

Sum Frequency Generation Investigation of Water at the Surface of H₂O/H₂SO₄ Binary Systems

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Structural data about water at the air/water interface of sulfuric acid solutions have been obtained with sum frequency generation spectroscopy. Sulfuric acid significantly affects the orientation of water at the interface. With as little as 0.01x (mole fraction) sulfuric acid, water is more highly oriented compared with the pure water surface. Surface water with one hydrogen free of hydrogen bonding, a “free OH”, decreases in concentration as the sulfuric acid concentration is increased. Finally, there are no sulfuric acid free OH groups projecting out of the surface for solutions from 0.01x to 0.9x sulfuric acid. Observations of the structure of water are consistent with the fact that sulfuric acid/water solutions change from ionic in nature at low concentrations (<0.01x) to ion pair complexes/hydrates at high concentrations (>0.4x).

Introduction

Water is a ubiquitous material, playing important roles in areas as diverse as biology, corrosion, and the environment. Hence, the structure and partitioning of water at aqueous interfaces is a subject of great importance. Recently, the vibrational structure of interfacial water at the neat air/liquid interface has been determined.¹ Also, the effect of neutral organic molecules on the water surface has been investigated.^{2–4} However, the influence of inorganic ions on surface water has not been examined with molecular sensitivity despite their importance in atmospheric chemistry⁵ and biological systems.

Aqueous interfaces are important in a variety of atmospheric chemistry issues ranging from cloud formation to ozone depletion. In the stratosphere, the major condensed phase consists of sulfuric acid solutions with a concentration of 0.1x to 0.4x or 40–80 wt %. (Table 1 has conversions for several H₂SO₄ solutions.^{6,7}) The surface of this condensed phase is believed to serve as a condensation site for polar stratospheric cloud formation and to play an important role in heterogeneous chemistry at midlatitudes. Understanding the chemical composition and structure of the air/H₂SO₄(aq) interface is critical to developing models of the surface chemistry occurring on them. This paper discusses the influence of H₂SO₄ on the orientation and concentration of surface water as determined by sum frequency generation (SFG).

The SFG studies here demonstrate that sulfuric acid tends to increase the order of surface water molecules at low mole fraction concentrations ($\leq 0.1x$) by increasing the hydrogen-bonding network. Water is increasingly bound in hydrates and displaced from the surface as H₂SO₄ bulk concentration increases, as demonstrated by a smooth decrease in the free OH peak of water. A free OH group is one which is projecting out of the liquid surface into the vapor, so that it is free of hydrogen bonding. At concentrations above 0.4x H₂SO₄, uncomplexed water does not appear at the surface and is completely bound into hydrates/complexes. Finally, there are no sulfuric acid free OH groups projecting out of the surface for solutions from 0.01x to 0.9x sulfuric acid.

TABLE 1: Conversions for Some Common H₂SO₄ Solutions

mole fraction (x)	molality (m)	molarity (M)	wt %	hydrate no.	density (g/mL)
0.01	0.56	0.55	5	99.00	1.03
0.02	1.13	1.09	10	49.00	1.07
0.05	2.92	2.63	22	19.00	1.16
0.10	6.17	4.93	38	9.00	1.28
0.11	6.94	5.40	40	8.00	1.31
0.13	8.55	6.29	46	6.50	1.35
0.14	9.26	6.66	48	6.00	1.37
0.17	11.11	7.53	52	5.00	1.42
0.20	13.89	8.66	58	4.00	1.47
0.25	18.52	10.18	64	3.00	1.55
0.33	27.78	12.30	73	2.00	1.65
0.40	37.04	13.67	78	1.50	1.71
0.50	55.56	15.27	84	1.00	1.77
0.90	500.00	18.36	98	0.11	1.84

Background

SFG is an ideal technique for probing air/liquid interfaces. In the electric dipole approximation, SFG, a $\chi^{(2)}$ process, is forbidden in bulk media but allowed at the surface where inversion symmetry is broken. Hence, SFG is a surface-specific technique. As a result of this surface specificity, SFG is sensitive to a few hundredths of a monolayer.

Surface SFG is described extensively in the literature;^{8–11} therefore, only a brief summary is given here. Sum frequency generation occurs when two laser beams are overlapped on the surface in space and time. The resultant signal occurs at the sum of the infrared, ω_{IR} , and visible, ω_{VIS} , input frequencies

$$\omega_{\text{SF}} = \omega_{\text{IR}} + \omega_{\text{VIS}} \quad (1)$$

The SFG signal intensity, I_{SFG} , is mediated by the macroscopic hyperpolarizability tensor $\chi^{(2)}$

$$I_{\text{SFG}} \propto |\chi^{(2)} : \mathbf{E}_1 \mathbf{E}_2|^2 \quad (2)$$

where \mathbf{E}_1 and \mathbf{E}_2 are the electric fields of the input visible and infrared laser beams, respectively. The infrared frequency is scanned, and as it comes into resonance with a vibrational mode

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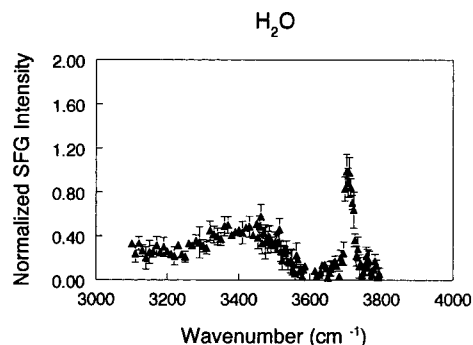


Figure 1. SFG spectrum of the neat water interface. Spectrum is normalized to the free OH peak at 3710 cm^{-1} .

of the molecule, $\chi^{(2)}$ increases to a maximum, resulting in a peak in the SFG spectrum.

The SFG intensity, I_{SFG} , is proportional to the square of the macroscopic hyperpolarizability, $\chi^{(2)}_{IJK}$, which is related to the microscopic hyperpolarizability, β_{IJK} , by

$$\chi^{(2)}_{IJK} = N\langle\beta_{IJK}\rangle \quad (3)$$

where N is the number of molecules contributing to the SFG signal, IJK refers to the surface-fixed coordinate system, and $\langle...\rangle$ indicates an ensemble average over the orientational distribution. Hence, the square root of the intensity is not only proportional to the number of molecules but also depends on their orientation.

Experimental Section

The SFG setup has been described in detail previously.³ Briefly, the experiment involves a KTP-based OPO/OPA (LaserVision) pumped by the fundamental of a 10 Hz Nd:YAG laser (Spectra-Physics GCR 150). The OPO/OPA is tunable from 2500 to 4000 cm^{-1} with energy from 0.4 to 6 mJ/pulse. The infrared bandwidth is $\approx 4 \text{ cm}^{-1}$ at 3100 cm^{-1} .

Sulfuric acid (GFS, 96–98 wt %) is evacuated at 20 mTorr for 24 h before making solutions. Solutions are handled under UHP N_2 in glass or Teflon containers and made with 18 $\text{M}\Omega\cdot\text{cm}$ water (Barnstead Nanopure). The sample surface is determined to be clean when an SFG spectrum in the CH region produces no resonant signal, indicating a coverage of less than 0.05 monolayer.

The quartz/water interface is probed by directing the laser beams through the backside of an IR quartz disk (Esco) and overlapping at the liquid/quartz interface. The pH of the solution is controlled with NaOH or HCl (Fluka).

Spectra are recorded at $273 \pm 2 \text{ K}$. The temperature is regulated with a home-built temperature feedback controller. Solutions remained liquid during the course of the experiment. The SFG data are gathered in 4 cm^{-1} increments from 3450 to 3800 cm^{-1} where resonances are expected to be narrow due to free OH groups and in 10 cm^{-1} increments from 3100 to 3450 cm^{-1} where hydrogen bonding broadens peaks. Each spectrum is collected by averaging 400 laser shots per data point. The presented spectra are an average of four separate spectra with error bars plotted at one standard deviation, 1σ . The deviation is typically $\pm 10\%$ of the signal intensity. All spectra are corrected for infrared intensity fluctuations and are normalized to the free OH peak of the neat water interface.

Results

Figure 1, the *ssp* spectrum of pure water, is in good agreement with the results of Du et al.¹ for water at the air/liquid

interface. *ssp* refers to the polarization of the sum frequency, visible, and infrared beams, respectively. Three features are seen in this spectrum: a sharp resonance at 3710 cm^{-1} , a broad peak at 3450 cm^{-1} , and a peak at $\approx 3200 \text{ cm}^{-1}$, which is not fully resolved but appears as a shoulder on the low-energy side of the spectrum. The peak at 3710 cm^{-1} is due to a free OH group of water. A free OH group is an OH group that projects out of the surface into the vapor so that it is free of hydrogen bonding. Water with only one of its free OH groups projecting from the surface has a surface coverage of ≈ 0.25 monolayer.^{1,2}

Due to the importance of water, there have been numerous investigations into the structure of bulk water using vibrational spectroscopy.^{12–16} Surprisingly, there is a lack of complete agreement on the peak assignments in the hydrogen-bonded region, 3100–3600 cm^{-1} . The following interpretation of the SFG spectrum is based on the infrared data and Raman polarization experiments of bulk water and ice. The peak at 3450 cm^{-1} is assigned to a combination of hydrogen-bonded water molecules in an asymmetrical environment and to the asymmetric stretch of symmetrically bonded water.^{12,15–17} The asymmetrical environment for water is where the two hydrogens are in different hydrogen-bonded environments. Thus, the 3450 cm^{-1} peak is a convolution of water in two environments, symmetrical and asymmetrical, which cannot be resolved in this experiment. The 3200 cm^{-1} resonance is due to the symmetric stretch of water hydrogen-bonded in a symmetrical environment. Evidence for this model is found in the infrared spectrum of single-crystal ice where the 3200 cm^{-1} peak dominates the ice spectrum, and water is highly ordered in a symmetrical, tetrahedral environment.¹³ Further, the 3200 cm^{-1} peak appears in the polarized Raman spectrum of liquid water but does not in the depolarized spectrum.^{14,15}

The addition of H_2SO_4 to water has a substantial effect on the *ssp* spectra as shown in Figure 2 where several sulfuric acid concentrations between 0.01x and 0.9x are shown. In Figure 2A (0.01x) the peak intensity at $\approx 3200 \text{ cm}^{-1}$ increases to about 5 times that of pure water while the peak intensity at 3450 cm^{-1} increases 1.5 times. The 3710 cm^{-1} peak height decreases to 70% of its value in pure water. At a higher concentration of sulfuric acid (0.05x), Figure 2B, the peak intensity at $\approx 3200 \text{ cm}^{-1}$ decreases slightly from the 0.01x solution. The 3450 cm^{-1} peak increases to over twice the intensity of that in water, and the 3710 cm^{-1} peak intensity decreases to 50% of that in water. At 0.1x H_2SO_4 , Figure 2c, the 3200 cm^{-1} peak intensity decreases by approximately 30% compared to the 0.05x solution, and the 3450 cm^{-1} peak intensity decreases to the value it had in the 0.01x solution. However, the 3710 cm^{-1} peak height in 0.1x H_2SO_4 has diminished to 0.2 of the intensity in water. The spectrum of the 0.2x solution, Figure 2D, has changed dramatically from that of the 0.1x solution. The two peaks in the 3100–3500 cm^{-1} region have nearly the same intensity as water; however, the 3710 cm^{-1} peak intensity is at 5% of that in water, which is at the edge of the detection limit. Increasing the concentration to 0.4x H_2SO_4 (Figure 2E) has another large effect on the spectrum. The 3450 cm^{-1} peak has disappeared into the noise, and the 3200 cm^{-1} peak is near the noise level at about 10% of the water spectrum. At 3710 cm^{-1} , no resonances can be seen. The 0.9x solution, Figure 2F, is spectrally indistinguishable from the 0.4x solution in the 3100–3800 cm^{-1} region. The peak intensities as a function of sulfuric acid mole fraction are plotted in Figure 3. The data plotted in Figure 3 are peak heights at approximately 3200, 3450, and 3710 cm^{-1} taken from the spectra in Figure 2.

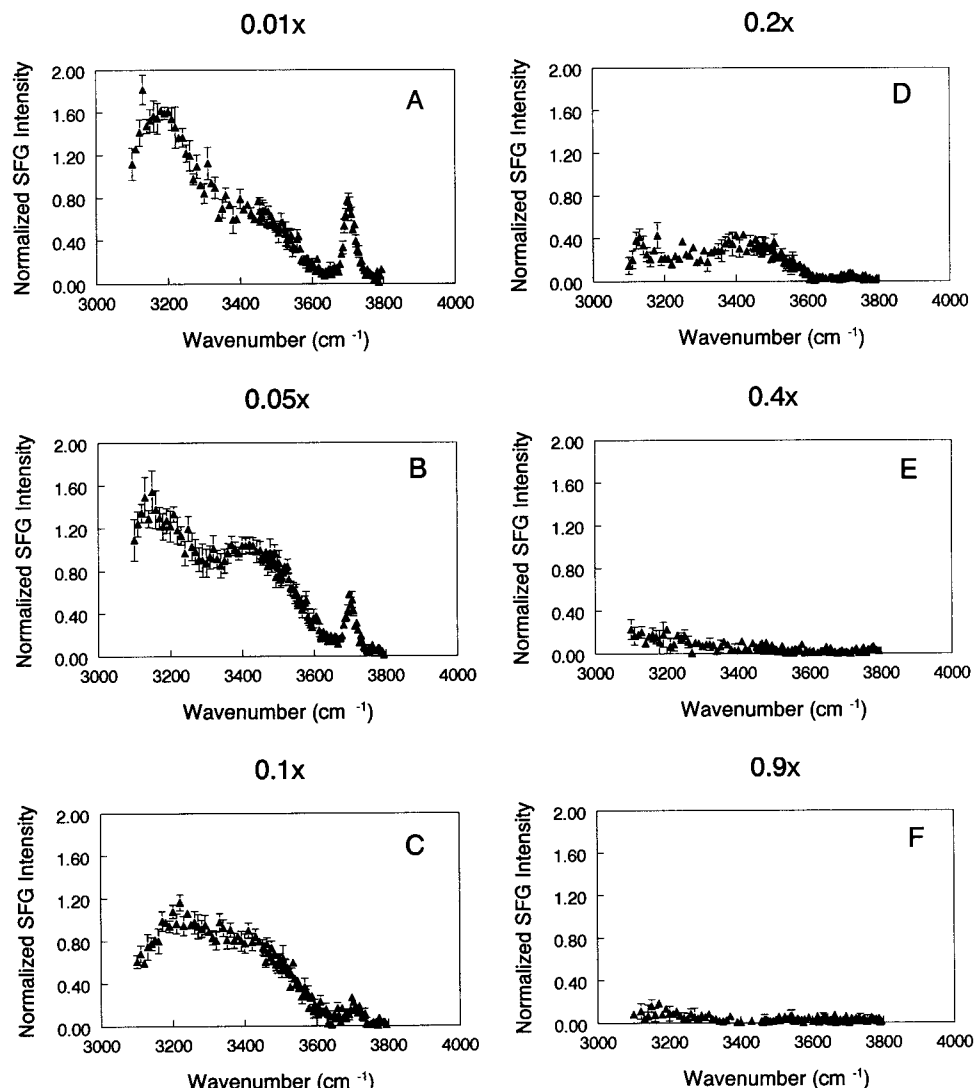


Figure 2. SFG spectra of $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ solutions at the air/liquid interface. Spectra are normalized to the free OH peak of water. Error bars are at 1σ and are typically $\approx 10\%$. Spectra are for *ssp* polarization.

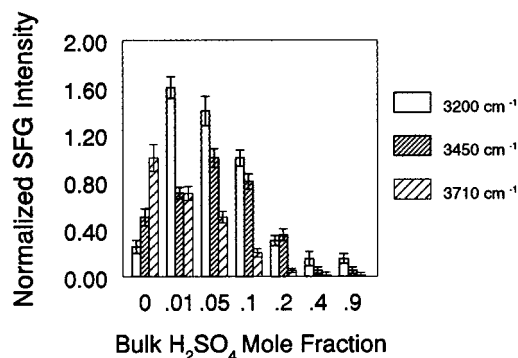


Figure 3. Summary of SFG intensity vs sulfuric acid concentration. Note x axis is not linear, and peaks are normalized to the free OH peak of the neat water interface.

Discussion

Sulfuric acid/water solutions have been the subject of much research over the past several decades. Properties such as conductivity,¹⁸ freezing point,^{7,19} vapor pressure,²⁰ and techniques such as NMR,^{21,22} calorimetry,⁷ and Raman and infrared spectroscopy^{23–26} have been used to elucidate the structure and composition of $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ solutions. There are two major descriptions of these solutions in the literature. One description is ion formation; the other is formation of hydrates or complexes.

The most appropriate description depends on the technique used to study the system, the focus of the investigators, and the concentration of acid. Both of these will be discussed and used to interpret the SFG results.

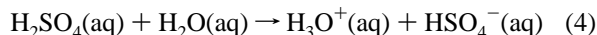
Bulk Solution. At low concentrations of H_2SO_4 , $\leq 0.01x$, the majority of sulfuric acid is ionized.^{24,27,28} Ion pairing begins to dominate when the sulfuric acid concentration is increased to $0.01–0.1x$. Finally, as the solution becomes more concentrated, $>0.1x$, molecular hydrates of the form $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ become the predominate species.^{7,18,27,29} These bulk species each have a noticeable effect on the surface water.

At concentrations $\leq 0.01x$, sulfuric acid is predominantly ionic in solution. The ions that have been identified in bulk solution at these concentrations are SO_4^{2-} , HSO_4^- , and H_3O^+ .^{24,27,28} However, even at this relatively low sulfuric acid concentration, the extent of dissociation by eq 4 is only about $0.5–0.6$. Thus, significant ion pairing/complex formation is occurring.^{7,18,27,29}

By $0.1x$ H_2SO_4 , the formation of complexes and ion pairs begins to dominate the bulk solution. Stable hydrates have been observed, for example $\text{H}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$,⁷ and extensive ion pairing is observed with Raman spectroscopy²¹ as well as calculated from conductance data.¹⁸ The distinction between species as ion pairs, as close-contact ion pairs, or as complexes is complicated and, in some cases, not agreed upon for species such as $\text{H}_3\text{O}^+ \cdot \text{SO}_4^{2-}$ or $\text{H}_2\text{O} \cdot \text{HSO}_4^-$.²¹ As solutions become

more concentrated, a mixture of lower hydrates $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ ($n = 6.5, 6, 4, 2, 1$) becomes the predominate species in solution.⁷ Identification of these hydrates as molecular or as ion pairs is not made, however. As the solution water content decreases, there is simply not enough water to solvate ions as evidenced by conductivity data, which show a decrease in conductivity with increasing H_2SO_4 concentration.³⁰

Ionic Model. When sulfuric acid is placed in water at low concentration, ionization occurs:



These ions are surrounded by solvation shell(s) of water molecules which are oriented with their negative dipole end toward the cation and positive end toward the anion.^{31–33} As the ions approach the air interface, they increase in free energy. Thus, their approach to the surface is a function of hydration energy. That is, the ions begin to lose their outer solvation shell(s) near the surface and therefore increase in energy. The anion (sulfate or bisulfate) ion can penetrate closer to the surface due to its “softer”, more polarizable, nature, lower hydration energy, and lower hydration number compared with that of the cation.^{32–35} Molecular dynamics calculations also indicate that negative ions, Cl^- and F^- , preferentially partition to the surface over Na^+ in dilute solution.³⁶ Surface potential experiments support this partitioning of negative ions toward the surface.³⁷ In the $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ system, the negative ions approach closer to the surface with the positive ions behind them. This sets up an electric double layer which causes surface water molecules to be oriented by the negative ion charge.

Electric Double Layer. The preference for negative ions in solution to partition closer to the surface creates an electric double layer which perturbs the structure of the neat water interface. The permanent dipole of a water molecule responds to this negative electric field by reorienting with its hydrogen atoms pointing down into the bulk. This orienting effect is most pronounced for water closest to the electric double layer. Evidence for this model can be found in the SFG spectra. In the pure water spectrum, Figure 1, the peak at $\approx 3200 \text{ cm}^{-1}$ is attributed to OH_{sym} stretch of water in a symmetric environment.¹⁶ This is also observed for water in a single-crystal ice lattice which is in a similar environment.¹³ The peak at 3450 cm^{-1} may be interpreted as water in a hydrogen-bond disordering environment.³⁸

Addition of H_2SO_4 to water to make a $0.01x$ solution has a dramatic effect on the SFG spectrum. The 3200 cm^{-1} peak increases in intensity by a factor of 5. The 3450 cm^{-1} peak intensity increases 1.5 times that in water. This indicates that addition of a small amount of sulfuric acid induces a significant amount of order in the interfacial region. The intensity of the free OH peak, 3710 cm^{-1} , decreases to about 70% of the value in pure water. The significance of the free OH feature is discussed below. While it is difficult to quantitate peak intensity in the hydrogen-bonded region, the increases at 3200 and 3450 cm^{-1} exceed the decrease of the free OH. Therefore, the increase in the hydrogen-bonded region is not only due to water going from a free to hydrogen-bonded OH group. Rather, since SFG intensity depends on the number of molecules and their orientation, the intensity increase is a convolution of two effects. First, water molecules in subsurface layers are being oriented by the negative electric field of the double layer. Second, the greater electric field leads to the dipole of water with a greater average vertical alignment along the surface normal with their hydrogen atom pointing down into the bulk.

This intensity increase has also been observed with SFG for water at a known negatively charged quartz/water interface,

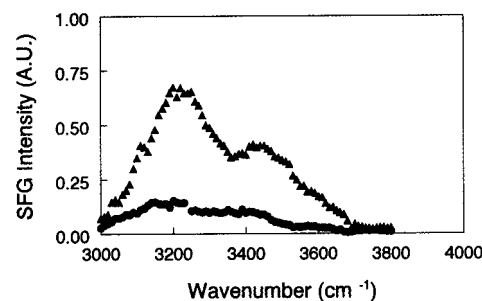


Figure 4. SFG spectra at the quartz/water interface: (●) pH = 2; (▲) pH = 12. The polarization is ssp and the temperature is 294 K.

where the electric field orients several layers of water.³⁸ This experiment has been reproduced in this laboratory, and the spectra are shown in Figure 4. At low pH values, the surface is protonated and electrically neutral, while at a basic pH the surface is negatively charged. The negatively charged interface creates about a 5-fold increase in peak intensity over the water spectrum at a neutral interface. A comparison between Figure 4 and the spectra in Figures 1 (water) and 2A ($0.01x \text{ H}_2\text{SO}_4$) suggests that the negative electric field can orient several layers of water at the air/liquid interface. This has also been observed in ferroelectric ice³⁹ and at the charged surfactant/water interface.⁴⁰ In the $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ system, the ions HSO_4^- and H_3O^+ are responsible for the electric double layer.

Several experimental^{37,41} and theoretical⁴² investigations of water at the air/liquid interface of ionic solutions have been explored with different techniques. The surface tension of the $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ system is essentially unchanged for $0.01x \text{ H}_2\text{SO}_4$ from pure water.³⁰ In contrast, surface tension measurements show that for most aqueous electrolyte solutions the air/liquid interface surface tension increases from that of pure water.⁴¹ This indicates a negative adsorption of ions at the surface and therefore a relative excess of water. Thus, the unchanged surface tension of $0.01x \text{ H}_2\text{SO}_4$ implies there is no change in the surface coverage of water. This agrees with calculations by Phillips⁴³ and AES experiments⁴⁴ which indicate the surface and bulk compositions are the same. The advantage of SFG is that it is sensitive to the molecular environment of water. Hence, at $0.01x \text{ H}_2\text{SO}_4$, water molecules at the surface and immediate subsurface have reoriented to a more regularly structured environment.

An increase in concentration of H_2SO_4 to $0.05x$ decreases the order of the water compared to the $0.01x$ solution. Decreased order is seen as a decrease in the tetrahedrally bonded OH peak intensity with a concurrent increase in the 3450 cm^{-1} resonance. More concentrated solutions show a gradual decrease in the hydrogen-bonded peaks until $0.4x$ sulfuric acid where all spectral features are gone. These decreases are associated with the formation of several stable hydrates in solution and are correlated with a decrease in the extent of dissociation from 0.36 at 0.05 bulk mole fraction, to 0.01 at $0.4x \text{ H}_2\text{SO}_4$.¹⁸

Complexed Surface Water. The increase in the formation of molecular complexes or ion pairs leads to both a decrease in the concentration of uncomplexed surface water and an increase in the randomization of surface water. Note that the formation of either ion pairs or molecular hydrates would have a similar effect on the spectrum of surface water. As the association of ions increases, the strength of the electric field due to the double layer decreases. Associated ion pairs are able to approach closer to the air/water interface since they possess more molecular character. The interaction of water with these ion pairs breaks up the hydrogen-bonded structure of this interfacial region and causes water to become more randomized in its orientation.

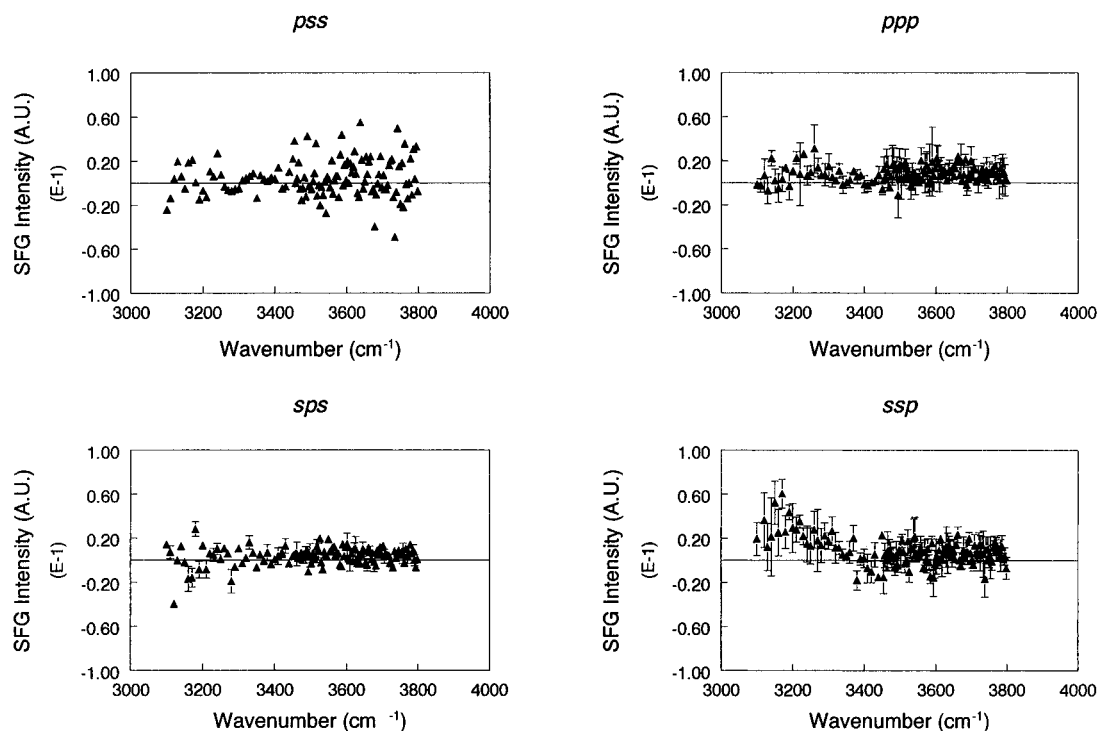


Figure 5. Polarization data for 0.9x H₂SO₄ solution. Note the scale on the y-axis is in arbitrary units.

Similarly, formation of hydrated complexes disrupts the hydrogen-bonded structure of the interface. Since SFG intensity is determined by H₂O surface concentration and orientation, either a decrease in surface concentration or a change in orientation can lead to a decrease in SFG intensity at high concentrations of acid (Figure 2). Nathanson and co-workers have performed molecular beam scattering experiments of D₂O on concentrated (98 wt %) H₂SO₄. They have discovered that water interacts very strongly with the surface,⁴⁵ which agrees with water being bound into complexes with sulfuric acid.

The lack of an SFG signal at high acid concentration (>0.4x) indicates not only a lack of uncomplexed water on the surface but also that complexed water has a random orientation. Removal of uncomplexed water from surface to the bulk or near surface region is demonstrated by the polarization data shown in Figure 5. The polarization data indicate that water does not assume a net orientation that would be invisible to the *ssp* polarization combination. If water were bound into complexes that had a preferential orientation at the surface, then changing the polarization of input and output laser beams would reveal water in a new surface orientation. However, the lack of SFG signal for these polarization combinations indicates that water orientation is random and subsurface. Therefore, water is being removed from the surface by complexation with H₂SO₄.

The orientation of sulfuric acid at the surface is also relevant to the chemistry which occurs there. Therefore, a search for the presence of the free OH due to sulfuric acid was made. A free OH is expected at 3610 cm⁻¹ from gas-phase infrared experiments.²⁵ No peak due to free OH of H₂SO₄ was found at concentrations between 0.01x and 0.9x. Recently, Roberts and co-workers⁴⁶ prepared pure sulfuric acid films in situ in a UHV chamber. Reflectance FTIR did not detect any free OH at the vacuum/solid interface of sulfuric acid but did detect a very broad hydrogen-bonded peak centered near 3000 cm⁻¹. Other FTIR experiments on H₂O/H₂SO₄^{7,26} show broad absorptions in the 3500–2500 cm⁻¹ region. The fact that this feature is not apparent in the SFG spectra also supports the conclusion that H₂O/H₂SO₄ complexes have no preferred orientation at the air/solution interface.

SFG Compared with Previous Work. SFG results and theoretical calculations for the H₂O/H₂SO₄ surface are in qualitative agreement with each other. SFG spectra indicate that between 0.2x and 0.4x H₂SO₄ the surface of the solution is depleted of uncomplexed water. This is consistent with the formation of hydrates. Phillips⁴³ calculates the mole fraction composition of solutions for H₂O, H₂SO₄, and hydrates H₂SO₄·*n*H₂O (*n* = 1–4). He finds significant hydrate formation occurs at a 1:4 H₂SO₄:H₂O mixture (0.2x), and these hydrates are oriented at the surface. This is also the concentration range where the SFG spectra indicate the start of a dramatic surface depletion of uncomplexed water. As the water to sulfuric acid ratio decreases, the hydrate concentration increases with an increasing shift toward the lower hydrates. These SFG results agree with the calculated result that the surface water concentration is dramatically reduced at bulk concentrations above ≈0.2x H₂SO₄. From these calculations, Phillips concludes that water must be oriented in sulfuric acid/water complexes at the surface.⁴³ This conclusion is not consistent with the spectra presented here. Specifically, the water must be isotropic in its orientation in the complex and subsurface since it is not detected in the polarization experiments (Figure 5).

The true power of surface science is to bring multiple techniques together for investigating chemistry or structure of a particular system. For example, combining AES and SFG results here enables the determination of the structure of water at the surface which neither technique alone could do. Recently, in an elegant experiment, Somorjai and co-workers⁴⁴ used XPS and AES to study the H₂O/H₂SO₄ system (25–100 wt % H₂SO₄) and determined, within 15%, the surface composition reflects that of the bulk. Utilization of specially constructed differentially pumped spectrometers enabled these experiments to be conducted under equilibrium conditions while maintaining surface sensitivity. The majority of the signal is reported to originate from the first three layers below the surface.⁴⁴ The XPS and AES results are complementary with these SFG results. For example, both SFG and AES experiments are consistent with an electric double-layer model. From the AES data the interfacial composition of 0.01x bulk solution would be ap-

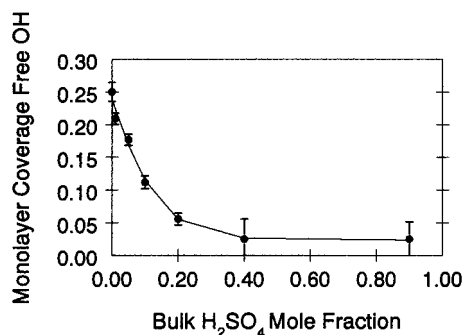


Figure 6. Monolayer water free OH coverage vs bulk mole fraction sulfuric acid. Free OH of the pure water surface is estimated at 0.25 monolayer.^{1,2} The detection limit is approximately 0.05 monolayer. The line is a guide for the eye.

proximately one sulfate for every 99 waters. The SFG intensity of water in the interface is dramatically altered relative to neat water, which supports the model of negative ions exhibiting long-range effects through an electric double layer, rather than penetrating to the surface. Sulfate (bisulfate) in the interface would have a structure-breaking effect similar to that in bulk solution.^{34,47} Further, since SFG provides structural information and AES the composition, utilizing both techniques enables conclusions concerning the amount of structure making/breaking at the interface as the solution composition is changed.

Free OH groups are necessarily at the first layer of the interface. At the surface of neat water, Shen and co-workers^{1,2} have shown that approximately 25% of surface water molecules contain a free OH group. In studies of glycerol/water mixtures,³ it was demonstrated that the free OH could be used to determine the concentration of surface water. In sulfuric acid solutions, there is a smooth decrease in the free OH peak as sulfuric acid is added to water. Using the free OH of water as a qualitative indicator of surface coverage of uncomplexed water (Figure 6), water is apparently absent from the surface, i.e., <0.05 monolayer, at bulk concentrations $\geq 0.4x$ H₂SO₄. This is supported by the lack of signal not only at the free OH resonance, 3710 cm⁻¹, but also in the hydrogen-bonded region. Since the SFG intensity is determined by number density and orientation, it cannot be ruled out that water is in an orientation that makes it invisible to SFG, i.e., random. That is, the SFG data indicate that water must be either absent or random. Since AES experiments⁴⁴ show the surface and bulk compositions are the same, water must be randomly oriented. This analysis assumes that the free OH is not preferentially or exclusively perturbed over other surface water orientations. This assumption appears to be valid since these data are consistent with thermodynamic calculations based on vapor pressure.⁴³ Therefore, uncomplexed water is removed from the surface, and the free OH is a qualitative measure of this complexation.

While this paper was in review, a paper by Raduge et al. on the H₂SO₄/H₂O system has been published.⁴⁸ The data from the two experiments are in very good agreement; however, the interpretations are quite different. At low concentrations of acid, <0.1x, Raduge et al. emphasize the hydrogen-bonding nature of sulfuric acid while, in this report, the ionic nature of the solutions is stressed. The ionic interpretation is consistent with data about the structure of water on ionic solutions.^{49,50} At higher concentrations, Raduge et al. indicate a more crystalline surface structure whereas in this paper the data are interpreted as a more random and disordered surface.

Conclusion

The structure of surface water is affected by H₂SO₄ in solution. At relatively low concentrations, the water is more

ordered compared to that of the neat water/air interface. This increased order is attributed to a subsurface electric double layer where the negative field can orient several layers of water. Above 0.4x H₂SO₄, the SFG signal is gone since the H₂SO₄/H₂O complexes can move to the surface complexing the uncomplexed surface water molecules. Uncomplexed water becomes bound into hydrates, is below the first layer of the interface, and is random in orientation. The random orientation is supported by the polarization experiments which do not detect any water, indicating water molecules do not assume a preferential orientation at the surface. Further, between 0.01x and 0.9x there are no dangling free OH groups due to sulfuric acid. Finally, the free OH is a useful indicator of surface coverage for uncomplexed water.

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References and Notes

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