effective electrostatic field at the interface must be greater at the FDS surface than at ODS. Zeta potential measurements of FDS and ODS surfaces found that both surfaces had identical electrokinetic behavior, suggesting that the interfacial potential is driven by the SiO<sub>2</sub> substrate and not specific ion adsorption.<sup>71,72</sup> Therefore, we conclude that the interfacial electrostatic field comes primarily from the SiO<sub>2</sub> substrate, which has been shown to be only partially directly bonded with silane monolayers and unaffected by the functionality of the monolayer forming molecules.<sup>82,83</sup> Thus, a likely reason for a difference in the effective electrostatic field at the SAM/water interface is capacitance differences between the monolayers. The Stern model is commonly used to explain behavior at highly charged interfaces and detailed explanations of the model can be found in the literature.<sup>84,85</sup> The potential drop over a layer of constant capacitance is given by:

$$\psi_0 - \psi_d = \frac{-\sigma_0 d}{\epsilon \epsilon_0} \quad (5)$$

where  $\psi_0$  is the surface potential and  $\psi_d$  is the potential on the other side of the Stern layer. The surface charge is  $\sigma_0$ ,  $d$  is the layer thickness,  $\epsilon$  and  $\epsilon_0$  are the relative permittivity of the medium and the permittivity of free space. Taking the surface potential of SiO<sub>2</sub> as  $-35$  mV at near neutral pH,<sup>75,86</sup> and the charge density as  $-3.2 \times 10^{-4}$  C/m<sup>2</sup>,<sup>87</sup> chemical specific parameters of the monolayers can then be used to calculate the electric potential at the monolayer surface. We estimate the dielectric constants of FDS and ODS SAMs as those of polytetrafluoroethylene and polyethylene, which are 2.1 and 2.33, respectively.<sup>88</sup> The thickness of the FDS layer was assumed to be 1.1 nm and the ODS monolayer 1.9 nm, based on ellipsometry measurements by Hozumi et al.<sup>72</sup> Using these parameters, the potential at the FDS surface is  $-16$  mV and  $-5.5$  mV for the ODS layer. This large difference in interfacial potential partially explains why there are more oriented water molecules at the FDS/water interface than at the ODS/water interface. Additionally, fluorocarbons have larger van der Waals diameters than hydrocarbons, 5.6 and 4.2 Å, respectively,<sup>89</sup> which may create more strain on the Si–O–Si cross-links ( $\sim 4$  Å)<sup>90</sup> at the base of the monolayer and lead to more defects in the SAM, allowing more water to access the surface. This point charge model of the interface is not strictly applicable to the liquid/liquid interface, but important comparisons can be drawn between the behavior of the CCl<sub>4</sub>/H<sub>2</sub>O interface with added NaCl and the behavior of water at FDS and ODS.

Effects of different salts on the CCl<sub>4</sub>/H<sub>2</sub>O interface have been previously studied;<sup>7</sup> Figure 10 presents spectra from that analysis. The presence of NaCl decreases the VSFS intensity below



**Figure 10.** SSP polarized VSFS spectra of the neat  $\text{CCl}_4/\text{H}_2\text{O}$  interface at pH 5.8 and with 1 M NaCl. Solid lines are fits to the data. The spectra are offset for clarity.

$3600\text{ cm}^{-1}$  with the majority of the change occurring around  $3200\text{ cm}^{-1}$ . This reflects the fact that those molecules in the  $3200\text{ cm}^{-1}$  region are somewhat deeper in the interfacial region and are largely oriented by field effects that arise from the inherent orientation of water immediately in contact with the organic liquid. The intensity near  $3500\text{ cm}^{-1}$  which is due to the donor OH mode and other weakly hydrogen-bonded water molecules in the topmost layer are only slightly affected by the presence of  $\text{Cl}^-$ . The free-OH intensity is unaffected by the presence of the salt. It is clear that ions are attracted to this interface, but their overall effect on interfacial water structure is less dramatic than for either of the monolayer samples.

These NaCl experiments show that there are fundamental differences and similarities between the FDS, ODS, and  $\text{CCl}_4$  interfaces that are consistent with the pH studies. At all three hydrophobic interfaces, the free-OH remains unaffected by the addition of ions or acid. The fields produced at the substrate greatly enhance the orientation of water both at the substrate and just beyond the monolayer over those directly in contact with the hydrophobic portions of the monolayer. Reduction of this field by either pH or by the addition of high concentrations of salt reveals a spectrum at the monolayer/water interface that more closely mimics that found for the nonpolar organic liquids with much weaker interfacial water-bonding interactions. Clearly visible in the ODS spectra under these high salt conditions, and also apparent in the spectral fitting of the pH results, is a peak near  $3600\text{ cm}^{-1}$  that is not replicated in the FDS spectra. We attribute this feature, which was seen in the pH studies shown in Figure 4 to water molecules in the ODS chains, as was discussed earlier. Similar spectral features have been predicted by molecular dynamics studies of alkanes, and oriented water monomers penetrating into the  $\text{CCl}_4$  have been found in this spectral region also.<sup>57</sup> Recent molecular dynamics studies have shown that immersion of such monolayers in water affects the orientation of ODS chains in even ideal SAMs and that this effect becomes greater with increasing number of defects in the SAM.<sup>68</sup> Under high salt concentrations this additional feature is not apparent for FDS, consistent with the

greater hydrophobicity of FDS which prevents water from penetrating into the chains in monomeric form. A recent simulation of fluorocarbon monolayers in contact with water found that at the molecular areas used to prepare these SAMs water neither perturbs nor penetrates into the chains.<sup>74</sup>

The addition of salt has a smaller but non-negligible effect on the liquid/liquid interface. The neat  $\text{CCl}_4$  interface has been shown through experimental and computational results to be composed of water molecules with a relatively high degree of molecular orientation.<sup>7,63</sup> At the topmost layer, water molecules at the  $\text{CCl}_4$  interface adopt a specific orientation due to contact with the hydrophobic phase. Additionally the nonaqueous phase also can adopt a preferred and layered orientation.<sup>7,10</sup> The result is that the orientation on both sides of the interface contributes to interfacial potential and orient additional water molecules somewhat deeper in the interfacial region. These more highly coordinated water molecules are the ones most affected by the added salt.

At the  $\text{CCl}_4/\text{H}_2\text{O}$  interface, different ions were found to have different effects on the interfacial structure based on their size and polarizability.<sup>7</sup> This ion-specific behavior is something not seen in the SAM studies within. However, the effects of pH and ionic strength on the  $\text{CCl}_4/\text{H}_2\text{O}$  interface are much weaker than at the SAM surfaces, which shows that the electrostatic field at the interface is much smaller and that ions have to reach a higher concentration to perturb interfacial water structure at the  $\text{CCl}_4$  interface. For the SAM systems, the large coordinated water signals with their high dependency on bulk pH and ionic strength show that water orientation extends deep into liquid phase, and the behavior observed gives rise to the ability to model the interface using the method above. It may be that at sufficiently low surface charge or at high ionic strength, specific ion adsorption behavior is present, but those studies are beyond the scope of this paper.

It is worth noting that when the FDS and ODS interfaces were exposed to dilute solutions of NaCl ( $1 \times 10^{-4}\text{ M}$ ), the intensity of the VSFS spectra in the coordinated water region increased slightly. This can be attributed to a small preferential attraction of  $\text{Cl}^-$  ions to the interface which increases the net electrostatic field and thus the number and/or degree of water orientation. This fits with the recent conclusions drawn by Tian and Shen, that  $\text{Cl}^-$  and  $\text{OH}^-$  ions are attracted to hydrophobic interfaces.<sup>33</sup> However, it seems unlikely that the presence of ions alone, given the known chemistry of the  $\text{SiO}_2$  substrate, can explain the observations here.

## CONCLUSION

These studies have examined the behavior of water at the surface of hydrocarbon and fluorocarbon SAMs in solutions containing different concentrations of ions and acids. The motivation for these studies has been to understand how the interfacial water might be affected by these added electrolytes, and if effects are observed, the origin of these effects. To achieve these goals we have taken a systematic approach to measuring the vibrational spectroscopy of interfacial water via VSFS from different regions of the interface. This has been facilitated by comparative studies of similar electrolyte solutions in contact with related organic liquids where the influence of a substrate is not present. Such liquid/liquid studies also assist in deriving information about water interactions and the possible presence of ions at the hydrophobic

terminus of the monolayers. Understanding the contribution of water from the monolayer bound substrate has been aided by ionic strength studies where high concentrations of ions minimize the electrostatic fields generated at the substrate surface that can influence water and ions well beyond the terminus of the monolayers.

Some striking similarities can be found between the water/monolayer interface and the water/hydrophobic liquid interface. The interface between water and the hydrophobic terminus of the monolayers is relatively sharp, as is found to be general behavior for water adjacent to nonpolar liquids. This is manifested in the measurement of interfacial water molecules at higher frequencies that weakly bond to the organic monolayer, similar to what is observed at related liquid/liquid interfaces. The degree of interaction is dependent on the molecular form of the hydrophobic phase, with a progressively stronger interaction as one moves from fluorocarbon monolayers, to hydrocarbon monolayers and alkanes, to more polarizable liquids like  $\text{CCl}_4$ . This weak interaction is identical in strength for water bonded to the hydrocarbon SAMs and various alkanes examined. The presence of ions and acids has no significant impact on this weak interaction between water and the free-OH mode in all cases.

Beyond that, the behavior of more highly coordinated water, which appears at lower frequencies in the VSFS spectra, displays very different behavior at the SAM interfaces relative to the  $\text{CCl}_4$ /water interface. We attribute this to the influence of electrostatic fields at the  $\text{SiO}_2$ /monolayer interface that is present due to water molecules and ions permeating the monolayers. For the monolayer films, there is an abundance of highly coordinated and highly oriented water molecules that dominate the VSFS spectra in this lower frequency region ( $<3600\text{ cm}^{-1}$ ). These water molecules are strongly affected by the presence of various ions and any alteration in pH. In contrast, for the liquid/liquid interface, the presence of such electrolytes is measurable but small, and the observed trends in intensity are often opposite to what is observed for the monolayers. The presence of  $\text{OH}^-$  ions increases water bonding and orientation at the monolayer containing interfaces examined, but had the opposite effect on the  $\text{CCl}_4$ /H<sub>2</sub>O interface. At the liquid/liquid interface,  $\text{OH}^-$  serves to disrupt the hydrogen-bonding network and  $\text{H}^+$  enhances that network, just as at the air/water interface. For the monolayer surfaces,  $\text{OH}^-$  deprotonates substrate silanols, which creates and electrostatic field to orient water molecules. Salt screening experiments remove this electrostatic component and reveal those water molecules whose interactions are governed by their direct interactions with their nonaqueous neighbors. As the salt concentration is raised and the electrostatic field increasingly screened, the spectra from the SAMs start to resemble the  $\text{CCl}_4$ /water spectra where interfacial fields are significantly lower and largely a result of water-organic interactions and the much smaller fields generated by these oriented dipoles. For the liquid/liquid interface, the observed trends are consistent with both hydroxide ions and protonated species migrating to the interface to a much greater degree than has been observed at the air/water interface. Garnering such detail about whether the ions from the aqueous ion, acid or basic solution are present at the terminus of the monolayers is difficult due to the dominating effect of the substrate generated fields.

As interest continues to grow in understanding how ions can affect the surface of water and in particular, water near

hydrophobic media, it is important to recognize the many complex factors that can contribute. The type of charged species and how they interact with water molecules and the solid or liquid system has a significant impact on interfacial behavior. For monolayer interfaces such as these, treating ions at these interfaces as one would treat ions at a fluid hydrophobic interface is a start but is clearly insufficient to describe the behavior accurately. Rather, full consideration of all interfacial components is required to understand the breadth and depth of behavior at hydrophobic surfaces.

## ■ ASSOCIATED CONTENT

§ **Supporting Information.** AFM, contact angle, and XPS analysis of ODS and FDS SAMs; the isotherm for FDS deposition; VSFS spectra of the SAMs in air and  $\text{D}_2\text{O}$ ; the full pH series of the  $\text{CCl}_4$ /H<sub>2</sub>O interface. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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