

Surface Propensities of Atmospherically Relevant Ions in Salt Solutions Revealed by Phase-Sensitive Sum Frequency Vibrational Spectroscopy

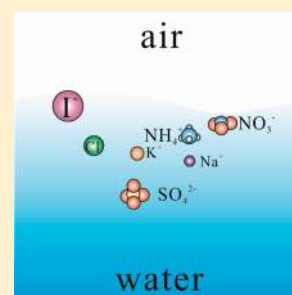
Chuanshan Tian,^{†,‡} Steven J. Byrnes,[‡] Hui-Ling Han, and Y. Ron Shen*

Department of Physics, University of California, Berkeley, California 94720, United States

S Supporting Information

ABSTRACT: We use phase-sensitive sum-frequency vibrational spectroscopy (PS-SFVS) to study the air/water interfaces of a set of salt solutions. The spectra reveals the presence of an electric double layer formed by cations and anions at the interfaces, and allow us to find the *relative* surface propensities of different ions in the following decreasing ranking order: I^- , NO_3^- , NH_4^+ , Cl^- , K^+ , Na^+ , and SO_4^{2-} . Most of our results agree with predictions of MD simulations, but NO_3^- and NH_4^+ do not.

SECTION: Surfaces, Interfaces, Catalysis



Ions at the air/water interface can undergo heterogeneous reactions that play key roles in atmospheric and environmental chemistry.^{1–4} The distribution of soluble ions at air/water interfaces is important for understanding the kinetics and dynamics of such interfacial reactions. Contrary to the traditional thermodynamic model that suggests ions in water should be repelled from the air/water interface, recent molecular dynamics (MD) simulations have predicted that some simple ions, such as I^- and Br^- , could accumulate at the interface.⁵ The predictions were confirmed by experiments.^{6–8} More complex ions, including ammonium (NH_4^+), nitrate (NO_3^-), and sulfate (SO_4^{2-}) that are abundant and active in atmospheric and environmental chemistry,^{6,9} however, are less well studied. MD simulations have also predicted the surface propensity of these ions at the air/water interface,^{3,6,9–13} but experimental results have not provided a ranking order of their surface propensities, which are important for understanding specific ion effects at air/water interfaces.¹⁴ To study the emergence of ions at a water interface, surface-specific sum-frequency vibrational spectroscopy (SFVS) has recently been used widely. It probes the spectral changes in the OH stretch region resulting from the presence of ions that form an electric double layer (EDL) at the interface. From the spectral change, one can deduce the structural change of the hydrogen-bonding network at the interface due to the surface field in the EDL.^{6,8,11,15,16} Unfortunately, most of the published works report only measurement of SFVS intensity spectra, which cannot unambiguously provide information on the absolute orientation of different OH species contributing to the spectra. The missing information makes it difficult to interpret the spectra and to infer the ion distribution at the interface. With the development of phase-sensitive SFVS,¹⁷ we can now measure $\text{Im } \chi_S^{(2)}(\omega_{\text{IR}})$, instead of $|\chi_S^{(2)}(\omega_{\text{IR}})|^2$, where $\chi_S^{(2)}(\omega_{\text{IR}})$ is the

nonlinear susceptibility of the interface; this measurement directly characterizes the vibrational resonances and allow determination of the absolute orientation of a moiety. Thus we can find the direction of the surface field in the EDL at the interface and thereby learn about the *relative* surface propensities of different ions. We describe in this paper our phase-sensitive SFVS (PS-SFVS) study of the air/water interfaces of a set of solutions containing various ions: I^- , NO_3^- , NH_4^+ , Cl^- , K^+ , Na^+ , and SO_4^{2-} . Their surface propensities (in terms of their concentrations at the interface with respect to their bulk concentrations) appear to have the decreasing ranking order indicated.

Our PS-SFVS setup has been described elsewhere.¹⁷ Some details of the experimental arrangement and spectral analysis procedure are given in the Supporting Information. The measurements yield spectra of $|\chi_S^{(2)}(\omega_{\text{IR}})|^2$ and $\text{Im } \chi_S^{(2)}(\omega_{\text{IR}})$ for air/water interfaces after normalization against a reference quartz crystal and correction by complex transmission Fresnel coefficients. The OH stretch resonances of water in the spectra form a strongly inhomogeneously broadened continuum due to varying strengths of hydrogen bonds between water molecules. Therefore the expressions of $\chi_S^{(2)}(\omega_{\text{IR}})$ and $\text{Im } \chi_S^{(2)}(\omega_{\text{IR}})$ take the forms

$$\chi_S^{(2)}(\omega_{\text{IR}}) = \chi_{\text{NR}}^{(2)} + \int \frac{A_q \rho(\omega_q)}{\omega_{\text{IR}} - \omega_q + i\Gamma_q} d\omega_q \quad (1)$$

$$\text{Im } \chi_S^{(2)}(\omega_{\text{IR}}) \approx A_q \rho_q \tau$$

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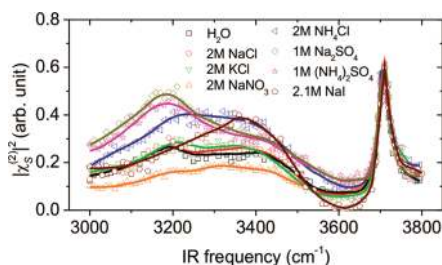


Figure 1. Sum-frequency $|\chi_S^{(2)}(\omega_{\text{IR}})|^2$ spectra of the air/water interfaces for neat water and various salt solutions.

Here, $\chi_{\text{NR}}^{(2)}(\omega_{\text{IR}})$ is the nonresonant background, A_q , ω_q , and Γ_q are, respectively, the amplitude, frequency, and damping constant of the q th vibrational resonance, and $\rho(\omega_{\text{IR}})$ is the density of modes at the input IR frequency ω_{IR} . We used in the experiment s , s , and p polarizations, respectively, for SF output, visible input, and IR input. This corresponds to measuring the tensor component $\chi_{S,yyz}^{(2)}(\omega_{\text{IR}})$, with z along the surface normal. In the spectra presented here, positive $\text{Im} \chi_S^{(2)}(\omega_{\text{IR}})$ refers to contributing OH species (assuming that they are decoupled from neighboring OHs) with a net polar orientation pointing toward the air.^{7,18–20}

Figure 1 shows the $|\chi_S^{(2)}(\omega_{\text{IR}})|^2$ spectra of the air/water interfaces for a set of solutions: neat water, 2.1 M NaI, 2 M NaCl, 2 M KCl, 2 M NaNO₃, 2 M NH₄Cl, 1 M Na₂SO₄, and 1 M (NH₄)₂SO₄. The neat water spectrum is the same as those of previous measurements reported in the literature.²¹ It displays a narrow peak at 3700 cm⁻¹ originating from dangling OH bonds protruding at the surface, and two broad bands around 3200 and 3450 cm⁻¹ due to bonded OH, often labeled as “ice-like” and “liquid-like” bands, respectively.^{7,18,22,23} The surface spectrum of 2.1 M NaI solution serves as another reference.⁷ It is significantly different from that of the neat water in the sense that the strength of the 3400 cm⁻¹ band is appreciably stronger and broader. The result is already well understood as being due to reorientation of water molecules in the negative field of the EDL formed by excess negative I⁻ ions and depleted positive Na⁺ ions at the interface.⁵ Generally, ions emerging at a surface may affect the surface spectrum in two ways: through molecular reorientation by the surface field in the EDL and through disruption of the interfacial structure. In the case of the 2.1 M NaI solution, the surface concentration of I⁻ is no more than a few percent,²⁴ so that its perturbation on the interfacial structure should be negligible. This is also the case for other solutions we have studied, and is supported by the observation that the dangling OH mode at 3700 cm⁻¹ is nearly the same in all cases. (Note that the dangling OH does not experience the surface field in the EDL.)

We now discuss the spectra for various solutions in Figure 1. We notice that dissolution of 2 M NaCl or KCl in water leads to a spectrum not very different from that of neat water, in agreement with previous experiments.^{6,8,11,15,16} This indicates the absence of a strong EDL at the interface of the solution. In other words, Na⁺, K⁺, and Cl⁻ are similarly repelled from the interface, and have nearly the same concentration profile at the interface. MD simulations have predicted that Na⁺, K⁺, are depleted at the interface, while Cl⁻ is neither depleted nor enhanced at the interface. They therefore suggest the presence of an EDL formed by Cl⁻/Na⁺ or Cl⁻/K⁺ with a negative surface field. This is not

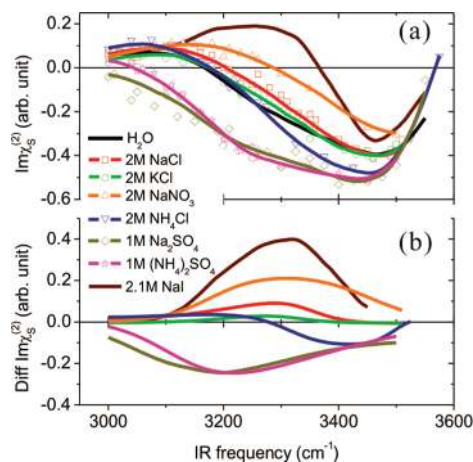


Figure 2. (a) $\text{Im} \chi_S^{(2)}(\omega_{\text{IR}})$ spectra of the air/water interfaces for neat water and various salt solutions. The solid curves serve as eye-guide. (b) Difference spectra of $\text{Im} \chi_S^{(2)}(\omega_{\text{IR}})$ for various salt solutions with reference to neat water.

obvious in the $|\chi_S^{(2)}(\omega_{\text{IR}})|^2$ spectra, but as we shall see later, it is detectable in the $\text{Im} \chi_S^{(2)}(\omega_{\text{IR}})$ spectra. For the solutions of NaNO₃, NH₄Cl, Na₂SO₄, and (NH₄)₂SO₄, the surface spectra in Figure 1 show appreciable differences from that of neat water, indicating the existence of an EDL surface field at the air/water interfaces. It is not easy, however, to know from the $|\chi_S^{(2)}(\omega_{\text{IR}})|^2$ spectra whether the surface field is positive or negative. We therefore turn next to the $\text{Im} \chi_S^{(2)}(\omega_{\text{IR}})$ spectra.

Figure 2a displays the $\text{Im} \chi_S^{(2)}(\omega_{\text{IR}})$ spectra of the set of solutions described above. The corresponding $\text{Re} \chi_S^{(2)}(\omega_{\text{IR}})$ spectra are given in the Supporting Information. In their comparison with the $\text{Im} \chi_S^{(2)}(\omega_{\text{IR}})$ spectrum of the air/neat water interface, positive increase of $\text{Im} \chi_S^{(2)}(\omega_{\text{IR}})$ means that interfacial water molecules contributing to the spectrum at ω_{IR} have been reoriented with more O→H pointing toward air. The reorientation is induced by the negative surface field of the EDL formed by negative ions closer to the interface than positive ions. Similarly, a decrease of $\text{Im} \chi_S^{(2)}(\omega_{\text{IR}})$ signifies a net reorientation of interfacial water molecules with more O→H pointing away from air. To see more clearly the change of $\text{Im} \chi_S^{(2)}(\omega_{\text{IR}})$ induced by surface field, we plot in Figure 2b the difference spectra of $\text{Im} \chi_S^{(2)}(\omega_{\text{IR}})$ for the various solutions with respect to the neat water. It is clear that a negative surface field exists at the interface of the 2.1 M NaI and 2 M NaNO₃ solutions, indicating the formation of an EDL near the interface by I⁻ or NO₃⁻ with Na⁺ that is repelled from the interface. The larger induced change in the spectrum of the NaI solution shows that I⁻ has more surface propensity than NO₃⁻. In the literature, the surface propensity of NaNO₃ is controversial. Earlier MD simulation using a polarizable force field did predict a surface excess of NO₃⁻ at the air/water interface.¹⁰ Recent MD simulations, dividing the polarizability of NO₃⁻ into three equal contributions placed on the oxygen atoms instead of one polarizable center on the nitrogen atom,¹⁰ however, suggested the opposite result.^{9,12,13} X-ray photoemission spectroscopy on a 3 M NaNO₃ solution also concluded that not much surface excess of NO₃⁻ existed at the interface.²⁵ Second harmonic generation measurement on a 2 M NaNO₃ solution, on the other hand, found appreciable surface excess of NO₃⁻ at the interface, but it was not as much as I⁻ in the case of the NaI solution.²⁶ Our result here indicates that NO₃⁻ has larger

surface propensity than Na^+ , although not as large as I^- , to form an EDL.

The $\text{Im } \chi_S^{(2)}(\omega_{\text{IR}})$ spectrum of the 2 M KCl solution, in comparison with that of the neat water, appears only barely more positive, and that of 2 M NaCl solutions are slightly more positive. The spectra suggest that Cl^- has a surface propensity close to, but little more than K^+ and Na^+ , leading to the formation of a weak EDL with a negative surface field. On the other hand, the $\text{Im } \chi_S^{(2)}(\omega_{\text{IR}})$ spectra of the 2 M NH_4Cl , 1 M Na_2SO_4 , and 1 M $(\text{NH}_4)_2\text{SO}_4$ solutions all appear clearly more negative than that of the neat water, indicating the existence of a clearly positive surface field at the interfaces. The NH_4Cl case is interesting. The positive surface field shows that, in contrast to the NaCl case, NH_4^+ has a surface propensity higher than that of Cl^- , and hence also Na^+ . This is opposite to what the MD simulation predicted.⁶ One may expect that the umbrella-bending-rocking combination mode of NH_4^+ at 3060 cm^{-1} could contribute to the low-frequency part of the spectrum.⁶ However, its symmetry suggests that the contribution, if any, should be very weak.

From the spectra in Figure 2, we notice that the effect of the EDL at the interfaces of the Na_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ solutions are relatively strong. The positive surface field in the case of Na_2SO_4 suggests that, while Na^+ should be repelled from the interface, SO_4^{2-} is repelled even further from the interface, presumably because, unlike I^- , the image charge effect on SO_4^{2-} dianions dominates over the dispersive force.^{3,5,6} Knowing that Na^+ should have surface depletion rather than excess at the interface, we must conclude that SO_4^{2-} also does not have a surface excess. The EDL in this case is formed because Na^+ has a larger surface propensity than SO_4^{2-} , but not because Na^+ has a surface excess. The same is true for the $(\text{NH}_4)_2\text{SO}_4$ solution. MD simulations did suggest that SO_4^{2-} should be strongly repelled from an air/water interface, much more appreciably than Na^+ and NH_4^+ .⁶ The $\text{Im } \chi_S^{(2)}(\omega_{\text{IR}})$ spectra of the two solutions are very close, indicating that the surface propensities of Na^+ and NH_4^+ are nearly the same with respect to SO_4^{2-} .

It is seen in Figure 2b that the spectral changes of $\text{Im } \chi_S^{(2)}(\omega_{\text{IR}})$ for the NaI, NaNO_3 , NaCl, and KCl solutions with respect to the neat water case, induced by surface field or potential in their EDL, all show a broad positive band in the liquid-like region with roughly the same profile, but different strengths that reflect the strengths of the EDL potential. Apparently, in these cases, the negative surface field reorients essentially the same group of more loosely hydrogen-bonded interfacial water molecules. The spectral changes for the Na_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ solutions are nearly the same. Both display a broad negative band induced by the positive surface field or potential in their EDL. In comparison with the above-mentioned positive band, the negative band appears to be broader and shifted to lower frequency, suggesting that the positive surface field has reoriented a different group or an additional group of interfacial water molecules than the negative surface field. The spectral change for the NH_4Cl solution is even more different: the relatively weak positive surface field seems to be able to reorient only the very loosely hydrogen-bonded interfacial water molecules that contribute to the higher vibrational frequencies. To truly understand the observed spectral changes, rigorous theoretical calculations are obviously needed. Here, we offer a simple conjecture. At the air/neat water interface, there might exist a group of water molecules that would straddle the top-layer water molecules with symmetric hydrogen bonds and contribute to the positive band in the ice-like region.⁷ They could be reoriented only by the negative

surface field if the field is strong enough. This would explain why the negative band is broader and shifts to lower frequency. However, in the weak-field cases, why the negative band (NH_4Cl) is shifted to higher frequency with respect to the positive band (NaCl and KCl) is still a mystery. It seems to suggest that the negative field is more effective to reorient water molecules in the liquid-like region.

From the spectra in Figure 2 and the deduced relative surface field strengths and signs for the set of solutions we studied, we can obtain the ranking order of surface propensity assuming that the cation–anion interactions in solution can be neglected. It is, in decreasing order: I^- , NO_3^- , NH_4^+ , Cl^- , K^+ , Na^+ and SO_4^{2-} . We believe that cation–anion interactions may make the surface propensity of selected ionic species somewhat different in different solutions, but the above ranking order of different ions is not likely to change. It is the relative surface propensity of the cation with respect to the anion that determines whether the EDL at the interface of a solution has a positive or negative surface field. The surface excess of the cation, anion, or both in a solution can be positive or negative to form an EDL. Because K^+ and Na^+ should be repelled from the interface by image charges, they should have negative surface excess. Since SO_4^{2-} has less surface propensity than Na^+ , it should have even more negative surface excess. Among the other ions, NH_4^+ and Cl^- have surface propensities that are similar to, although somewhat larger than, those of Na^+ , and therefore are likely to also have negative surface excess. On the other hand, I^- is known to have positive surface excess, but it is not clear whether NO_3^- has a positive or negative surface excess. All we can be sure is that it has a larger surface propensity than the other ions in our study except I^- .

In summary, we show that the $\text{Im } \chi_S^{(2)}(\omega_{\text{IR}})$ spectra obtained from PS-SFVS allow us to qualitatively deduce the relative strengths and directions of the surface field at the interfaces of different salt solutions, and hence determine the relative surface propensities of different ions in water. Some of our results on the solutions we have studied agree with predictions of MD simulations, and others do not. We note, however, that the interfacial EDL should exist when cations and anions have different surface propensities, but not necessarily have surface excess of opposite signs.

■ ASSOCIATED CONTENT

Supporting Information. Experimental details and spectral analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: yrshen@berkeley.edu.

Present Addresses

[†]Department of Physics, Fudan University, Shanghai 200433, China.

Author Contributions

[‡]These authors contributed equally.

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