Evidence for an Enhanced Hydronium Concentration at the Liquid Water Surface

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The recent demonstration of enhanced surface anion concentrations for aqueous electrolyte solutions strongly contrasts current textbook descriptions. Small cations are still expected to be repelled from the surface, but recent simulations predict that hydronium (H_3O^+) cations are instead preferentially adsorbed at the interface. Here we describe a comparative second harmonic generation (SHG) study of aqueous solutions of hydriodic acid (HI) and alkali iodides (NaI and KI), which establish lower limits of 55% and 34% larger surface iodide concentrations for HI solutions relative to NaI and KI solutions, respectively. This result implies that hydronium ions must exist in much higher densities near the liquid surface than do the alkali ions, in support of the theoretical predictions.

I. Introduction

The outermost layer of an aqueous solution surface is conventionally viewed as being devoid of ions.[1,2] This concept embodies both the surface tension increase measured for salt solutions relative to pure water[3] and dielectric continuum models of the surface that date back to the original Onsager−Samaras description.[4−6] Lately, there has been renewed interest in the possible existence of polarizable ("soft") ions at the water−air interface due to potential implications for atmospheric aerosol chemistry.[7−9] Furthermore, a few theoretical[10−12] and our own experimental[13,14] studies have recently confirmed enhanced concentration of "soft" anions (e.g., I^-) at the outermost layer of the liquid water surface. In this case, the large size and high polarizablility of the anions compensates for the incomplete solvation through the field-induced dipole interactions that maximize at the interface. Smaller and less polarizable ("hard") cations are still expected to be repelled from the outermost layer of the interface. The addition of simple inorganic acids to water is known to *reduce* the surface tension[3] and should thus be present in excess at the interface. However, such macroscopic measurements offer no molecular-level insight into the nature of the observed surface excess.

Recent theoretical calculations have proposed that hydronium (H_3O^+) is preferentially localized at the outermost liquid layer of the water−air interface[15−17] due to the amphiphilic nature of this unique and ubiquitous cation. Neutral water molecules are capable of forming four hydrogen bonds, whereas hydronium can only form three due to a less negative charge on the oxygen. At the interface, however, the hydrophilic protons are directed into the liquid and form strong hydrogen bonds, while the hydrophobic oxygen is directed toward the vapor. This predicted "directional hydrophobicity", if confirmed, could help explain several aspects of the intriguing surface behavior of water and aqueous solutions, viz. the opposite surface tension change effected by salts and acids[3] and the enigmatic Jones-Ray effect,[18] wherein nearly all salts are found to effect a minimum in the surface tension at bulk concentrations of ca. 10^{-3} M.

Surface sensitive experiments offer another venue to provide detailed molecular insight to the identity and distribution of species at the interface. The first sum frequency generation (SFG) experiments on electrolyte solutions, performed by the Shen[19] and Schultz[20] groups, compared the surface hydrogen bonding networks of salt and acid solutions by probing the OH-stretch vibrations of the solvent. These studies revealed that acids generally perturb the surface hydrogen bonding structure more strongly than do salts and ascribed the observed spectral changes to interfacial broadening via electric double layer formation and to ion pair formation that excludes water molecules from the interface. No conclusive evidence for the presence of hydronium ions at the interface was presented, however, and because of problems with overlapping bands and uncertain assignment of spectral features, these earlier experiments remain somewhat inconclusive and controversial. However, a recent study comparing molecular dynamics simulations with new SFG experiments on acidic solutions[17] strongly supports an enhanced hydronium concentration at the interface, in agreement with the SHG results presented here.

We present results obtained with the surface-specific technique of resonance-enhanced SHG, directly probing the iodide concentration of alkali iodide and hydriodic acid solutions. The experiments reveal a lower bound of a $55 \pm 10\%$ and $34 \pm 7\%$ larger surface concentration of iodide for HI solutions compared to the NaI and KI solutions of the same bulk concentration, thereby indicating that hydronium approaches closer to and may even penetrate into the outermost layer of the liquid water surface, in agreement with the recent theoretical predictions.[15−17]

II. Experimental Details

A. Laser System. The relatively weak SHG response of aqueous electrolyte surfaces is probed using sub-100 fs laser pulses from a regenerative Ti:sapphire laser system. The laser system and experimental setup will be described in detail in a later publication[21] and only a brief description is presented here. A home-built Ti:sapphire oscillator seeds a commercial amplifier (Spectra Physics, Spitfire) after which a commercial OPA (Light Conversion, TOPAS) is used to tune the wavelength. After the OPA, dichroic mirrors and optical filters are used to purify the beam and a variable ND filter is used to attenuate the laser power. The fundamental beam is focused onto to the sample at

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45° and recollimated before the SHG beam is separated from the fundamental by dichroic mirrors and a prism and collected by a solar blind PMT (Hamamatzu, R7154PHA).

B. Sample Preparation. All glassware is cleaned with hot chromic acid or Nochromix (a chromic acid substitute) before each experiment and rinsed with 18.2 MΩ water with ≤4 ppb total organic content (Millipore, MilliQ gradient). Samples are prepared using regent grade chemicals (99+%) and Millipore water. During the experiment, the sample is kept in a closed box purged with pure nitrogen. The nitrogen flow is also responsible for gently stirring the surface without causing significant deviations to the laser beam. The water was purged thoroughly with pure nitrogen for at least 1 h before making the solutions. Solutions were made fresh before each experiment. Since the iodide solutions are light- and oxygen-sensitive, it is important to use fresh solutions and limit contact with air and ambient light.

C. Second Harmonic Generation. SHG is a second-order process that is dipole-forbidden in bulk centrosymmetric media and widely used as a surface specific probe for liquids,[22,23] with probing depth of a few monolayers.[24] Due to the coherent nature of the response, the generated SHG intensity depends on the square of the source terms, as expressed in terms of the second-order susceptibility:[25,26]

$$I_{2\omega} \propto |\chi^{(2)}|^2 I_\omega^2 \tag{1}$$

$$\chi^{(2)} = \chi^{(2)}_{\text{water}} + \chi^{(2)}_{\text{iodide}} \tag{2}$$

$$\chi^{(2)}_{\text{iodide}} = N_S \langle \beta \rangle_{\text{Or}} \tag{3}$$

Here I_ω and $I_{2\omega}$ are the incident and SHG intensity, respectively, $\chi^{(2)}$ is the second-order susceptibility, N_S is the number of molecules probed at the surface, and $\langle \beta \rangle_{\text{Or}}$ is the orientationally averaged first-order hyperpolarizability. Second-order susceptibilities are generally complex quantities and contain both resonant and nonresonant contributions. For the wavelengths used in this experiment, the water susceptibility is nonresonant and thus real, but it changes with variations in the ion concentration to produce a concentration-dependent water background. The nonresonant part of the iodide susceptibility is negligible compared to the water background response, so the complex iodide susceptibility can be described by eq 3.

III. Results

We utilize the strong charge-transfer-to-solvent (CTTS) transition of iodide in the UV to directly probe the surface concentration of iodide by resonant-enhanced femtosecond SHG. The bulk absorption spectrum of iodide, comprising two CTTS bands at 195 and 225 nm, is shown in Figure 1.

Our recent SHG studies of sodium and potassium iodide solutions have characterized three distinct concentration regimes.[13] At low concentrations (<0.1 M), individual iodide anions adsorb strongly to the surface with a Gibbs free energy of −6.2 kcal/mol. This produces a saturated surface at millimolar bulk concentrations and is an example of the Jones-Ray effect,[18] viz. an initial enhancement in the ion surface concentration that saturates around 10^{-3} M, independent of the nature of the salt. The intermediate range (between 0.1 and 2 M) is dominated by a change in the nonresonant water background and, at high concentrations (>2 M), the SHG intensity increases further due to increasing concentrations of interfacial iodide anions. The wavelength dependence of the high concentration iodide responses for NaI, KI, and HI solutions are compared in Figure
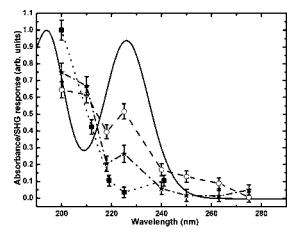

Figure 1. Iodide spectral dependence. The solid line is the bulk absorption spectrum of iodide, comprising two CTTS transitions centered at 195 and 225 nm. The solid squares are the nonlinear surface responses of iodide from HI solutions at molar concentrations. For comparison, the open circles and solid stars are the corresponding responses from NaI and KI, respectively. The HI and NaI spectra are averaged over 4 and 5 M while the KI spectrum is average over 3 and 4 M. These high concentration spectra are different than the low concentration spectra published previously[13] due to the different adsorption mechanism and increased interionic interaction at high concentrations. Error bars are estimated from the reproducibility of the data.

1. These high concentration spectra are different than the previously published low concentration spectra[13] due to the different solvation environments and adsorption mechanisms. A clear implication of this is the notable cation effects on the spectra, absent at low concentrations, and manifested as spectral shifts. Due to these shifts, the spectral intensities should be compared at their maxima rather than at a fixed wavelength. However, the HI response is shifted farther to the UV, outside of the spectral coverage of our experiment. The concentration comparisons are made at 200 nm, which is the maximum response observed for all solutions. If it were possible to compare the spectral intensities at their spectral maxima, even larger surface enhancements of hydronium would be observed. The quoted surface enhancements of HI compared to NaI and KI are thus lower bounds.

HI solutions show a very weak Jones-Ray effect compared to NaI and KI (approximately 5 times smaller). This is, in itself, quite interesting, since NaI and KI show an identical Jones-Ray effect, implying individual anion adsorption with no cation dependence.[13] The reduced Jones-Ray effect for HI implies that the hydronium cations "poison" the active surface sites that the anions bind to, providing additional evidence for hydronium cations in the outermost surface layer. The Jones-Ray effect appears as an initial offset in the SHG response at certain wavelengths and has, for simplicity in the following analysis, been normalized out.

The measured SHG intensity contains contributions from both the water background and the iodide anions at the interface. The SHG intensity is proportional to the norm square of these contributions. The water background is nonresonant and thus real, whereas the iodide response contains a complex phase that depends on the wavelength. The nonresonant contribution changes with salt concentration and, in principle, no distinction can be made between the nonresonant water background and a possible nonresonant contribution from iodide. However, the nonresonant contribution from iodide is most probably negligible compared to the water background, and since the total nonresonant contribution is separated from the resonant iodide contribution in the analyses below, it would not affect the result
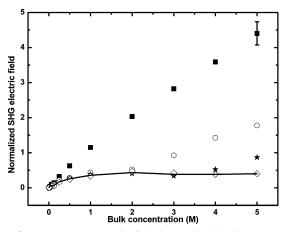
Figure 2. Nonresonant water SHG background. The bulk concentration dependence of the SHG electric field is normalized to pure water and corrected for the small initial offset from the Jones-Ray effect. Shown are results from four different probe wavelengths: solid squares (200 nm), open circles (212 nm), solid stars (219 nm), and open diamonds (225 nm). All wavelengths reveal a change in the nonresonant water background, represented by the black line, whereas only the resonant wavelengths exhibit the iodide response, as shown in Figure 1. Error bars are estimated from the reproducibility of the data.
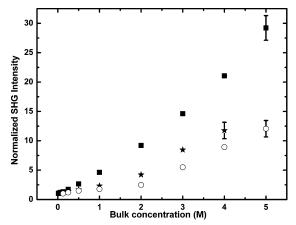

Figure 3. Evidence for enhanced surface hydronium concentration. This graph show the measured SHG intensity normalized to the pure water response. When the SHG intensity at 200 nm of HI (black squares) is compared to that of NaI (open circles) the surface concentration of iodide is found to be 55 ± 10% larger for HI than for NaI and 34 ± 7% higher than for KI (solid stars). The larger surface iodide concentration observed for HI compared to NaI and KI is evidence that hydronium is much more easily accommodated at the liquid−water surface than are either sodium or potassium cations, in accord with the recent computer simulations.[15−17] Error bars are estimated from the reproducibility of the data.

if the total nonresonant response contained a contribution from iodide.

By tuning the wavelength out of resonance with the iodide response, the change in the water SHG background with ion concentration can be measured independently, as shown in Figure 2. Once the water background is known, it can then be incorporated into the total SHG intensity in order to extract the iodide response. Figure 3 shows the total SHG response at 200 nm of HI, NaI and KI solutions as a function of bulk concentration. The SHG response of the HI solution is much stronger than those of either NaI or KI solutions.

To compare the iodide concentrations of the solutions we need to extract the iodide part (the resonant contribution) of the total SHG intensity. This requires the knowledge of the complex phase of the iodide susceptibility and the magnitude of the nonresonant water background. A diagram describing the
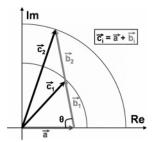

Figure 4. Complex susceptibility. The measured SHG intensity is the square vector c_i, which is the sum of the two contributions from the water background (*a*) and the iodide response (*b_i*). The water background is real but the iodide susceptibility contains an unknown complex phase as determined by the angle θ. The two circles represent the length of the total second-order susceptibility as measured in the experiment. The length of the real water susceptibility (a) is determined by the nonresonant experiments. The length of the iodide susceptibility (b) as determined by measured intensities, depends on the complex phase of the iodide susceptibility.

complex nature of the problem is shown in Figure 4. At a given concentration the total SHG intensity (c) is measured, and from the off-resonant experiment the contribution from the water background (a) is known. However, the magnitude of the iodide response that would give rise to the total SHG intensity will depend on the complex phase (θ) of the iodide signal. From the cosine relation we obtain

$$b = a \times \cos(\theta) + \sqrt{c^2 - a^2(1 - \cos^2(\theta))} \qquad (4)$$

The magnitude of the iodide response (b) that is extracted from a measured SHG intensity (c) and a known water background (a) is show for an arbitrary complex angle of the iodide susceptibility in Figure 5a. When the surface concentrations are compared, the relative enhancement of iodide in HI and KI solutions over NaI at the same bulk concentration can be calculated. This is shown in Figure 5b. Although the magnitude of the relative surface concentration changes with the complex angle of the iodide susceptibility, the HI enhancement over NaI is always around three times larger than the KI enhancement over NaI. Fortunately, the complex angle of the iodide suscep-tibility (θ) can be estimated from the fits to the concentration profiles. The fitted angles are shown in Figure 6. At 200 nm, the angle is in the range 60−83°. For this angle range the surface concentration increase of iodide of HI and KI, compared to NaI solutions of same bulk concentration, is 55 ± 10% and 16 ± 4%, respectively, as shown in Figure 5. The latter corresponds to an increase of the surface iodide concentration of HI solutions relative to KI of 34 ± 7%.

IV. Discussion

The larger surface iodide concentration of HI compared to NaI and KI can be rationalized by considering the electrostatic interactions occurring in the interfacial region. For salts comprising a highly polarizable anion and an unpolarizable cation (e.g., NaI), the anions are enhanced at the interface, which, in turn, electrostatically attracts the cations toward the interface. From Newton's Third Law, the cations then impose a bulk-directed force on the anions, drawing them away from the surface and thereby limiting their ultimate surface concentra-tion. The surface concentrations of anions and the cations are thus strongly correlated, creating a neutral interface in order to satisfy long range charge neutrality. The much larger surface iodide concentration found for HI compared to both NaI and
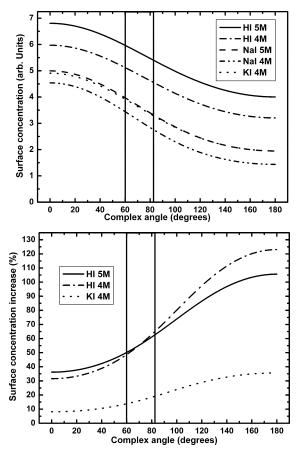
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Figure 5. Surface concentration of iodide. Panel a shows the magnitude of the iodide susceptibility, in units of the normalized SHG electric field, for an arbitrary complex angle. The magnitude of the iodide susceptibility, as derived using eq 4, is proportional to the surface concentration. The black vertical lines enclose the range of the complex angle at 200 nm as shown in Figure 6. Panel b shows the surface concentration increase of iodide for HI and KI solutions compared to a NaI solution at same bulk concentration, calculated for an arbitrary angle of the complex susceptibility of iodide. The solid line compares solutions at 5 M and the dash dotted and dotted lines at 4 M. The vertical lines enclose the range of the complex angle at 200 nm as shown in Figure 6. Within this range the surface increase of HI compared to NaI is 55 ± 10% where as KI is 16 ± 4%.

KI implies that the hydronium cations must be less strongly repelled from the surface than are sodium or potassium cations, and considering the magnitude of the difference, hydronium could well be positively adsorbed to the outermost molecular layer at the water surface. This picture thus supports the recent theoretical predictions.[15−17] The mechanism that attracts the hydronium cation to the surface is quite different than that operating for anions. Ordinary water molecules are capable of forming four hydrogen bonds (two acceptor and two donor bonds), whereas the hydronium cation is only able to form three hydrogen bonds due to the less negative charge on the oxygen.[16,17] The hydronium cation can, in this picture, be viewed as a defect, disrupting the hydrogen bonding network in the bulk, and, like defects in solid state, it is expelled to the surface where the reduced coordination number is more easily accommodated.[16] A sketch of the proposed hydrogen bonding network around water and hydronium, is shown in Figure 7. While this classical picture captures the essential chemical behavior, one should keep in mind, however, that the hydronium ion can quantum mechanically rearrange to other forms.

An enhanced surface concentration of hydronium ions could have a significant and general influence on the chemical and
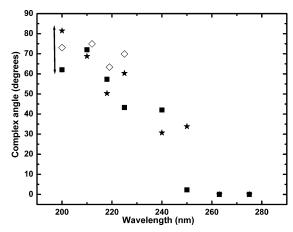

Figure 6. Complex angle of the iodide susceptibility. The concentration dependence of the total SHG intensity can be fit to a combination of Equation 2 and 3, allowing the surface concentration of iodide to change with bulk concentration. From the fit, the real and complex part of the iodide susceptibility, at the given wavelength, is obtained and the complex phase derived. The solid squares are the complex angles obtained for NaI, solid stars for KI, and the open diamonds for HI. The intensity comparisons are made at 200 nm, where the complex angle of iodide is in the range 60−83°.
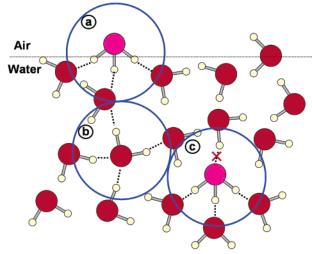

Figure 7. Surface hydrogen bonding network predicted by Voth and co-workers.[16] The blue circles show characteristic hydrogen bonding environments of water and hydronium. Circle b shows the hydrogen bonding network around a water molecule in the bulk solution capable of forming four hydrogen bonds (two donor and two acceptor). Due to the reduced negative charge on the oxygen, the hydronium cation is capable of forming only three strong hydrogen bonds (all donor), as shown in circle c.[16,17] This disrupts the hydrogen bonding network in the bulk and the hydronium cation migrates to the surface, where the lower coordination number is more easily accommodated (circle a).

physical properties of aqueous surfaces. For example, many chemical reactions are pH dependent and could thus occur more easily or more rapidly at the liquid surface than in bulk. This may have important implications for atmospheric processes involving aerosols and ocean surfaces.[7−9] The interesting Jones-Ray effect could be a direct result of surface H_3O^+ ions, which could subsequently bind anions. However, this would contradict the currently observed reduced Jones-Ray effect for the hydriodic acid unless other effects, such as saturation or a larger water autoionization, dominate the surface properties of acidic solutions. The recent continuum surface models by Karraker and Radke[5] and Manciu and Ruckenstein[6] can reproduce the Jones-Ray effect by postulating an initial surface layer of OH^- ions, which are replaced by other anions when a salt is added to water.

The surface hydroxide layer could then be neutralized by the surface protons and reduce the Jones-Ray effect. In any case, it is clearly of much interest to further investigate the surface properties of acidic electrolyte solutions.

V. Conclusion

Using the surface specific technique of SHG we have directly measured the surface concentration of iodide of HI, KI, and NaI solutions. By comparing solutions at the same bulk concentration we find the surface iodide concentration of HI solutions is $55 \pm 10\%$ and $34 \pm 7\%$ larger than NaI and KI, respectively, as a lower bound. This enhancement of the surface iodide concentration for HI is indicative of an enhanced hydronium concentration, as predicted by recent theoretical calculations.[15-17]

The hydronium ion exhibits other unique properties in aqueous systems. As the "water cation" it takes a far more profound role in the hydrogen bonding network and its dynamics than do simple cations. This manifests itself in the high proton diffusion rate governed by the Grotthus mechanism or proton hopping.[27,28] Due to the quantum mechanical nature of the solvated proton, it is difficult to model theoretically, as evidenced by the large differences in the classical simulation of Dang[15] and Jungwirth[17] and the quantum mechanical simulation by Voth.[16] Detailed microscopic experiments, such as presented here, are needed to test and elaborate currently evolving theoretical models of the solvated proton.

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