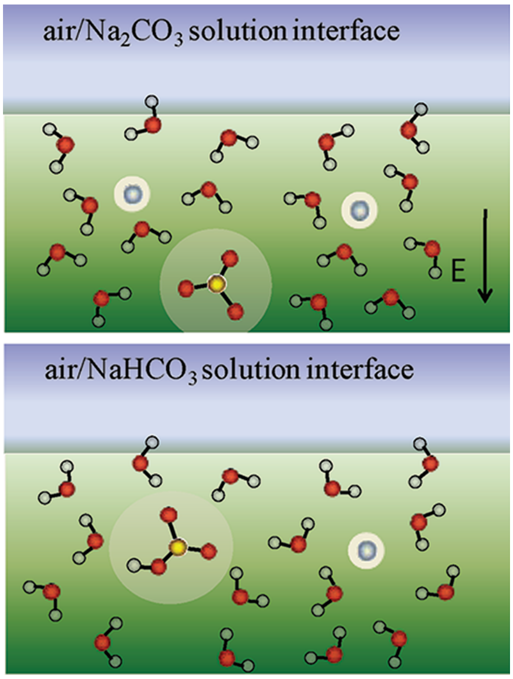
ACCOUNTS
of chemical research

Organization of Water and Atmospherically Relevant Ions and Solutes: Vibrational Sum Frequency Spectroscopy at the Vapor/Liquid and Liquid/Solid Interfaces

AARON M. JUBB, WEI HUA, AND HEATHER C. ALLEN*
Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210, United States

RECEIVED ON JUNE 7, 2011

CONSPECTUS



The nature of water's hydrogen-bonding network is a vital influence on the chemistry that occurs at interfaces, but a complete understanding of interfacial water has proven elusive. Even-order nonlinear optical spectroscopies, such as vibrational sum frequency generation (VSFG) spectroscopy and heterodyne detected phase-sensitive sum frequency generation (PS-SFG) spectroscopy, are inherently surface specific. With the advent of advances in these spectroscopic techniques, researchers can now explore many longstanding questions about the dynamics and structures present at the vapor—water and water—solid interfaces. Of special interest to the atmospheric chemistry community is the accommodation of ions and solutes by water's hydrogen-bonding network. A better understanding of how ions and solutes behave in hydrogen-bonded water has afforded a fresh perspective of aqueous aerosols, because the interactions involved therein drive phenomena such as the hydrolysis of atmospheric chemical species. In this Account, we present work from our laboratory focusing on applying VSFG and the recently developed PS-SFG techniques to probe the perturbation of water's hydrogen-bonding network at the vapor—water interface by a variety of ions and solutes. We also present very recent results from our laboratory on the direct observation of the adsorption of ions at the water—CaF_2 interface.

We begin by discussing the influence of ions and solutes on interfacial water structure. Results for halide salts and the acid analogs on interfacial water structure are shown to be quite different, as would be expected from differences in surface tension measurements that have been known for a long time. Also examined are systems with the largely polarizable molecular anions nitrate (NO_3^-), sulfate (SO_4^{2-}), carbonate (CO_3^{2-}), and bicarbonate (HCO_3^-).These systems feature more complicated influences on interfacial water structure than halide-containing solutions; however, our conventional VSFG results for both nitrate and sulfate solutions are in agreement with recent PS-SFG results and molecular dynamics simulations.

We also discuss recent PS-SFG work on carbonate and bicarbonate systems in which the accommodation of the bicarbonate ion at the vapor—water interface is in stark contrast to the carbonate results. Perturbation of interfacial water by solutes is examined for solutions of dimethyl sulfoxide and methylsulfonic acid. PS-SFG results for these systems are striking: they illustrate the dramatic changes that interfacial water molecules undergo in the presence of solutes that are not observed with conventional VSFG. Finally, we discuss direct sulfate ion adsorption for the aqueous sodium sulfate—CaF_2 interface, with the goal of elucidating water behavior at this surface.

Introduction

Water's ubiquity on Earth and the vital role it plays in all aspects of life make the necessity of scientific inquiry into its properties both obvious and practical. Beyond practical concerns, however, water is a fascinating subject that displays many unique and subtle properties, which are still not

10.1021/ar200152v

completely understood and are the subject of much diverse and intense experimental and theoretical work.[1−10] Many of water's important properties stem from its large hydrogen-bonding nature such as its uncommonly high boiling point to the ability to solvate ions and solutes. The hydrogen-bond network at the asymmetric two-dimensional vapor/water interface is particularly interesting because much chemistry is controlled by interactions at this interface.[11,12] The advancement of surface-specific even-order nonlinear optical spectroscopic techniques, such as VSFG and surface second harmonic generation (SHG), in the past two decades along with theoretical work has enabled elucidation of many questions on interfacial water.[10,13−20] Of particular importance to fields such as atmospheric chemistry is the accommodation of ions and solutes by water's hydrogen-bond network. Work in the Allen laboratory has focused on elucidating the behavior of water's hydrogen-bonding network in the bulk and at the vapor/liquid and liquid/solid interfaces for a variety of systems relevant to atmospheric aerosol chemistry, geochemistry, and biology through the use of vibrational linear (Raman and infrared) and nonlinear (VSFG) optical spectroscopies.[17,21−29]

Here we present primarily our most recent work, published and unpublished, on the roles that ions and solutes play in perturbing the hydrogen-bond network at the vapor/liquid and solid/liquid interfaces, as well as comment on contributions from other researchers working in this field. Motivation for this work stems from a knowledge gap with regard to atmospheric particulate matter (aerosols), both liquid, inclusive of water, and solid phase matter, primarily mineral, and how the surfaces of these aerosols influence chemistry that occurs in the atmosphere.[12] Surface effects of atmospheric aerosols have been the focus of scientific inquiry since the 1990s, with emphasis on tropospheric aerosols.[30]

Because probing the asymmetric two-dimensional hydrogen bond network of water found at interfaces necessitates a surface-specific technique, VSFG is widely utilized within our laboratory because it is an even-order nonlinear optical spectroscopy that provides information on the vibrational character of molecules at surfaces. Conventional VSFG intensity is proportional to the square modulus of the second-order nonlinear susceptibility, $|\chi^{(2)}|^2$, multiplied by the intensities of the input visible and infrared beams, eq 1.

$$I_{\text{SFG}} \propto |\chi^{(2)}|^2 I_{\text{vis}} I_{\text{IR}} \propto |\chi_{\text{NR}}^{(2)} + \chi_{\nu}^{(2)}|^2 I_{\text{vis}} I_{\text{IR}} \tag{1}$$

$$\chi_{\nu}^{(2)} = \sum_{\nu} \frac{A_{\nu}}{\omega_{\text{IR}} - \omega_{\nu} + i\Gamma_{\nu}} \tag{2a}$$

$$\text{Im}\,\chi^{(2)} = -\sum_{\nu} \frac{A_{\nu}\Gamma_{\nu}}{(\omega_{\text{IR}} - \omega_{\nu})^2 + \Gamma_{\nu}{}^2} \tag{2b}$$

$$\chi_{\nu}^{(2)} = \int \frac{A_{\nu}\rho(\omega_{\nu})}{\omega_{\text{IR}} - \omega_{\nu} + i\Gamma_{\nu}} \mathrm{d}\omega_{\nu} \tag{3}$$

Here I_{SFG}, I_{vis}, and I_{IR} are the intensities of the output sum frequency beam, the visible excitation beam, and the infrared excitation beam, respectively, and $\chi_{\text{NR}}^{(2)}$ and $\chi_{\nu}^{(2)}$ refer to the nonresonant and resonant components of the second-order nonlinear susceptibility. Equations 2a and 2b reveal the Lorentzian line-shape character of the second-order nonlinear susceptibility when the VSFG resonances are discrete where A_{ν} is the SFG transition moment strength, ω_{ν} is the frequency of the SFG active vibration, ω_{IR} is the frequency of the incident infrared laser beam, and Γ_{ν} is the line-width of the VSFG transition. Equation 2b is the imaginary term from the expansion of eq 2a. For continuum modes, such as the collective OH vibrations of interfacial water, eq 3 more accurately represents $\chi_{\nu}^{(2)}$ where $\rho(\omega_{\nu})$ is the density of VSFG modes at ω_{ν}.[31]

While eqs 2a and 2b inherently contain information on the sign of the VSFG transition moment and thus the orientation of the induced dipole moment, we can see from eq 1 that this information is lost when collecting the conventional VSFG intensity spectrum. It becomes impossible then to directly measure the orientation (phase) of the VSFG transition moment utilizing conventional VSFG techniques. This issue has been recognized for many years as a shortcoming of the conventional VSFG technique and, previous to direct measurement of SFG phase, researchers have attempted to address this both experimentally and through theoretical simulations.[32,33] The first direct measurement of the phase of $\chi^{(2)}$ was completed using SHG in 1986 by Kemnitz et al.[18] It was not until 1990 that the phase of $\chi_{\nu}^{(2)}$ was measured with VSFG by Superfine et al. for a pentadecanoic acid monolayer on water;[34] however, this method saw limited adoption due to the added experimental complexity. In the following years, several groups reported the Im $\chi_{\nu}^{(2)}$ (eq 2b) spectra for water at a variety of interfaces;[32,35] however, a widely applicable experimental approach to directly measure Im $\chi_{\nu}^{(2)}$ was lacking until recently. This technique, pioneered by Ji et al. and referred to from here as heterodyne detected phase-sensitive sum frequency generation (PS-SFG), allows the measurement of the Im $\chi_{\nu}^{(2)}$

spectra for molecules at the interface of two centrosymmetric media.[36] This marks a huge step forward for VSFG instrumentation, and the ideas of Ji et al. are being quickly adopted by both experimentalists and theoreticians within the surface spectroscopy community.[9,10,25,27−29,37−40]

PS-SFG is an excellent tool to investigate the effect that ions and solutes exert upon the hydrogen-bond network of water because PS-SFG can show whether the transition dipole moment of water reorients due to the presence of an ion or solute, even if the VSFG power spectrum remains unchanged. As such, the majority of the work presented in this Account utilizes the PS-SFG technique where an existing conventional femtosecond broad-band VSFG spectrometer in our laboratory was adapted for phase detection using the design demonstrated first by Nihonyanagi et al.[37] In this design, collecting both conventional VSFG (power spectrum) and PS-SFG is possible. The broad-bandwidth VSFG spectrometer used for this work has been described in greater detail elsewhere along with a more recent description of the PS-SFG setup utilized for this work.[25,27] Briefly, a titanium:sapphire oscillator (792 nm)/double regenerative amplifier (1 kHz) (Spectra-Physics) generates both the picosecond visible and femtosecond infrared light. The full spectral bandwidth for the infrared beam was 800 and 500 cm^{-1} in the water hydrogen-bonding region for the conventional VSFG and PS-SFG setups, respectively. Average energies for the visible and infrared beams were ~300 and ~10 μJ, respectively. For the liquid/solid work, a scanning VSFG spectrometer (20 Hz, Ekspla) was used. Details of the 20 Hz scanning VSFG system can be found elsewhere.[21] Briefly, a Nd:YAG laser is used to produce the visible beam (532.1 nm, ~500 μJ) and to pump an OPA/OPG/DFG system, which produces the tunable infrared beam (2.5−12 um, >50 μJ).

Results and Discussion

Vapor/Neat Water Interface. In order to understand the role that solvated ions and solutes play in perturbing water structure at the vapor/liquid interface, it is vital to have an understanding of neat water structure both in the bulk and at the vapor/water surface.[17] Bulk vibrational studies using Raman and infrared spectroscopies are useful in helping to assign the complicated hydrogen-bonding continuum region located from 3000 to 3650 cm^{-1}. This region is generally attributed to the collective OH stretching modes of hydrogen-bonded water molecules, from a more strongly to a more weakly hydrogen-bonding network. The most apparent difference between VSFG spectra for the vapor/liquid interface and Raman and infrared spectra for bulk water occurs at 3700 cm^{-1}, where a sharp, narrow peak is observed for the vapor/water interface VSFG spectrum. This peak is assigned to the free OH stretch of water molecules that straddle the vapor/liquid interface. These water molecules have one OH bond pointing toward the vapor phase and the other OH bond pointing toward the liquid where it is free to interact with other water molecules via hydrogen-bonding.[14]

A precise assignment for the origin of the hydrogen-bonding continuum from 3000 to 3650 cm^{-1} has proven to be elusive and as such is a large source of controversy within the community.[9,10,14,17,32,39,41] Explanations for this region range from the presence of several hydrogen-bound water species, to the prevailing effects of large dynamic fluctuations in water, to intramolecular coupling between the overtone of the OH bending mode and the OH stretch fundamental.[7,39,41] The recent development of PS-SFG, as well as thorough theoretical studies, has provided much additional information toward resolving this issue;[9,10,36] however the controversy persists.

Ion Effects at Vapor/Water Interface. The relationship and effect that solvated ions have upon the structure of water's hydrogen-bonding network is of special interest to the atmospheric chemistry community because aqueous aerosols are involved in a wide range of atmospherically important processes such as the heterogeneous hydrolysis of atmospheric chemical species.[11,12] The use of surface specific vibrational spectroscopic techniques such as VSFG has been actively pursued by a number of groups to help elucidate long-standing questions on the surface structure of water containing a wide variety of ions.[6,15−17,19,20,24,29,31,40,42−44] Provided here is a brief synopsis of the major findings from work on vapor/ion−water interfaces using VSFG completed by our laboratory in the past as well as the major unresolved questions from this work that we seek to address using the PS-SFG technique. Very recent results for the aqueous sodium carbonate and sodium bicarbonate systems utilizing PS-SFG are also presented and summarized.[28]

Previous work has primarily focused on the effect that halide ions (Cl^-, Br^-, and I^-) with mono- and divalent countercations (Na^+ and Mg^{2+}, Ca^{2+}, and Sr^{2+}) have upon the water structure near the vapor/liquid interface and how these results compare with results for acidic solutions (HCl, HBr, and HI).[19,20,22,24] From surface tension measurements, Figure 1, it is known that acidic solutions exhibit very different behavior than solutions of the salt analogue, and addressing this behavior was a central goal in past work. Introduction of the halide salts was seen to manifest as a slight decrease in the strong hydrogen-bonding region at

$3200\ cm^{-1}$ and a significant increase in the weak hydrogen-bonding region at $3400\ cm^{-1}$, for example, Figure 2b. These spectral changes increased with increasing polarizability of the anion, $Cl^- < Br^- < I^-$, and were interpreted as an indication of surface enrichment of solvated anions at the vapor/liquid interface recognizing that an increase in the $3400\ cm^{-1}$ region intensity is also a signature for the halide's solvation shell water molecules.[15,20,24] For acidic solutions, it was seen that both the 3200 and $3400\ cm^{-1}$ regions were enhanced, for example, Figure 2c, with the increase in the $3400\ cm^{-1}$ peak again being attributed to the enrichment of polarizable anions within the interface and the $3200\ cm^{-1}$ enhancement assigned to the presence of H_3O^+ or $H_2O_5^+$ in the interface, which both increases the interfacial depth and orders the interface.[17,19,20,22] Recent PS-SFG results from Tian et al. support this interpretation for the interfacial structure of acidic solutions.[31] The spectra for the acid analogs of the monovalent halide salts exhibited very different behavior for the free OH at $3700\ cm^{-1}$ where a decrease in the intensity was observed indicating a decrease in free OH oscillators at the surface. This finding was consistent with additional polarization studies in our laboratory, the results of Shultz and co-workers, and molecular dynamics simulations.[20,24,45]

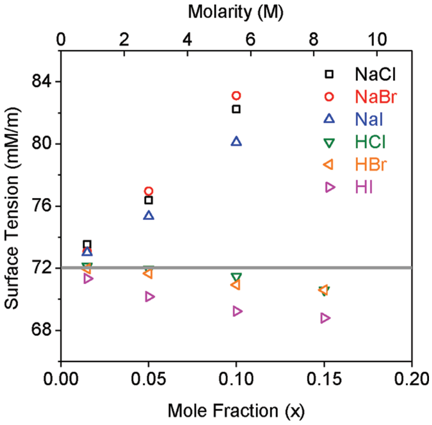


FIGURE 1. Surface tension values of sodium salts and monoprotic acids as a function of concentration. Figure adapted from ref 24.

Our laboratory has also investigated the effects of large, polarizable molecular anions such as nitrate (NO_3^-) and sulfate (SO_4^{2-}) on the hydrogen-bonding structure of water.[21,23,24] Although interpretation for the nitrate and sulfate systems appeared to be more difficult, recent PS-SFG work from Tian et al. and our laboratory have provided further insight into these systems.[29,40] For divalent cation and sodium nitrate systems, there is a severe depletion of intensity in the $3200\ cm^{-1}$ region and an enhancement for

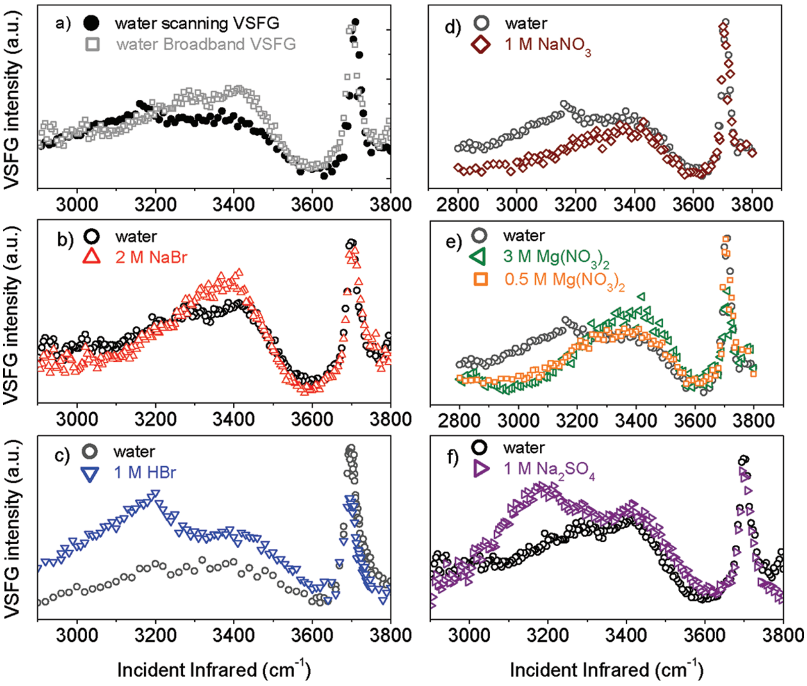


FIGURE 2. The ssp polarized conventional VSFG spectra of aqueous solutions of (a) neat water (scanning and broad band system), (b) 2 M NaBr (broad band system), (c) 1.2 M HBr (scanning system), (d) 1 M $NaNO_3$ (scanning system), (e) 0.5 and 3 M $Mg(NO_3)_2$ (scanning system), and (f) 1.1 M Na_2SO_4 (broad band system). Neat water VSFG spectrum is shown in black (broad band system) and dark gray (scanning system) for reference in each spectrum. Differences in spectral shape of neat water spectra are due to slight differences in SFG systems and Fresnel factors (incident angle changes).

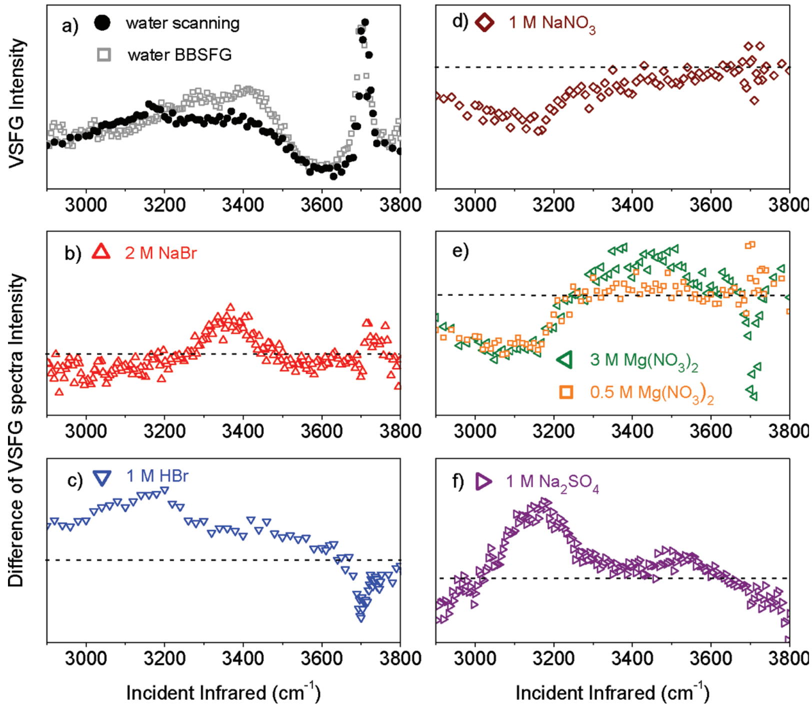


FIGURE 3. (a) The ssp conventional VSFG spectra for neat water (scanning and broad band system). (b–f) The difference spectra (VSFG salt or acid spectrum minus VSFG water spectrum) for the indicated salts. Because the spectra are convoluted with cross-terms containing nonresonant contributions, they are not comparable to other solution difference spectra; the difference spectra are merely a qualitative guide for the eyes. Dashed line represents the water zero for each respective spectra.

~3 M divalent cations ($Sr^{2+} > Ca^{2+} > Mg^{2+}$) and no enhancement for $NaNO_3$ of the 3400 cm^{-1} region, Figure 2d,e, while for the sodium and other monovalent sulfate systems (divalent cation systems have not yet been completed), a large enhancement is found for both the 3200 and 3400 cm^{-1} regions, Figure 2f. These results are interpreted as follows: For nitrate systems, the significant depletion of the 3200 cm^{-1} region and enhancement of the 3400 cm^{-1} region is attributed to the existence, but not an enrichment, of the nitrate ion at the interface, with comparable surface activity to that of the chloride ion, which is supported by recent PS-SFG measurements by Tian et al.[21,24,40,46] For the divalent cation series, the spectral changes are exaggerated as the size of the cation increases, $Mg^{2+} < Ca^{2+} < Sr^{2+}$, where the larger and more polarizable cation affects the interfacial water the most significantly, although cations are typically considered as hard ions. We have postulated that the larger divalent cations create additionally complex concentration gradients when paired with nitrate (and chloride) and so the interfacial region experiences a widening (i.e., thickening).[24,46] We ruled out the possibility of a wider electric double layer created by a simpler picture of nitrate surface concentration enhancement because of the observed 3200 cm^{-1} intensity decrease, although additional PS-SFG studies need to be completed on $Mg(NO_3)_2$, $Ca(NO_3)_2$, and $Sr(NO_3)_2$ salt solutions to support this interpretation. For sodium sulfate systems, Figure 2f, the intensity enhancement extends to the lower frequency region, in agreement with work from Tarbuck et al.[43] and consistent with the simpler picture, although reversed in ordering where sulfate is buried deeper in the interface and the cations reside on average above sulfate thus creating a local electric field resulting in water alignment as evidenced by the 3200 cm^{-1} enhancement. This interpretation is supported by recent PS-SFG studies on Na_2SO_4 solutions and is consistent with molecular dynamics simulations.[23,29,40,45] As a qualitative guide to highlight changes to the hydrogen bonding network, Figure 3 shows the difference spectra obtained from subtracting the water VSFG spectrum in Figure 2 with the associated salt or acid VSFG spectrum.

For aqueous solutions of sodium carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-), we have recently completed conventional VSFG and PS-SFG studies.[28] Early VSFG work on sodium bicarbonate and sodium carbonate containing solutions were carried out by Tarbuck et al.[43] who reported that bicarbonate did not significantly perturb the water hydrogen bonding network whereas carbonate presence caused a large intensity enhancement of the 3200 cm^{-1} spectral region. These results were interpreted as arising from a

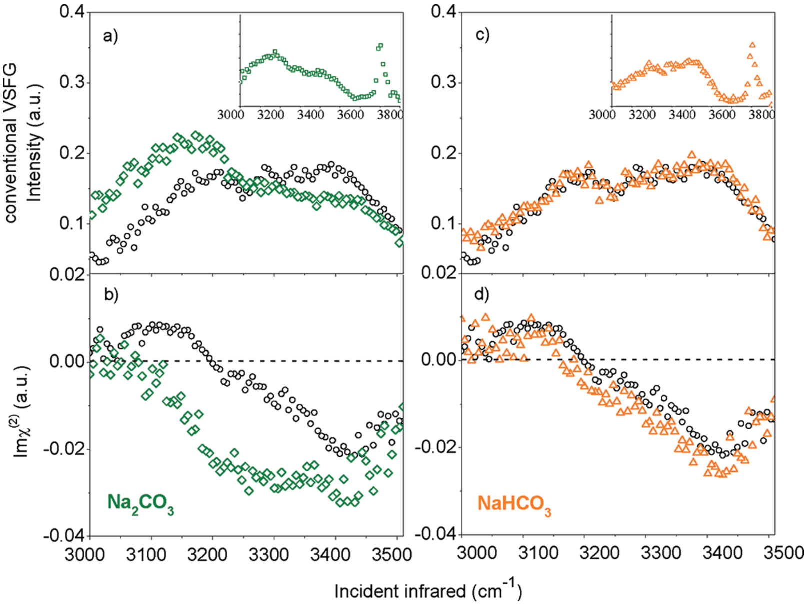


FIGURE 4. Conventional VSFG spectra (top panel) and Im $\chi_{\nu}^{(2)}$ SFG spectra (bottom panel) corresponding to the vapor/aqueous salt solutions interfaces for 1.1 M Na_2CO_3 (a,b) and 0.8 M $NaHCO_3$ (c,d) salt solutions Water spectra are shown as a reference (black circles). The insets in the top panels are conventional VSFG spectra showing the full 3000−3800 cm^{-1} region. All spectra were obtained under the ssp polarization combination. Figure adapted from ref 28.

convolution of an increase in the cooperative OH stretching of tetrahedrally coordinated water molecules, the ordering effects of the ion induced field, and strong ion−dipole interactions.[43] Tarbuck et al.'s results were found to be consistent with subsequent work from Du et al. and our conventional VSFG data on sodium carbonate and sodium bicarbonate solutions.[28,44]

PS-SFG spectra for sodium carbonate and bicarbonate are shown in Figure 4. For the left column corresponding to the carbonate sample, the increase in the low-frequency region centered at 3200 cm^{-1} for the conventional VSFG power spectrum, Figure 4a, indicates an increase in strong hydrogen-bonding. Figure 4b displaying the Im $\chi_{\nu}^{(2)}$ spectra for the carbonate solution and neat water, however, indicates that in addition to an increase in the hydrogen-bonding strength, there are several additional effects at play. Relative to the neat water surface, the sign flip from 3000 to 3200 cm^{-1} from positive to negative and the increased negative intensity of the 3200−3500 cm^{-1} region for the carbonate solution reveals that carbonate ions have a strong orienting effect on the ensemble average water OH transition moment causing water molecules to align with their OH transition moments pointing toward the bulk solution. In order for these results to make physical sense, carbonate ions must reside at the bottom edge of the interfacial region and the sodium ions relatively near to the surface. This could generate the field necessary to orient the water molecules. While it has been suggested that sodium ions are repelled from the interface, our data indicates that the sodium ions, on average, should reside above the carbonate ions within the interface in order to generate the necessary local field to orient the interfacial water.[23,43] This is in contrast to the sodium bicarbonate results where there are no significant differences between the measured power spectrum, Figure 4c, and the imaginary spectra, Figure 4d, for neat water and the bicarbonate solution. These results strongly suggest that sodium and bicarbonate ions are dispersed throughout the interface and are accommodated by water's existing hydrogen-bonding network. These results are particularly interesting since the relative acidity of an atmospheric aerosol will then dictate the interfacial water structure if the acidity is controlled by the increases in atmospheric CO_2, which then affects the equilibrium balance of HCO_3^- and CO_3^{2-} in the aerosol.

Solute Effects at Vapor/Water Interface. The effect that nonionic solutes have on water hydrogen-bond structure is also of large interest for atmospheric chemistry. This is especially true for sulfur-containing molecules because the sulfur cycle is the dominant factor in the gas-to-particle conversion process in the marine boundary layer (MBL) due to the wide availability of biogenic dimethyl sulfide via algal metabolic byproduct.[47] Sulfur-containing molecules produced by the sulfur cycle such as dimethyl sulfoxide (DMSO), methane sulfonic acid (MSA), and the final oxidation

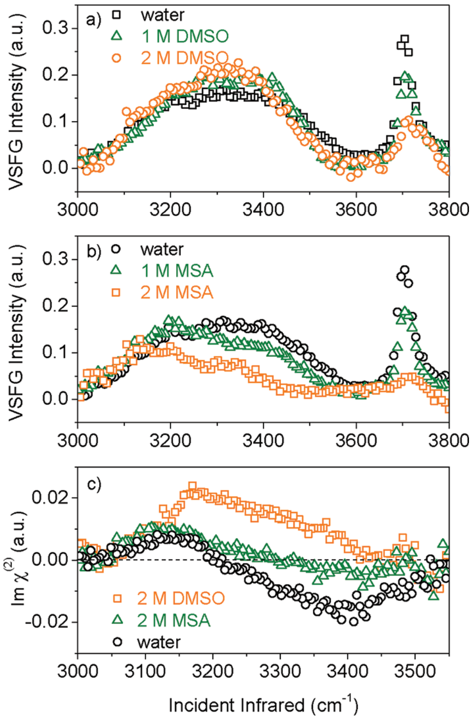


FIGURE 5. Conventional VSFG and Im $\chi_{\nu}^{(2)}$ spectra in water stretch region of (a) DMSO–water mixtures and (b) MSA–water mixtures. (c) Im $\chi_{\nu}^{(2)}$ spectra in water region of 2 M DMSO, 2 M MSA, and neat water. Figure adapted from ref 25.

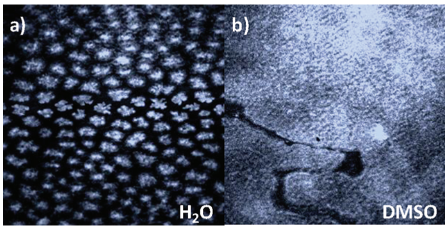


FIGURE 6. BAM images of DPPC monolayer on (a) neat water and (b) 0.1× DMSO subphases at 10 mN/m. Figure adapted from ref 26.

product H_2SO_4 demonstrate a strong affinity for water, which allows sulfur-containing aerosols to serve as cloud condensation nuclei. This in turn modifies the formation of global cloud cover effecting the Earth's albedo and climate.[48] PS-SFG measurements on water's hydrogen-bond network at the vapor/liquid interface for DMSO- and MSA-containing solutions are therefore presented.[25] Shown in Figure 5 are the conventional VSFG spectra for DMSO solutions (Figure 5a) and MSA solutions (Figure 5b), as well as the PS-SFG results (Figure 5c) for these solutions at the vapor/liquid interface. Conventional VSFG results for DMSO-containing solutions (Figure 5a) show the hydrogen-bonding network of water only slightly perturbed by the presence of DMSO while the free OH peak at 3700 cm^{-1} decreases, where the latter is attributed to the replacement or hydrogen-bonding of topmost water molecules by DMSO. For the MSA/water VSFG results, Figure 5b, a significant decrease in the 3400 cm^{-1} peak is seen and the overall hydrogen-bonding region is slightly red-shifted; this has been assigned to an enhancement in the hydrogen-bonding strength of surface water in the past.[49]

Yet, the PS-SFG results for 2 M DMSO solutions (Figure 5c) indicate the surface water's hydrogen-bonding network is greatly perturbed, in contrast to the conventional VSFG results. This is also contrary to what one would predict from Raman spectroscopic results from bulk studies of these aqueous solutions.[25] Easily interpreted from the PS-SFG spectra and the fact that DMSO is a surface-active (surface concentration enhancement) molecule,[50] the presence of DMSO causes a reorientation of the interfacial water structure where the OH transition moment of surface OH oscillators now on average point toward the surface. For MSA, the PS-SFG intensity is observed to decrease across the hydrogen-bonding region where the intensity is nearly zero beyond 3200 cm^{-1} revealing lack of a net OH orientation. This is attributed to the conflicting influences of the hydrated methane sulfonate anions and the hydrated hydronium ions in the interfacial region, which have both been shown to have preferred interfacial residence.[22,49] Hence the PS-SFG spectrum for the MSA–water solution reveals a much thinner surface electric double layer relative to DMSO, a very different result compared with the speculative interpretations from previous conventional VSFG results.

An elegant example of consequences that solutes such as DMSO have is seen in Figure 6. Here two Brewster angle microscopy (BAM) images for a compressed (~10 mN/m) phospholipid monolayer (1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC)) on a neat water subphase (Figure 6a) and a 0.1× (mole fraction) DMSO solution subphase (Figure 6b) are shown.[26] For Figure 6a, the formation of multilobed DPPC domains when the monolayer is compressed to ~10 mN/m is very clear. However, when DMSO is introduced to the subphase and the monolayer is again compressed to ~10 mN/m, the phospholipid fails to form distinct domains, instead immediately condensing into a film. Future work in our laboratory is focused on elucidating the hydrogen bonding structure for such complex systems.

Neat Water/Mineral Interface. Beyond the vapor/liquid interface, there is a wide interest in understanding water's behavior near the liquid/solid interface.[51,52] From an atmospheric perspective, the water/mineral interface is particularly important to understand because interactions at this boundary influence the aqueous phase chemistry of the mineral aerosol.[53] VSFG is an attractive tool to investigate water/mineral systems because the inherent interfacial sensitivity of the technique avoids contributions from bulk species. Due to increased experimental complexity in accessing a buried interface and the relative novelty of the technique, PS-SFG has only seen limited application to water/mineral systems.[35,52] The majority of VSFG studies on water/mineral systems have focused on insoluble oxide minerals such as quartz (α-SiO_2), fused silica (SiO_2), and corundum (α-Al_2O_3).[35,52,54–56] These minerals are very abundant and important in the environment as well as being experimentally attractive for VSFG because they are insoluble and feature large transmission in both mid-infrared and visible frequency ranges. The other common mineral phase in water/mineral VSFG studies has been fluorite (CaF_2), which is a slightly soluble ($K_{sp} \approx 3.9 \times 10^{-11}$) ionic mineral with environmental and industrial relevance.[57,58] A common finding for all water/mineral systems studied by VSFG is that as the solution pH moves farther away from the mineral isoelectric point (ISP), inducing mineral surface charge enhancement, the intensity of the detected VSFG for the hydrogen-bonding region of water increases. This signal intensity enhancement reflects the increased hydrogen-bond order due to ordering effects from the charged water/mineral interface.

Salt Effects at the Water/Mineral Interface. Much like the vapor/liquid interface, the role that ions play on the water hydrogen-bond network at the water/mineral interface has been the focus of intense studies.[54,55,58] Unlike the vapor/liquid interface, however, the water/mineral interface generally features a charged surface at environmentally relevant pH values, which exerts an electric field some distance away from the surface. For salt water/mineral systems, this electric field, commonly approximated by the Gouy–Chapman model, attracts ions, which in turn screen the effective interface potential of the mineral.[59] Screening of the mineral interface potential by ions limits the ordering influence of the mineral on water hydrogen-bonding network. The application of VSFG to study how the hydrogen-bonding network of water responds to the screening of charged mineral surfaces and the behavior of the ions themselves near charged mineral surfaces is being actively pursued by several reseach groups, including ours. Here we discuss literature results[58] for the water hydrogen-bonding region for the sulfate–water/CaF_2 interface in the context of atmospheric chemistry and present very recent, unpublished work directly probing sulfate interaction with the solid CaF_2 surface at the water/CaF_2 interface from our laboratory.

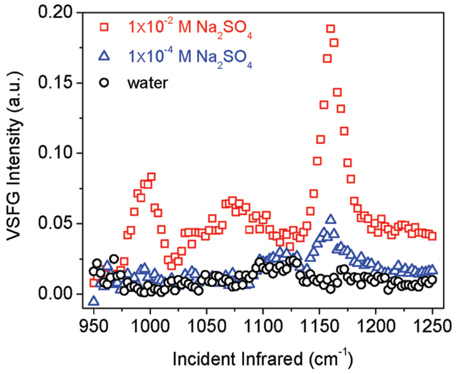


FIGURE 7. The ssp polarized conventional VSFG spectra in S–O region for water/CaF_2 interface of two Na_2SO_4 solutions in 1 *m* NaCl at pH 7. Neat water VSFG spectrum is shown in black.

Recent work in our laboratory has directly measured sulfate anion adsorption at the water/CaF_2 interface, Figure 7, with VSFG. Here the S–O modes of the adsorbed sulfate anion are directly probed for Na_2SO_4 solutions in 1 *m* (moles solute per kg solvent) NaCl solutions at a pH of 7. NaCl is chosen as a background electrolyte to ensure the total ionic strength of the solution does not change with increased sodium sulfate additions. From Figure 7, it can be seen that direct sulfate adsorption, not solvated sulfate anions residing within the interface, is detectable for Na_2SO_4 concentrations as low as 1×10^{-4} *m*. That only adsorbed sulfate anions are contributing to the VSFG spectra is apparent from the multiple peaks present within the S–O bond frequency range, indicating the symmetry lowering from T_d to C_{2v}/C_{3v} that occurs for the sulfate anion upon adsorption.[60] These results indicate that the surface charge of CaF_2 is neutralized by inner-sphere complexation of the sulfate anion at the water/CaF_2 interface, as well as sulfate ions that reside in the interfacial electric double layer.

Hopkins et al. have examined the influence of ions on the water structure at the water/CaF_2 interface at a near neutral pH (5.8) with VSFG and have demonstrated that the addition of sodium sulfate is more disruptive toward the hydrogen-bonding network than the addition of NaCl, NaBr, and NaF.[58] The comparatively large intensity changes for Hopkin et al.'s Na_2SO_4 VSFG spectra suggests that the sulfate anion is involved in interactions that are more disruptive to water's hydrogen-bonding network at the solution/CaF_2 interface than simply screening the surface potential, which our results support. The direct adsorption of sulfate may describe, beyond a divalent versus monovalent explanation, why the sulfate anion exhibits a larger effect on the hydrogen-bonding network of water at the water/CaF_2 interface than salts such as NaCl as was observed by Hopkins et al.[58]

Conclusions

Work presented here has focused upon efforts to elucidate the perturbation of water's hydrogen-bonding network by ions and solutes at a variety of interfacial regimes. Surface-sensitive vibrational spectroscopic methods such as VSFG and PS-SFG are the primary tools that are utilized in our laboratory to interrogate interfacial water. However, understanding perturbation of water arising from interactions with various ions and solutes is nontrivial. Results for the vapor/water interface of ionic solutions indicate that, in general, the hydrogen-bond network is less accommodating of ions as size, polarizability, and charge increases. However, results for bicarbonate that show little perturbation indicate that predicting ion effects based on these parameters is not sufficient and direct measurements are nessessary. Direct phase measurement is even more vital for understanding perturbation orginating from solutes because the complex molecular character of these compounds makes predicting their influence even more tenuous. For water near charged interfaces, such as water/mineral systems, a large enhancement of the hydrogen-bonding network as observed by others due to an increased surface potential of the mineral may be screened by the presence of ions in the solution. The direct adsorption of ions to the mineral, as was shown for Na_2SO_4 solutions at the water/CaF_2 interface, may explain why some ions show increased shielding abilities over others.

We acknowledge the NSF-CHE (Grant No. 0749807), DOE-BES Geochemistry (Grant No. DE-FG02-04ER15495), and the Camille and Henry Dreyfus Foundation (Camille Dreyfus Teacher-Scholar Award) for funding of this work.

BIOGRAPHICAL INFORMATION

Aaron M. Jubb was born in Fort Hood, TX, in 1984. In 2006, he received a B.A. in chemistry from Lawrence University and is currently working toward a Ph.D. in chemistry at The Ohio State University under the supervision of Dr. Heather Allen. His research interests include the application of physical chemistry methodology to study environmental systems.

Wei Hua received her B.S. in chemistry in 2005 and M.S. in Environmental Science in 2008 from Peking University, China. Since 2008, she has been pursuing her Ph.D. degree under the direction of Professor Heather C. Allen. Her research interests are focused on aqueous surface structure and molecular interactions in atmospheric chemistry and biologically relevant monolayer systems.

Heather C. Allen received her B.S., M.S., and Ph.D. degrees from University of California, Irvine, and was advised by F. S. Rowland and D. Blake as an undergraduate and J. C. Hemminger (advisor) and B. J. Finlayson-Pitts (co advisor) as a graduate student. Her research interests have focused on molecular organization at interfaces of environmental interest and more recently biological applications of such in addition to optical spectroscopy instrumentation development.

REFERENCES

1 Fecko, C. J.; Eaves, J. D.; Loparo, J. J.; Tokmakoff, A.; Geissler, P. L. Ultrafast Hydrogen-Bond Dynamics in the Infrared Spectroscopy of Water. *Science* **2003**, *301*, 1698–1702.

2 Asbury, J. B.; Steinel, T.; Stromberg, C.; Corcelli, S. A.; Lawrence, C. P.; Skinner, J. L.; Fayer, M. D. Water Dynamics: Vibrational Echo Correlation Spectroscopy and Comparison to Molecular Dynamics Simulations. *J. Phys. Chem. A* **2004**, *108*, 1107–1119.

3 Xantheas, S. S. Cooperativity and Hydrogen Bonding Network in Water Clusters. *Chem. Phys.* **2000**, *258*, 225–231.

4 Buch, V.; Milet, A.; Vacha, R.; Jungwirth, P.; Devlin, J. P. Water Surface Is Acidic. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 7342–7347.

5 Verlet, J. R. R.; Bragg, A. E.; Kammrath, A.; Cheshnovsky, O.; Neumark, D. M. Observation of Large Water-Cluster Anions with Surface-Bound Excess Electrons. *Science* **2005**, *307*, 93–96.

6 Petersen, P. B.; Saykally, R. J. On the Nature of Ions at the Liquid Water Surface. *Annu. Rev. Phys. Chem.* **2006**, *57*, 333–364.

7 Smith, J. D.; Cappa, C. D.; Wilson, K. R.; Cohen, R. C.; Geissler, P. L.; Saykally, R. J. Unified Description of Temperature-Dependent Hydrogen-Bond Rearrangement in Liquid Water. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 14171–14174.

8 Luzar, A.; Chandler, D. Hydrogen-Bond Kinetics in Liquid Water. *Nature* **1996**, *379*, 55–57.

9 Auer, B. M.; Skinner, J. L. Vibrational Sum-Frequency Spectroscopy of the Water Liquid/Vapor Interface. *J. Phys. Chem. B* **2009**, *113*, 4125–4130.

10 Ishiyama, T.; Morita, A. Vibrational Spectroscopic Response of Intermolecular Orientational Correlation at the Water Surface. *J. Phys. Chem. C* **2009**, *113*, 16299–16302.

11 Jungwirth, P.; Tobias, D. J. Specific Ion Effects at the Air/Water Interface. *Chem. Rev.* **2006**, *106*, 1259–1281.

12 Finlayson-Pitts, B. J.; Pitts, J. N., Jr. *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments and Applications*; Academic Press: San Diego, CA, 2000.

13 Eisenthal, K. B. Liquid Interfaces Probed by Second-Harmonic and Sum-Frequency Spectroscopy. *Chem. Rev.* **1996**, *96*, 1343–1360.

14 Du, Q.; Superfine, R.; Freysz, E.; Shen, Y. R. Vibrational Spectroscopy of Water at the Vapor Water Interface. *Phys. Rev. Lett.* **1993**, *70*, 2313–2316.

15 Bian, H. T.; Feng, R. R.; Xu, Y. Y.; Guo, Y.; Wang, H. F. Increased Interfacial Thickness of the NaF, NaCl and NaBr Salt Aqueous Solutions Probed with Non-Resonant Surface Second Harmonic Generation (Shg). *Phys. Chem. Chem. Phys.* **2008**, *10*, 4920–4931.

16 Johnson, C. M.; Tyrode, E.; Baldelli, S.; Rutland, M. W.; Leygraf, C. A Vibrational Sum Frequency Spectroscopy Study of the Liquid-Gas Interface of Acetic Acid-Water Mixtures: 1. Surface Speciation. *J. Phys. Chem. B* **2005**, *109*, 321–328.

17 Gopalakrishnan, S.; Liu, D. F.; Allen, H. C.; Kuo, M.; Shultz, M. J. Vibrational Spectroscopic Studies of Aqueous Interfaces: Salts, Acids, Bases, and Nanodrops. *Chem. Rev.* **2006**, *106*, 1155–1175.

18 Kemnitz, K.; Bhattacharyya, K.; Hicks, J. M.; Pinto, G. R.; Eisenthal, K. B.; Heinz, T. F. The Phase of Second-Harmonic Light Generated at an Interface and Its Relation to Absolute Molecular Orientation. *Chem. Phys. Lett.* **1986**, *131*, 285–290.

19 Baldelli, S.; Schnitzer, C.; Shultz, M. J. The Structure of Water on HCl Solutions Studied with Sum Frequency Generation. *Chem. Phys. Lett.* **1999**, *302*, 157–163.

20 Shultz, M. J.; Schnitzer, C.; Simonelli, D.; Baldelli, S. Sum Frequency Generation Spectroscopy of the Aqueous Interface: Ionic and Soluble Molecular Solutions. *Int. Rev. Phys. Chem.* **2000**, *19*, 123–153.

21 Xu, M.; Tang, C. Y.; Jubb, A. M.; Chen, X. K.; Allen, H. C. Nitrate Anions and Ion Pairing at the Air—Aqueous Interface. *J. Phys. Chem. C* **2009**, *113*, 2082–2087.

22 Levering, L. M.; Sierra-Hernandez, M. R.; Allen, H. C. Observation of Hydronium Ions at the Air—Aqueous Acid Interface: Vibrational Spectroscopic Studies of Aqueous HCl, HBr, and HI. *J. Phys. Chem. C* **2007**, *111*, 8814–8826.

23 Gopalakrishnan, S.; Jungwirth, P.; Tobias, D. J.; Allen, H. C. Air—Liquid Interfaces of Aqueous Solutions Containing Ammonium and Sulfate: Spectroscopic and Molecular Dynamics Studies. *J. Phys. Chem. B* **2005**, *109*, 8861–8872.

24 Allen, H. C.; Casillas-Ituarte, N. N.; Sierra-Hernandez, M. R.; Chen, X. K.; Tang, C. Y. Shedding Light on Water Structure at Air-Aqueous Interfaces: Ions, Lipids, and Hydration. *Phys. Chem. Chem. Phys.* **2009**, *11*, 5538–5549.

25 Chen, X. K.; Allen, H. C. Water Structure at Aqueous Solution Surfaces of Atmospherically Relevant Dimethyl Sulfoxide and Methanesulfonic Acid Revealed by Phase-Sensitive Sum Frequency Spectroscopy. *J. Phys. Chem. B* **2010**, *114*, 14983–14988.

26 Chen, X. K.; Huang, Z. S.; Hua, W.; Castada, H.; Allen, H. C. Reorganization and Caging of DPPC, DPPE, DPPG, and DPPS Mono-Layers Caused by Dimethylsulfoxide Observed Using Brewster Angle Microscopy. *Langmuir* **2010**, *26*, 18902–18908.

27 Chen, X. K.; Hua, W.; Huang, Z. S.; Allen, H. C. Interfacial Water Structure Associated with Phospholipid Membranes Studied by Phase-Sensitive Vibrational Sum Frequency Generation Spectroscopy. *J. Am. Chem. Soc.* **2010**, *132*, 11336–11342.

28 Hua, W.; Chen, X. K.; Allen, H. C. Phase-Sensitive Sum Frequency Revealing Accomodation of Bicarbonate Ions, and Charge Separation of Sodium and Carbonate Ions within the Air/Water Interface. *J. Phys. Chem. A* **2011**, *115*, 6233–6238.

29 Hua, W.; Jubb, A. M.; Allen, H. C. Electric Field Reversal of Na_2SO_4, $(NH_4)_2SO_4$, and Na_2CO_3 Relative to $CaCl_2$ and NaCl at the Air/Aqueous Interface Revealed by Phase-Sensitive Sum Frequency. *J. Phys. Chem. Lett.* **2011**, *2*, 2515–2520.

30 Odum, J. R.; Hoffmann, T.; Bowman, F.; Collins, D.; Flagan, R. C.; Seinfeld, J. H. Gas/Particle Partitioning and Secondary Organic Aerosol Yields. *Environ. Sci. Technol.* **1996**, *30*, 2580–2585.

31 Tian, C. S.; Ji, N.; Waychunas, G. A.; Shen, Y. R. Interfacial Structures of Acidic and Basic Aqueous Solutions. *J. Am. Chem. Soc.* **2008**, *130*, 13033–13039.

32 Raymond, E. A.; Tarbuck, T. L.; Brown, M. G.; Richmond, G. L. Hydrogen-Bonding Interactions at the Vapor/Water Interface Investigated by Vibrational Sum-Frequency Spectroscopy of HOD/H_2O/D_2O Mixtures and Molecular Dynamics Simulations. *J. Phys. Chem. B* **2003**, *107*, 546–556.

33 Sovago, M.; Vartiainen, E.; Bonn, M. Determining Absolute Molecular Orientation at Interfaces: A Phase Retrieval Approach for Sum Frequency Generation Spectroscopy. *J. Phys. Chem. C* **2009**, *113*, 6100–6106.

34 Superfine, R.; Huang, J. Y.; Shen, Y. R. Experimental Determination of the Sign of Molecular Dipole Moment Derivatives: An Infrared-Visible Sum Frequency Generation Absolute Phase Measurement Study. *Chem. Phys. Lett.* **1990**, *172*, 303–306.

35 Ostroverkhov, V.; Waychunas, G. A.; Shen, Y. R. New Information on Water Interfacial Structure Revealed by Phase-Sensitive Surface Spectroscopy. *Phys. Rev. Lett.* **2005**, *94*, No. 046102.

36 Ji, N.; Ostroverkhov, V.; Tian, C. S.; Shen, Y. R. Characterization of Vibrational Resonances of Water-Vapor Interfaces by Phase-Sensitive Sum-Frequency Spectroscopy. *Phys. Rev. Lett.* **2008**, *100*, No. 096102.

37 Nihonyanagi, S.; Yamaguchi, S.; Tahara, T. Direct Evidence for Orientational Flip-Flop of Water Molecules at Charged Interfaces: A Heterodyne-Detected Vibrational Sum Frequency Generation Study. *J. Chem. Phys.* **2009**, *130*, No. 204704.

38 Stiopkin, I. V.; Jayathilake, H. D.; Bordenyuk, A. N.; Benderskii, A. V. Heterodyne-Detected Vibrational Sum Frequency Generation Spectroscopy. *J. Am. Chem. Soc.* **2008**, *130*, 2271–2275.

39 Tian, C. S.; Shen, Y. R. Sum-Frequency Vibrational Spectroscopic Studies of Water/Vapor Interfaces. *Chem. Phys. Lett.* **2009**, *470*, 1–6.

40 Tian, C. S.; Byrnes, S. J.; Han, H. L.; Shen, Y. R. Surface Propensities of Atmospherically Relevant Ions in Salt Solutions Revealed by Phase-Sensitive Sum Frequency Vibrational Spectroscopy. J. Phys. *Chem. Lett.* **2011**, *2*, 1946–1949.

41 Sovago, M.; Campen, R. K.; Bakker, H. J.; Bonn, M. Hydrogen Bonding Strength of Interfacial Water Determined with Surface Sum-Frequency Generation. *Chem. Phys. Lett.* **2009**, *470*, 7–12.

42 Baldelli, S.; Schnitzer, C.; Shultz, M. J.; Campbell, D. J. Sum Frequency Generation Investigation of Water at the Surface of H_2O/H_2SO_4 Binary Systems. *J. Phys. Chem. B* **1997**, *101*, 10435–10441.

43 Tarbuck, T. L.; Richmond, G. L. Adsorption and Reaction of CO_2 and SO_2 at a Water Surface. *J. Am. Chem. Soc.* **2006**, *128*, 3256–3267.

44 Du, H.; Liu, J.; Ozdemir, O.; Nguyen, A. V.; Miller, J. D. Molecular Features of the Air/Carbonate Solution Interface. *J. Colloid Interface Sci.* **2008**, *318*, 271–277.

45 Jungwirth, P.; Winter, B. Ions at Aqueous Interfaces: From Water Surface to Hydrated Proteins. *Annu. Rev. Phys. Chem.* **2008**, *59*, 343–366.

46 Casillas-Ituarte, N. N.; Callahan, K. M.; Tang, C. Y.; Chen, X. K.; Roeselova, M.; Tobias, D. J.; Allen, H. C. Surface Organization of Aqueous $MgCl_2$ and Application to Atmospheric Marine Aerosol Chemistry. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 6616–6621.

47 Schwartz, S. E. Are Global Cloud Albedo and Climate Controlled by Marine-Phytoplankton? *Nature* **1988**, *336*, 441–445.

48 Charlson, R. J.; Schwartz, S. E.; Hales, J. M.; Cess, R. D.; Coakley, J. A.; Hansen, J. E.; Hofmann, D. J. Climate Forcing by Anthropogenic Aerosols. *Science* **1992**, *255*, 423–430.

49 Allen, H. C.; Raymond, E. A.; Richmond, G. L. Surface Structural Studies of Methanesulfonic Acid at Air /Aqueous Solution Interfaces Using Vibrational Sum Frequency Spectroscopy. *J. Phys. Chem. A* **2001**, *105*, 1649–1655.

50 Allen, H. C.; Raymond, E., A.; Richmond, G. L. Nonlinear Vibrational Sum Frequency Generation Spectroscopy of Atmospherically Relevant Molecules at Aqueous Solution Surfaces. *Curr. Opin. Colloid Interface Sci.* **2000**, *5*, 74–80.

51 Schrodle, S.; Richmond, G. L. In Situ Non-Linear Spectroscopic Approaches to Understanding Adsorption at Mineral-Water Interfaces. *J. Phys. D: Appl. Phys.* **2008**, *41*, No. 033001.

52 Ostroverkhov, V.; Waychunas, G. A.; Shen, Y. R. Vibrational Spectra of Water at Water/α-Quartz (0 0 0 1) Interface. *Chem. Phys. Lett.* **2004**, *386*, 144–148.

53 Usher, C. R.; Michel, A. E.; Grassian, V. H. Reactions on Mineral Dust. *Chem. Rev.* **2003**, *103*, 4883–4939.

54 Jena, K. C.; Hore, D. K. Variation of Ionic Strength Reveals the Interfacial Water Structure at a Charged Mineral Surface. *J. Phys. Chem. C* **2009**, *113*, 15364–15372.

55 Yang, Z.; Li, Q. F.; Chou, K. C. Structures of Water Molecules at the Interfaces of Aqueous Salt Solutions and Silica: Cation Effects. *J. Phys. Chem. C* **2009**, *113*, 8201–8205.

56 Zhang, L.; Tian, C. S.; Waychunas, G. A.; Shen, Y. R. Structures and Charging of α-Alumina (0001)/Water Interfaces Studied by Sum-Frequency Vibrational Spectroscopy. *J. Am. Chem. Soc.* **2008**, *130*, 7686–7694.

57 Becraft, K. A.; Richmond, G. L. In Situ Vibrational Spectroscopic Studies of the CaF_2/H_2O Interface. *Langmuir* **2001**, *17*, 7721–7724.

58 Hopkins, A. J.; Schrodle, S.; Richmond, G. L. Specific Ion Effects of Salt Solutions at the CaF_2/Water Interface. *Langmuir* **2010**, *26*, 10784–10790.

59 Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*; Wiley: New York, 1997.

60 Hug, S. J. In Situ Fourier Transform Infrared Measurements of Sulfate Adsorption on Hematite in Aqueous Solutions. *J. Colloid Interface Sci.* **1997**, *188*, 415–422.