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# Hydronium and Hydroxide at the Air–Water Interface with a Continuum Solvent Model

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## Abstract

The distribution of hydronium and hydroxide ions at the air–water interface has been a problem of much interest in recent years. Here we explore what insights can be gained from a continuum solvent model. We extend our model of ionic solvation free energies and surface interaction free energies to include hydronium and hydroxide. The hydronium cation is attracted to the air–water interface, whereas the hydroxide anion is repelled. If the cavity size parameters required by the model are adjusted to reproduce solvation energies, quantitative agreement with experimental surface tensions is achieved. To the best of our knowledge, this is the most accurate theoretical prediction of this property so far. The results indicate that even if ‘water structure’ is important, its effects can be captured with a relatively simple model. They also contradict the inference from electrophoresis that there is strong hydroxide enhancement at the air–water interface.

*Keywords:* Implicit Solvent, Surface Tensions, Adsorption, Aqueous, Ion–Surface, pH

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## 1. Introduction

Any improvement in our understanding of the properties of the hydronium and hydroxide ions in water represents important progress because of the central role they play in chemistry. An explicit example that concerns us is the distribution of hydronium and hydroxide at the air–water interface. A problem that has received renewed attention lately,[1, 2, 3, 4] and reasonably so, as the air–water interface plays a central role in a range of chemical and physical processes. In addition, the air–water interface serves as a relatively simple case against which to test models of ion–surface interactions. These models can then be used to better understand the interaction between ions and more complex surfaces.[5]

This is currently a contentious topic. The long known apparent strong hydroxide enhancement has been put forward as the reason behind unexplained phenomena such as electrophoretic mobility of bubbles and oil droplets,[6, 2] thin film disjoining pressure,[7] and surface relaxation of water.[8] Although appealing in its simplicity, theoretical and spectroscopic techniques have found little evidence of this enhancement.[9, 1, 4] A number of reviews provide a summary of this debate and the research on this topic.[9, 1, 2, 10, 3, 11, 12, 13, 4]

Classical molecular dynamics (MD) simulation of these properties is highly sensitive to the parameters chosen.[14] This means it is difficult to reach any firm conclusions or to make quantitative predictions from MD. *Ab initio* molecular dynamics (AIMD) has shown promise,[15, 16, 17, 18, 14] but it has not yet been able to resolve this problem conclusively due to high computational demands. Comparison of MD simulation with experimental surface tensions increments has generally shown relatively poor agreement[19] and is often neglected in these studies.

On the other hand, continuum solvent models, which are the alternative to explicit solvent simulation, have previously almost always required ion–specific parameters that are adjusted to reproduce the very experiments that they are trying to explain. This makes it very difficult to test their physical accuracy and limits their predictive power. For instance, the model of Levin et al.[20] is a sophisticated alternative continuum solvent model of these properties. However, to reproduce acidic surface tension increments this model has to assume a square well interaction potential of the ion with the air–water interface with the well depth adjusted to reproduce experimental surface tensions.[21] This means that the critical question of what causes this attraction has not been answered. Other promising continuum solvent models of ionic interaction with the air–water interface have recently been developed[22, 23, 24] but have not been applied to the hydronium and hydroxide ions.

In a series of recent papers, we have developed a continuum solvent model that explains a range of properties of

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alkali halide solutions quantitatively.[25, 26, 27, 28, 29, 30] An essential point of departure is the inclusion of quantitative *ab initio* ionic dispersion interactions omitted from other theories, along with cavity energies.

For interactions of the alkali halide ions with the air–water interface the model shows agreement with the surface tension increments of these salts.[29] It also reproduces the known enhancement of the iodide anion at the air–water interface. The model calculates the solvation free energy of the ions as a function of distance from the air–water interface. It is therefore essentially a generalization the ionic solvation model developed in Ref. 26 to include the effect of the interface. Crucially the model uses the continuum solvent approximation, so it has low computational demand and can provide clear physical insight into the source of surface tension increments. The model does not require that parameters be explicitly adjusted to make it match experimental surface tensions. The obvious next challenge is to further test the model by generalizing it to new solutes and surfaces in order to establish how well the model accurately represents the underlying physics.

Hydronium and hydroxide are perfect candidates. They are arguably the most important ions in water and are anisotropic; hence they differ significantly from the alkali halide ions and are a good test of the model. Here we test the hypothesis that our continuum solvent model of electrolyte solutions can reproduce experimental solvation energies and surface interactions of these ions. Moreover, we explore whether agreement with experimental surface tensions increments can be improved by adjusting the ionic cavity radii of hydronium and hydroxide to match experimental solvation energies precisely. This is similar to classical MD, where the Lennard Jones parameters are adjusted to reproduce experimental solvation energies and then used to calculate surface interactions.[31]

## 2. Theory

Our solvation and surface interaction models are developed in detail in Ref. 26 and 29. A brief overview is provided here. We shall treat the proton as being purely in the form of the hydronium cation. This seems a reasonable assumption as there is spectroscopic evidence indicating that it is primarily in this form at the interface.[32]

### 2.1. Solvation Energies

The solvation model[26] separates the solvation free energy into three contributions, electrostatic, dispersion and cavity formation energies:

$$G_S = G_{ES} + G_{disp} + G_{cav} \quad (1)$$

#### 2.1.1. Electrostatic

The electrostatic solvation energy in our previous model[26] was taken to be the Born energy for a spherical monatomic solute. Here to calculate the electrostatic solvation free energy for the hydronium and hydroxide ions we use COSMO.[33,

34] This calculates the energy change on solvating the ion in a dielectric continuum with the dielectric constant of water, including the contributions from the anisotropic charge distribution and any electrostatic polarization effects. It gives the same value that the Born equation does for a monatomic ion. The size of the cavity in the dielectric medium ( $R_{cav}$ ) is crucial to calculate this contribution and is determined below.

#### 2.1.2. Dispersion

The model of the dispersion solvation energy described in Ref. 25 and used in Ref. 26 requires that a damping ( $b$ ) parameter be determined for the ion to account for the ion–water wave–function overlap. These parameters are known for the noble gas atoms and a simple interpolation as a function of the crystal size was used to determine these parameters for the isoelectronic alkali-halide ions.[25] It is not at all clear that it is reasonable to apply this interpolation to determine the damping parameters for the polyatomic hydroxide and hydronium ions, which have a significantly more complex electronic structure. If we did apply such an interpolation we would conclude that hydroxide has a very similar  $b$  parameter to fluoride, as it has a similar crystal radius to fluoride.[35] But the orientationally averaged polarizability of hydroxide is significantly larger than that of fluoride. As a result the model would predict that hydroxide would have a very large dispersion solvation energy, which disagrees with *ab initio* calculation.

We therefore use an alternative method of calculating the dispersion contribution. We calculate the dispersion interaction of an ion–water dimer using Symmetry Adapted Perturbation Theory with Density Functional Theory (DFT-SAPT) and multiply it by the coordination number of the ion. The ion–water separation is taken to be  $R_S$  where this is determined by the distance from the ion to the first peak in the ion–oxygen radial distribution function.

$$G_{disp} = N_c U_{disp} \quad (2)$$

where  $U_{disp} = E_{disp}^{(2)} + E_{exch-disp}^{(2)}$ . [36] We have previously shown[28] that this method and the method of Ref. 25 agree well with each other for the monatomic and monovalent ions. From AIMD[14] the coordination number ( $N_c$ ) of hydroxide is 4.6 and for hydronium is 3.1.

#### 2.1.3. Cavity

For the cavity formation energy we multiply the surface area by the surface tension of the bulk air–water interface.

$$G_{disp} = 4\pi\sigma R_S^2 \quad (3)$$

where  $\sigma = 0.178 k_B T \text{ \AA}^{-2}$ . Although this ansatz could be disputed due to the microscopic size of the cavity, we have provided a justification for it in Ref. 26. Essentially the argument is that the reduction in surface tension around small hydrophobic cavities does not occur for ions as the water molecules at the cavity surface are constrained by

the electric field of the ion, similarly to their constrained orientation at the bulk air-water interface. This means that the hydrogen bonded network, a cause of this lower surface tension will not form. The ultimate justification however is the good experimental agreement with ionic solvation free energies.

## 2.2. Surface Interaction

As the ion approaches the air-water interface all three of the contributions to the solvation energy change and contribute to the interaction free energy of the ion with the air-water interface. There are also additional contributions that arise from the presence of the interface. We assume that these contributions are additive:

$$G(z, \theta, \phi) = \Delta G_{\text{ES}}(z, \theta, \phi) + \Delta G_{\text{disp}}(z) + \Delta G_{\text{cav}}(z) + \Delta G_{\text{int}}(z) \quad (4)$$

We describe how each of these contributions is calculated in the following sections.

### 2.2.1. Cavity/Surface Area Contributions

There is a change of surface area of the cavity as the ion crosses the air-water interface. This is given by the following expression:

$$\Delta A_{\text{cav}}(z) = \begin{cases} -2\pi R_{\text{S}} (R_{\text{S}} - z + R_{\text{adj}}) & z < R_{\text{S}} + R_{\text{adj}} \\ 0 & z \geq R_{\text{S}} + R_{\text{adj}} \end{cases} \quad (5)$$

where  $R_{\text{adj}} = 0.84 \text{ \AA}$ , which gives the difference between  $R_{\text{S}}$  and  $R_{\text{cav}}$ . The interaction free energy associated with this area change is given by:

$$\Delta G_{\text{cav}}(z) = \sigma \Delta A_{\text{cav}}(z) \quad (6)$$

There is also an additional contribution from the change in surface area of the air-water interface,[37] this does not contribute to the solvation energy but does give the following contribution to the interaction free energy:

$$\Delta G_{\text{int}}(z) = \begin{cases} -\pi\sigma (R_{\text{S}}^2 - (z - R_{\text{adj}})^2) & z < R_{\text{S}} + R_{\text{adj}} \\ 0 & z \geq R_{\text{S}} + R_{\text{adj}} \end{cases} \quad (7)$$

### 2.2.2. Electrostatic contribution

The electrostatic contribution can be broken up into three separate terms.

$$\Delta G_{\text{ES}}(z, \theta, \phi) = G_{\text{image}}(z, \rho) + G_{\text{SP}}(z) + G_{\text{COSMO}}(z, \theta, \phi) \quad (8)$$

#### Image Charge Contribution:

The image charge contribution gives the repulsion of the ion from the air-water interface at large separations where the solvation layer does not overlap with the interface. This contribution becomes screened by the background electrolyte as concentration increases. It is given by:[38]

$$G_{\text{image}}(z, \rho) = \begin{cases} \frac{1}{4\pi\epsilon_0\epsilon_r} \frac{e^2}{4z} \exp^{-2\kappa z} & z > R_{\text{S}} + R_{\text{adj}} \\ 0 & z \leq R_{\text{S}} + R_{\text{adj}} \end{cases} \quad (9)$$

where  $\kappa = \frac{\sqrt{\rho}}{3.04}$  is the inverse Debye length in  $\text{\AA}^{-1}$  and  $\rho$  has units of  $\text{mol L}^{-1}$ .

#### Surface Potential Contribution:

There is a contribution to the solvation energy from the surface potential of the air-water interface. This contribution was not included in the solvation energy as we compared with experimental estimates of the intrinsic solvation energy. This potential will however contribute to the distribution of ions at the interface and it is therefore necessary to include it. There is significant debate about what the size of this contribution is, but we use a value of  $\phi = +0.13\text{V}$ , consistent with Ref. 29 and Ref. 39. We assume the following functional form for this contribution:

$$G_{\text{SP}}(z) = eq\phi \frac{\Delta A_{\text{cav}}(z)}{2\Delta A_{\text{cav}}(0)} \quad (10)$$

$A_{\text{cav}}$  is defined above, this function means that at  $z = 0$  half of the surface potential is felt by the ion.

#### COSMO Contribution:

Finally as the ion crosses the interface we need to calculate how the Born solvation energy changes. We can use COSMO to do this if we allow our ion to gradually cross a flat dielectric interface and calculate how the total energy changes. We can create an effectively flat dielectric interface in COSMO by creating a dummy atom centered in a very large cavity. The  $G_{\text{COSMO}}$  term can then be calculated numerically. This amounts essentially to the change in electrostatic solvation energy of the ion as it crosses the interface.

### 2.2.3. Dispersion Energy Contribution

For the dispersion contribution we use the expression:

$$\Delta G_{\text{disp}}(z) = G_{\text{disp}} \frac{\Delta A_{\text{cav}}(z)}{(4\pi R_{\text{S}}^2)} \quad (11)$$

where  $G_{\text{disp}}$  is given above (Eq. 3).

### 2.2.4. Additional Contributions

A number of additional contributions to the interaction of an ion with the air-water interface have been hypothesized in the literature. We do not include these explicitly in this model but discuss them briefly here.

*Capillary Wave Suppression* Otten et al.[37] argue that changes in the configurational entropy of local water molecules cannot explain the experimentally observed entropic repulsion of ions from the air-water interface, and they provide simulation evidence that ions present at the interface can suppress capillary wave fluctuations, which would explain this observation. This is an interesting hypothesis, but including or assessing the importance of this effect is beyond the scope of the relatively simple model outlined in this paper.

*Fluctuation-Suppression Force* Gray-Weale and Beattie[40] argue that a postulated ‘‘fluctuation suppression’’ force strongly attracts hydroxide to the surface. We do not explicitly include this term for several reasons: Firstly,

any model with such a large attraction cannot be reconciled with surface tension data. This is discussed further below. Secondly, this force corresponds physically to the energy gained when an ion displaces water molecules from the energetically unfavorable interfacial region and returns them to bulk. This contribution is already calculated consistently in this model with the  $G_{\text{int}}$  term. Thirdly, this force is calculated by assuming dipoles in water interact with the Keesom force:

$$G(r) = -\frac{\langle |\mu'|^2 \rangle \langle |\mu|^2 \rangle}{3k_{\text{B}}Tr^6} \quad (12)$$

(See supplementary information of Ref. 40.) This force gives the thermally averaged interaction of two dipoles in vacuum.[41] The use of this expression for dipoles in condensed phase is questionable: firstly it is not clear why the factor of  $1/\epsilon_r$  does not need to be included to account for the dielectric response of the intervening water molecules, which will damp this interaction. Secondly, the pair-wise additive approximation breaks down for fixed dipole interactions in water where many-body contributions dominate. (Indeed the Keesom interaction in a condensed phase is proportional to temperature not its inverse.)[42] Finally, the dielectric decrement is used to estimate  $\langle |\mu'|^2 \rangle$ . This interpretation of the dielectric decrement is debatable[43] and there is significant experimental uncertainty associated with this property, which makes it difficult to assess how large this contribution is for various ions including hydronium.

*Water Structure* It is often argued that the explicit structuring of water molecules around ions will play a role in determining their free energies of interactions. This is examined further in the discussion section below, but obviously it is not possible to take these effects into account explicitly while preserving the continuum solvent approximation.

### 2.3. Statistical Angular Averaging

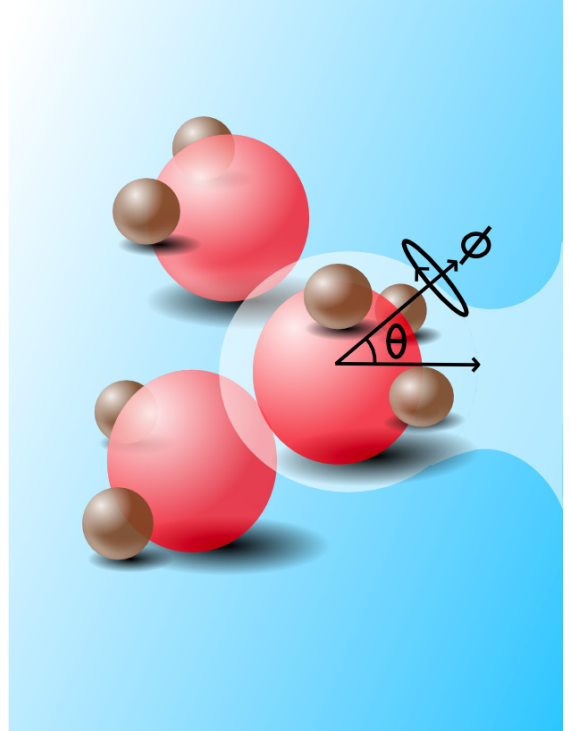
We can specify the orientation of the hydroxide anion with a single angle  $\theta$ . For the hydronium cation we need two angles  $\theta$  and  $\phi$ . The definition of these angles is given in Figure 1. The free energy of an ion in water is given by the Widom particle insertion formula:[44]

$$G(z) = -k_{\text{B}}T \ln \left\langle \left\langle \exp^{-\beta U_{XS}(z, \theta, \phi)} \right\rangle \right\rangle_0 \quad (13)$$

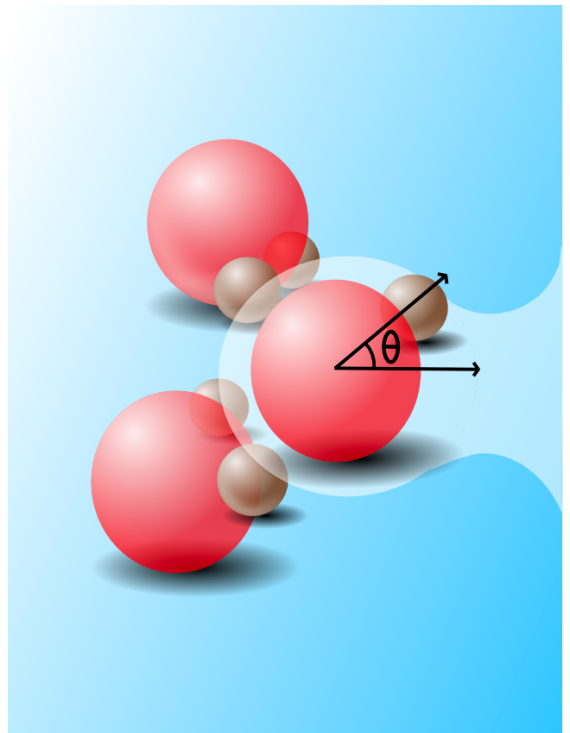
where the double brackets indicates averaging over both solute orientations and solvent configurations.

The average over solvent configurations can be treated by recognizing the fact that  $\left\langle \exp^{-\beta U_{XS}(z, \theta, \phi)} \right\rangle_0 = \exp^{-\beta G(z, \theta, \phi)}$ , where  $G(z, \theta, \phi)$  is simply the solvation energy of an ion at the point:  $(z, \theta, \phi)$ . We can calculate this using the method outlined above. The average interaction free energy of the ion with the surface can then be given by:

$$G(z) = -k_{\text{B}}T \ln \left( \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \exp^{-\beta G(z, \theta, \phi)} / (4\pi) \right) \quad (14)$$



(a) Hydronium



(b) Hydroxide

Figure 1: Hydronium and hydroxide at the air–water interface. Their angular positions are captured by the angles  $\theta$  and  $\phi$ .

For hydroxide there is no  $\phi$  dependence. For hydronium we can use the fact that  $\int_0^{2\pi} d\phi = 6 \int_0^{\pi/3} d\phi$  due to rotational symmetry. This reduces the number of free energy calculations required, and the average becomes:

$$G(z) = -k_B T \ln \left( \int_0^{\pi/3} d\phi \int_0^\pi d\theta \sin \theta \exp^{-\beta G(z, \theta, \phi)} / (2\pi/3) \right) \quad (15)$$

#### 2.4. Calculation Details

The TURBOMOLE package (v6.4)[45, 46] was used with an implementation of COSMO[33, 34]. Here we have used the aug-cc-pVQZ[47] basis sets for oxygen and hydrogen atoms. The calculations were performed at the Hartree-Fock level using the DSCF program[48] then at the MP2 level using the RIMP2 program.[49, 50, 51] The NPPA and NSPA parameters of the COSMO program were increased to 12962 and 7292 respectively. The dummy atom was placed in a cavity with a radius of 50 Å. The RSOLV parameter in COSMO was set to 0.84 Å. The epsilon parameter was set to 116.95. The calculations were performed without the overlapping charge correction and with an open cavity. These parameters are the same as in Ref. 29 where justification is provided.

The ionic solvation energy was calculated by taking the difference between the total energy of the ion in vacuum and the total energy of the ion in a spherical cavity in a dielectric medium calculated with COSMO. The geometry of the ion was optimized for both of these energy calculations separately. For the calculation of the ion-surface interaction energy the ion’s geometry was fixed to be the same as for the ion in the spherical cavity in bulk. The jobex program[48, 49, 50] was used to determine the optimized ionic geometry. The DFT-SAPT[36] calculations were performed using the PBE0 functional[52] on ion-water dimers using the MOLPRO 2012.1 software package.[53, 54]

#### 2.5. Solute Sizes

To determine the  $R_S$  parameter for the hydronium ion we use the values given by Ohtaki and Radnai in Ref. 55, determined from scattering data, as well as the value determined by Baer et al.[14] on the basis of AIMD. This is the only simulation estimate used as it represents the state of the art, including the dispersion corrections, which have been shown to be crucially important in reproducing the correct density of water and hence will likely be important in determining this parameter. This results in a value of  $R_S = 2.72 \pm 0.05$  Å. The size parameters for the hydroxide anion are significantly harder to determine as there seem to be no experimental estimates of this quantity.[55, 56] We therefore use the value of  $R_S = 2.55$  Å determined from AIMD[14]. We can use the expression  $R_{cav} = R_S - R_{adj}$  to determine the cavity sizes for these solutes, where  $R_{adj} = 0.84$  Å. This method of defining ionic radii is exactly the same as the one used previously in our continuum solvent model of ionic solvation energies.[25].

The resulting solvation energies and surface interactions are quite sensitive to the size values of the ions, and there is also significant uncertainty associated with these sizes. We therefore adjust these cavity size parameters to the nearest 0.01 Å to accurately reproduce the solvation energies. We can then use these adjusted cavity sizes to calculate surface interactions. This is an important test of the model. It means that any failure of the model to correctly reproduce solvation energies, either from incorrect cavity radii or from the approximations used, are corrected for and the quality of the surface interaction model alone can be tested. Obviously improving the physical accuracy of one aspect of the model should result in increased accuracy of other aspects. This same procedure was carried out in Ref. 29. The resulting adjusted cavity size parameters are referred to as  $R_{cavA}$ , and there is a corresponding shift in the  $R_S$  parameters:  $R_{SA} = R_{cavA} + 0.84$ . We also adjust the dispersion interactions to remove the very small remaining error after adjusting the cavity size to the nearest 0.01 Å.

##### 2.5.1. Experimental data

The solvation energy of the hydronium cation is  $-189.2 k_B T$ , at  $T = 293.15K$ . The solvation energy of the hydroxide anion is  $-179.4 k_B T$ . [57] These values are consistent with Tissandier’s value for the intrinsic hydrogen ion solvation free energy. This is the same choice of the intrinsic solvation energy we used in Ref. 26 where we justified this value. It is also consistent with the values recommended by Hünenberger and Reif on the basis of a comprehensive review of the literature.

The surface tension increments collated by Marcus[58] were used to determine the experimental surface excesses from the Gibbs adsorption isotherm.  $\Gamma_{exp1}$  is determined from the average of the values reported in the literature.  $\Gamma_{exp2}$  is determined by first assuming that the surface tension increments for a salt can be split into additive contributions from the cation and anion, which is a reasonable assumption at low concentration.

We do not compare with experimental surface potential changes since Slavchov et al.[59] have shown that the presence of ions significantly alters the intrinsic surface potential of water, meaning that the potential created by the ionic distributions is not the only contribution to  $\Delta\chi$ . This means that experimental agreement cannot be expected.

## 3. Results and Discussions

### 3.1. Solvation Free energies

Table 1 gives the adjusted and unadjusted cavity and  $R_S$  parameters for the hydronium and hydroxide ions. Interestingly adjusting the radii so that hydronium and hydroxide have the same radii gives the best agreement with experimental solvation energies. This common value is  $\approx 0.2$  Å smaller than the corresponding parameter for a water molecule.[60]

Table 2: Solvation Energies of ions with  $R_{\text{cav}}$  values.

Ion	$\beta G_{\text{exp}}$	$\beta G_{\text{the}}$	$\beta G_{\text{ES}}$	$(\beta G_{\text{Born}})$	$\beta G_{\text{cav}}$	$\beta G_{\text{disp}}$
$\text{H}_3\text{O}^+$	-189.2 <sup>a</sup>	-167.5	-175.0	-149.7	16.5	-9.01
$\text{OH}^-$	-179.4 <sup>a</sup>	-194.9	-159.1	-164.5	14.5	-50.3

<sup>a</sup> From Ref. 57

Table 1: Values of the ionic size parameters in water.

Ion	$R_{\text{cav}}(\text{\AA})$	$R_{\text{cavA}}(\text{\AA})$	$R_{\text{S}}(\text{\AA})$	$R_{\text{SA}}(\text{\AA})$
$\text{H}_3\text{O}^+$	1.88 <sup>a</sup>	1.79 <sup>b</sup>	2.72 <sup>c</sup>	2.63 <sup>e</sup>
$\text{OH}^-$	1.71 <sup>a</sup>	1.79 <sup>b</sup>	2.55 <sup>d</sup>	2.63 <sup>e</sup>

<sup>a</sup> From  $R_{\text{cav}} = R_{\text{S}} - 0.84 \text{ \AA}$     <sup>b</sup> From  $R_{\text{cavA}} = R_{\text{SA}} - 0.84 \text{ \AA}$ <sup>c</sup> Determined from average of values from Ref. 55 and 14<sup>d</sup> Determined from Ref. 14    <sup>e</sup> Determined by adjusting to reproduce experimental solvation energies.Table 3: Solvation Energies of ions with  $R_{\text{cavA}}$  values.

Ion	$\beta G_{\text{exp}}$	$\beta G_{\text{theA}}$	$\beta G_{\text{ESA}}$	$\beta G_{\text{cavA}}$	$\beta G_{\text{dispA}}$
$\text{H}_3\text{O}^+$	-189.2 <sup>a</sup>	-189.2	-192.6	15.5	-12.0
$\text{OH}^-$	-179.4 <sup>a</sup>	-179.4	-151.1	15.5	-43.7

<sup>a</sup> From Ref. 57

Tables 2 and 3 give the solvation energy contributions resulting from these size values. With  $R_{\text{cavA}}$  hydronium has a significantly more negative solvation free energy than hydroxide even though they are the same size. This is the opposite of what is normally observed for ions: anions are normally more strongly solvated than cations of similar size. This effect is commonly attributed to orientational properties of the water molecules. However, we have shown[26, 28] that a plausible explanation is the larger dispersion interaction of anions with the surrounding water. This mechanism is important for hydroxide and hydronium, where we see that the dispersion solvation energy of hydroxide is significantly more negative than that of hydronium. However, this effect is overwhelmed by a much larger electrostatic solvation energy for the hydronium cation. This is caused by the fact that these ions are not point charges in the center of a cavity, but have some charge distribution inside the cavity. Indeed Table 2 shows that the Born equation fails to accurately calculate the solvation energy of these ions compared with a COSMO calculation. In contrast, for spherical ions such as fluoride the Born equation is very accurate. This breakdown of the Born equation is much more dramatic for the hydronium cation than it is for the hydroxide anion. This is likely because the positive charge of the hydronium ion is concentrated around the hydrogen atoms. These are significantly closer to the water molecules than the central oxygen atom and therefore the electrostatic solvation energy is significantly larger. It is less clear why the Born

Table 4: Solvation Energies of Fluoride with adjusted ion size ( $R_{\text{cavA}} = 1.84 \text{ \AA}$ ).

Ion	$\beta G_{\text{exp}}$	$\beta G_{\text{theA}}$	$\beta G_{\text{ESA}}$	$\beta G_{\text{cavA}}$	$\beta G_{\text{dispA}}$
$\text{F}^-$	-179.2 <sup>a</sup>	-178.1	-152.9	16.1	-41.3

<sup>a</sup> From Ref. 61

equation gives an electrostatic energy that is too negative compared with the COSMO calculation for hydroxide.

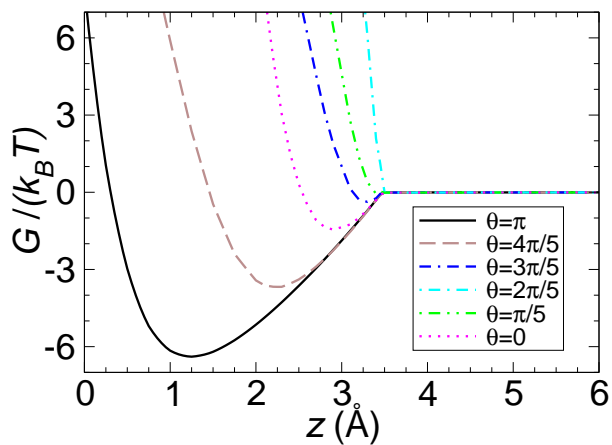
Table 4 provides the contributions to the solvation energy of the fluoride anion. We can compare this with hydroxide and see that the two anions behave almost identically. They have similar size and their dispersion and electrostatic solvation energies are the same. This results in very similar total solvation energies, which explains why they have such similar experimental solvation free energies. This has significant implications for the importance of water's structural properties as discussed below.

### 3.2. Surface Interaction Free energies

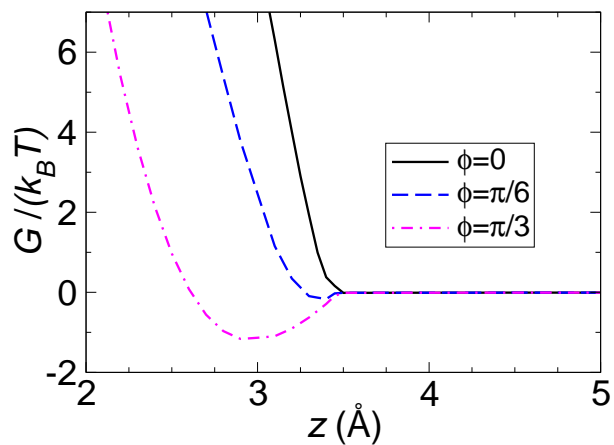
Figure 2 shows the interaction energy of a hydronium ion with the air-water interface as a function of orientation. The long range image charge coulomb repulsion is not shown as it is small and concentration dependent.

From the size and solvation energy of hydronium it would be expected to behave as a kosmotrope similar to sodium and be repelled from the interface. Figure 2a shows that with the anisotropic nature of this ion taken into account, a dramatically different picture emerges. It is clear that the energy depends dramatically on the orientation of the hydronium ion at the interface. There is a large minimum of approximately  $-6k_{\text{B}}T$  when the ion is oriented with its hydrogens pointing into bulk water ( $\theta = \pi$ ). The fact that this is the preferred orientation of the hydronium ion at the air-water interface is well established from spectroscopy and simulation.[32, 62] This is intuitive as the positive charge will be localized around the hydrogen atoms and keeping these atoms close to the surface of the water will minimize the loss of electrostatic solvation energy.

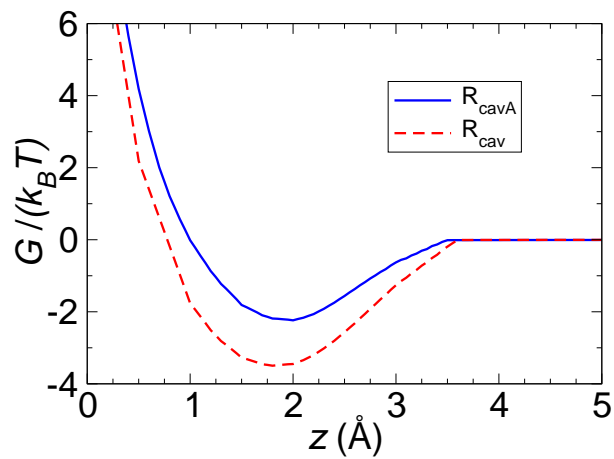
The interaction becomes strongly repulsive at  $\theta = 2\pi/5$ . This indicates that the hydrogen side of hydronium is behaving like a kosmotrope and the oxygen side behaves like a chaotrope and is enhanced at the interface. This kind of complex orientation dependent behavior of polyatomic ions has been observed in the solvation of iodate.[63]



(a)  $\theta$  dependence with  $\phi = 0$  and  $R_{\text{cavA}}$



(b)  $\phi$  dependence with  $\theta = \pi/2$  and  $R_{\text{cavA}}$



(c) Averaged interaction with  $R_{\text{cavA}}$  and  $R_{\text{cav}}$ .

Figure 2: Interactions of  $\text{H}_3\text{O}^+$  with the air–water interface.



The most repulsive potential arises with  $\theta = 2\pi/5$  and  $\phi = 0$ . This is because at this orientation one of the hydronium hydrogen atoms points directly upwards. The positive charge of the ion is centered around these hydrogen atoms and therefore removing the water from around them costs the most energy. At smaller  $z$ , i.e., closer to the interface these potentials change order, but the potential is so repulsive that it has no effect on the distribution profiles.

Using Eq. 15 we can calculate the thermally averaged potentials. These are shown in Figure. 2c. Adjusting the the cavity size from  $R_{\text{cav}}$  to  $R_{\text{cavA}}$  reduces the depth of the potential well. This is due to the larger ion–water interaction resulting from the smaller cavity. We can see that with  $R_{\text{cavA}}$  a potential well emerges of  $-2.2 k_{\text{B}}T$  at  $z = 2.0 \text{ \AA}$ .

Figure 3 shows the interaction of the hydroxide anion with the air–water interface as a function of  $\theta$ . Compared with hydronium the orientation dependence is dramatically weaker. The qualitative behavior of a large repulsion beginning at  $3.47 \text{ \AA}$  is the same for all  $\theta$ . There is however some puzzling non–monotonic angular dependence, i.e.,  $\theta = \pi/5$  shows the least repulsion whereas  $\theta = 0$  shows the most at the larger distances from the interface. Intuitively we would expect  $\theta = 0$  to be least strongly repelled as the negative charge should reside predominantly on the oxygen which should prefer to stay in bulk. Indeed  $\theta = 0$  does have the weakest repulsion below  $2.5 \text{ \AA}$ , and its large initial repulsion is presumably associated with dehydrating the hydroxides hydrogen. This unusual angular dependence does not dramatically affect the surface distributions and hence surface excess as when these interactions are thermally averaged a simple soft–sphere like repulsion results, as seen in Figure. 3b. Because there is no potential minimum, adjusting the cavity radii does not alter the potentials significantly. This resulting averaged behavior of the hydroxide anion is very similar to that observed for the the fluoride anion presented in Ref. 29.

Figure 4 breaks the interaction energies down into various contributions. We can see the primary explanation for the hydronium ion adsorption is that when  $\theta = \pi$ , the ion can begin to cross the interface without experiencing any electrostatic repulsion. This means that the two surface area terms and the surface potential contributions can overwhelm the dispersion repulsion and stabilize the ion at the interface. Hydroxide again essentially behaves identically to fluoride. The large electrostatic and dispersion repulsion overwhelms any attractive surface area terms and means that the first hydration layer cannot be removed, and the ion effectively feels a soft sphere repulsion.

Figure 5 presents the resulting ionic distribution profiles at the neat air–water interface. It shows a moderate enhancement of hydronium a depletion of hydroxide and the long range image charge repulsion, which acts on both ions.

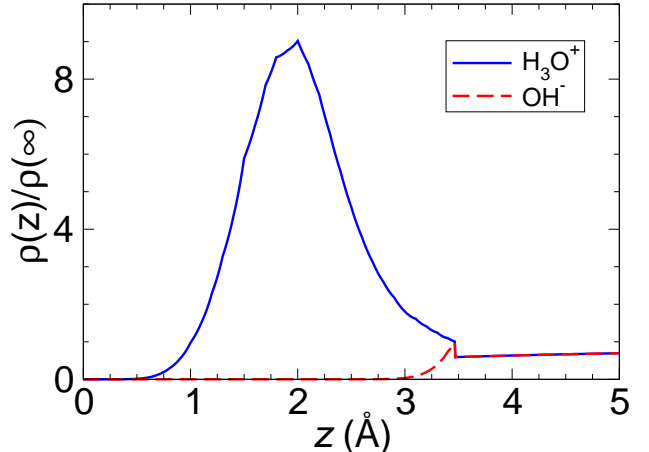


Figure 5: Densities of hydronium and hydroxide at the neat air–water interface calculated with  $R_{\text{cavA}}$ .  $\rho(\infty)$  is equal to  $10^{-7} \text{ M}$ .

### 3.3. Molecular Dynamics

As already mentioned estimates of these interactions on the basis of molecular dynamics simulation vary significantly depending on the model used[14] but many models indicate an enhancement of the hydrogen cation and a repulsion of the hydroxide anion similar to the results presented here.[64, 9, 65, 66] In particular, Lee and Tuckerman[18] use AIMD to predict a value of  $-2.2 k_{\text{B}}T$  for the minimum of the interaction potential of hydronium with the air–water interface, in excellent agreement with the value calculated here.

Notably however, our results disagree with state of the art AIMD calculations of these properties,[14] where a weak enhancement of hydroxide is observed and the interaction potential for the hydrogen ion is flat with no potential minimum. These calculations include dispersion corrections to the DFT functional and should be more accurate. This disagreement is therefore disconcerting.

One possibility is that the dispersion correction to the DFT functional used in the AIMD calculations are inadequate when applied to ions. Indeed, the Grimme correction, which Ref. 14 uses, was not parametrized for ions and does not incorporate the large change in polarizability that results from the charge on the ion, compared with the corresponding neutral atom. Table 5 presents the dispersion correction for ion–water and water–water dimers calculated with the Grimme method and the dispersion interaction energy of the same dimers calculated with DFT–SAPT. It is clear that the Grimme calculation does not capture the effect of changing the charge of the ion adequately. With DFT–SAPT the dispersion interaction becomes larger when the water molecule changes to hydroxide and become smaller when it changes to hydronium. The Grimme calculation shows the opposite trend. The fact that the Grimme correction is smaller than the DFT–SAPT calculation for the water dimer is to be ex-

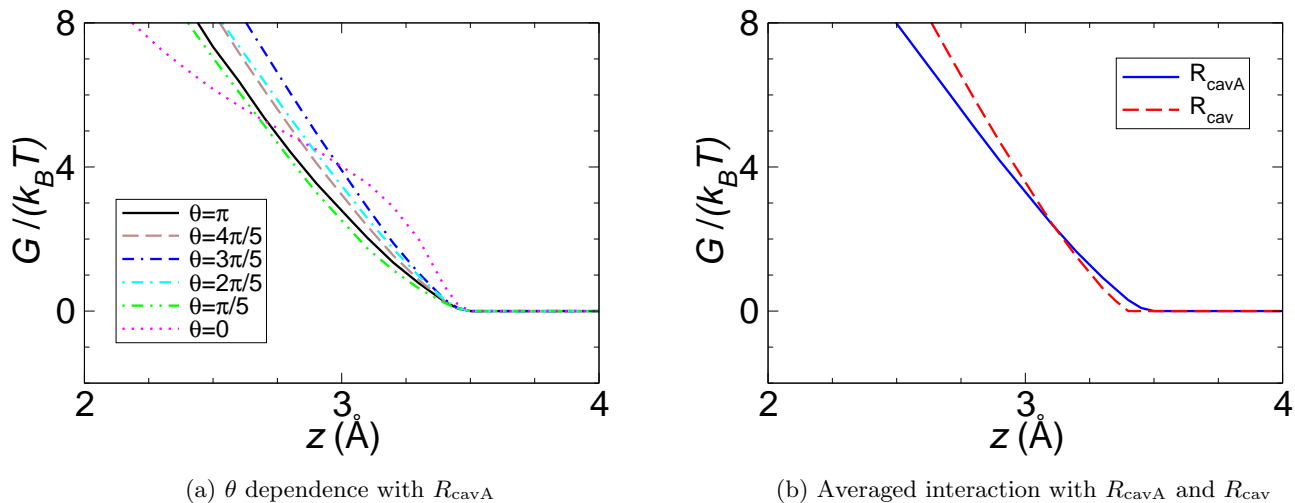


Figure 3: Interaction of  $\text{OH}^-$  with the air-water interface.

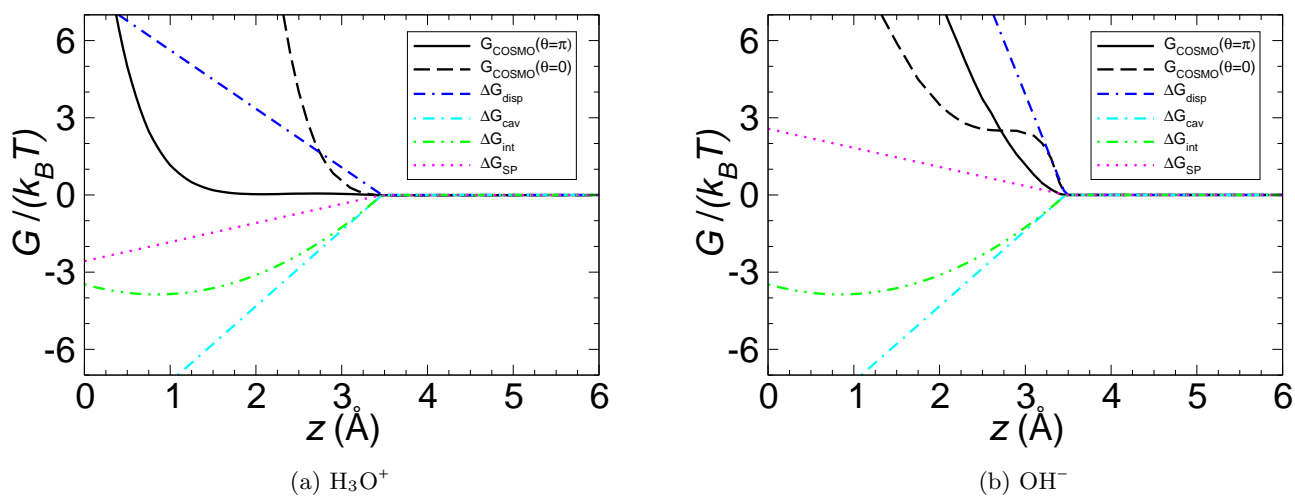


Figure 4: Contributions to the interaction of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  with the air-water interface calculated using  $R_{\text{cavA}}$ .

Table 5: Dimer dispersion interactions calculated at a separation of  $R_S$ . For the water dimer,  $R_S = 2.82 \text{ \AA}$  is used.[60] The values are in units of  $k_B T$ .

Dimer	D3 Correction <sup>a</sup>	DFT-SAPT
H <sub>2</sub> O-H <sub>2</sub> O	-2.16	-3.73
H <sub>3</sub> O <sup>+</sup> -H <sub>2</sub> O	-2.31	-2.91
OH <sup>-</sup> -H <sub>2</sub> O	-1.65	-10.94

<sup>a</sup>Using the method of Ref. 67 with the parameters for the BLYP functional.

pected. It is because the Grimme method has been specifically parametrized to correct the BLYP functional, which likely already includes a contribution from the dispersion interaction. The DFT-SAPT partitioning of energies is admittedly not incontrovertible. However, it is surely more accurate than the Grimme approach as rather than using only the atomic nuclei types and positions, it uses information from the electronic wavefunction. It is also consistent with independent theoretical calculations of this quantity.[28, 68]

In addition, the total binding energy of both the hydronium salts water dimer and the hydroxide-water dimer calculated with BLYP alone is too negative, adding the dispersion correction then makes this worse. This again implies that BLYP-D3 is inadequate for calculating ion-water interactions. Ionic free energies in solution obviously depend sensitively on the ion-water interaction energy and so this may be the source of significant error.

### 3.4. Spectroscopy

This enhancement of hydronium is consistent with second harmonic generation (SHG)[69, 1] and sum-frequency generation (SFG)[62, 70, 71, 32] experiments. The repulsion of hydroxide from the air-water interface is also generally consistent with these experiments, although Ref. 32 and Ref.72 use SFG and SHG respectively to argue for the presence of hydroxide at the air-water interface, at what concentration though is not clear. On the other hand pH dependent SFG[73] and photoelectron spectroscopy (PES)[74] have been used to argue for the absence of hydroxide at the interface. The ambiguity of the probe length of these experimental methods prevents quantitative comparison.

Electrospray mass spectrometry also provides evidence for an enhancement of hydronium[75] and a depletion of hydroxide[76] at the air-water interface.

### 3.5. Surface Tensions

The key experimental measurement to quantitatively test the ion interaction potentials are the surface excesses. These can be calculated from the experimental surface tension values given in Ref 58 using the Gibbs adsorption isotherm:

$$\Gamma = \frac{-\rho\beta}{N_A} \left( \frac{d\gamma}{d\rho} \right)_T \quad (16)$$

$\Gamma$  is the surface excess and is given by:

$$\Gamma = \sum_i \int_0^\infty dz (\rho_i(z) - \rho_i(\infty)) + \int_{-\infty}^0 dz \rho_i(z) \quad (17)$$

where the sum is over all ions present in the system.  $\rho_i(z)$  can be calculated theoretically using:

$$\rho_i(z) = \rho_i(\infty) \exp[-\beta(G_i(z) + q_i\phi(z))] \quad (18)$$

where  $G_i(z)$  is the interaction free energy of the ion with the interface described above and the potential  $\phi$  is determined by solving the Poisson-Boltzmann equation:

$$-\epsilon_r \epsilon_o \frac{d^2 \phi(z)}{dz^2} = \sum_i q_i \rho_i(z) \quad (19)$$

In order to calculate these surface excesses the interaction potentials calculated in Ref. 29 were used for the alkali halide counterions.

Table 6 compares the experimental and theoretical surface excesses of some simple acids and bases when compared with experiment. The surface excesses for all 29 salts modelled so far are presented in the appendix. If the  $R_{cavA}$  values are used, the hydroxides have the following Hofmeister ordering of their surface excesses:  $\Gamma_{LiOH} < \Gamma_{NaOH} \approx \Gamma_{KOH} \approx \Gamma_{RbOH} < \Gamma_{CsOH}$ . For the hydrogen ions the ordering is  $\Gamma_{HF} < \Gamma_{HCl} < \Gamma_{HBr} < \Gamma_{HI}$ .

A quite drastic overestimate of the enhancement of hydrogen ions at the interface results if the unadjusted cavity radii are used. This is caused by the larger interaction potential with  $R_{cav}$  shown in Figure 2c. Much better agreement is observed if the cavity radii are adjusted to reproduce experimental solvation energies. The theoretical values agree reasonably well with the experiment. We emphasize that the size parameters are adjusted to reproduce solvation energies not surface tensions, so this experimental agreement is significant. This is remarkable considering how sensitive the surface excess is to the depth of the adsorption minimum. To the best of our knowledge this is the most accurate theoretical estimate of this quantity in the literature.

The potential presented in Figure 2c for the hydronium ion is very similar to the one presented by dos Santos and Levin[21], where it was explicitly adjusted to reproduce experimental surface tensions. The good agreement with surface tensions is therefore not surprising, although it is very promising that fitting to reproduce the surface tensions was not required.

For the hydroxide salts again we see reasonable experimental agreement. The use of adjusted cavity radii here does not alter the theoretical values significantly as this simply shifts the position of the repulsive wall slightly rather than changing the depth of the interaction minimum. In addition the theoretical values are almost precisely the same as the values predicted for fluoride salts. (-7.7  $\text{\AA}$  was calculated for both NaF and KF in Ref. 29).

Table 6: Theoretical and experimental surface excesses in units of ( $\text{\AA}$ ) Theoretical values calculated at a concentration of  $\rho = 0.05$  M as in Ref. 29.

Electrolyte	$\Gamma_{\text{exp1}}/\rho(\infty)^{\text{a}}$	$\Gamma_{\text{exp2}}/\rho(\infty)^{\text{b}}$	$\Gamma_{\text{theory}}/\rho(\infty)^{\text{c}}$	$\Gamma_{\text{theoryA}}/\rho(\infty)^{\text{d}}$
HCl	$1.03 \pm 0.08$	$0.6 \pm 0.8$	13.1	0.5
HBr	$1.96 \pm 0.05$	$1.6 \pm 0.8$	13.4	1.2
NaOH	$-8.3 \pm 0.4$	$-9.2 \pm 0.8$	-7.8	-7.8
KOH	$-8.0 \pm 0.4$	$-8.8 \pm 0.8$	-7.7	-7.7

<sup>a</sup> Assuming additive contributions. <sup>b</sup> Average of the experimental values. <sup>c</sup> Calculated with  $R_{\text{cav}}$ .

<sup>d</sup> Calculated with  $R_{\text{cavA}}$ .

This was expected from the fact that their interaction potentials are very similar. This is fortuitous as hydroxide salts surface excesses are again similar to fluorides. ( $\Gamma_{\text{exp2}}/\rho(\infty) = -8.2$  and  $-7.8$  for NaF and KF. ) So any significant difference in the interaction potential would be difficult to reconcile with experiment.

As acknowledged in Ref. 14 the state of the art AIMD calculations of these properties appear to conflict with experimental surface excesses. They point to simulation evidence that indicates ion-pairing effects may play a non-negligible role in determining surface enhancements. This would mean that single-ion interaction potentials cannot on their own determine experimental surface excesses. It is certainly possible that dimers formed from  $\text{H}^+$  and an anion are adsorbing to the surface and explaining the surface excess of these acids.[77] However, as they acknowledge, spectroscopic evidence indicates otherwise for HCl at the air-water interface.[78] We would also expect to see stronger ion-pair dependence if this were occurring. We therefore believe that the model outlined here therefore provides a more satisfactory explanation.

It is also difficult to reconcile the AIMD minimum in the hydroxide interaction with surface tensions as this would require a larger concentration of ion-pairs in bulk than at the surface to be consistent with surface tensions. This would presumably result in low activity/osmotic coefficients for the hydroxide salts, but these coefficients are actually slightly higher than for the fluoride salts.[79] This indicates that there is less ion pairing than for fluoride salts and so hydroxide should be repelled from the interface just as fluoride is.

### 3.6. Implications

We remark that we have essentially taken the model of Ref. 29 and applied it to the hydronium and hydroxide ion without modification. The only complexity introduced is in dealing with the orientational dependence, but this does not require any significant new approximations or parameters. The model reproduces experimental surface excesses well, including a net surface enhancement of the hydronium ion. That behavior is qualitatively different to any of the alkali-halide ions for which the model was built. The key parameters needed are the ionic sizes, the coordination number and the surface tension. The values

used for these parameters can be independently derived, although the final justification is the good agreement with experiment, and the cavity sizes do have to be adjusted by a small amount to reproduce the surface tensions of hydronium quantitatively.

The surface interaction model was originally developed to reproduce the surface tensions and it is possible that knowledge of these values somewhat informed the subjective choices necessary in building a model. In this case however we have essentially applied the same process without modification and so the fact that the calculations agree with experiment is, to us, impressive. In addition, it is worth noting that adjusting the radii to correctly reproduce the solvation free energy improves experimental agreement with surface tension increments. The fact that improving the physical accuracy of one property improves the accuracy of this secondary property is a hopeful indication that the model is correctly capturing the underlying physics.

This good experimental agreement does provide a potential justification for neglecting the additional contributions discussed in the Theory section above. This does not however, conclusively prove that these contributions are not important, as fitting to reproduce solvation energies may have implicitly included them or a fortuitous cancellation of errors may have occurred, particularly if they are not ion specific.

#### 3.6.1. Water Structure

Explanations of the properties of hydronium and hydroxide in water frequently invoke the structural properties of water and the hydrogen bonding ability of these ions.[70, 9, 80, 14] These explanations imply that an understanding of the properties of ions in water is impossible without explicitly incorporating the orientation and position of many individual water molecules. If this is true it is unfortunate as it will mean understanding these properties is very challenging. This proposition should therefore be tested as rigorously as possible rather than simply assumed. We must be careful to avoid the problem Ball[81] identifies in regard to water structure: “Too often this becomes a mere *deus ex machina*, a kind of mantra that dispels any responsibility for more careful investigation.” An important means of testing the importance of

water structure is to build the best models we can that neglect it and see how accurate they are. This was the central motivation behind the work that has led to this paper.[82, 83] The successful prediction of the properties of the hydronium and hydroxide anion indicates that attributing the cause of these properties to water’s structural effects may not be justified. Obviously this claim depends on the interpretation of the term ‘structural,’ as the model does include information about the distribution of water molecules through the size and coordination numbers. In addition, some structural effects may be captured implicitly by the adjustment of cavity sizes to reproduce solvation energies. However, we can say that for the purpose of modelling interaction free energies of monovalent ions with an interface it seems that even if water structure is important, it can be captured relatively straightforwardly with a model that does not explicitly consider the structures formed by the surrounding water molecules.

More specifically, the unique structural properties of hydroxide are often emphasized.[84, 85, 86, 40, 80] However, what we have observed here is that hydroxide has essentially the same size and dispersion interaction energy as fluoride in water. As a result, theoretically it has almost an identical solvation energy. It also has a basically identical surface interaction and therefore an identical surface excess to fluoride. These theoretical results are consistent with experimental solvation energies and surface tension increments where hydroxide has the same solvation energy and surface tension increment as fluoride to within error. If hydroxide can have unique and unusual structural properties and yet behave essentially identically to fluoride, this necessarily implies that structural properties are not crucially important in determining these behaviors.

Obviously there will be experiments where these structural effects are important such as spectroscopic and dynamical properties and in diffusion. But there is some evidence indicating that monovalent ionic interaction free energies do not seem to depend very sensitively on water structure and hence reasonable experimental agreement can hopefully be achieved with simpler models that neglect it. Interaction free energies of ions are obviously a crucially important property in a multitude of applications and hence this is a hopeful if not exciting conclusion. In addition, the surface tension increments of non-aqueous electrolytes, such as methanol, appear to behave similarly to water.[87] This provides additional support for the notion that “water structure” is not crucial in determining these properties.

### 3.6.2. Hydroxide adsorption

The measured negative zeta potential of bubbles, oil droplets and solid particles has been interpreted in terms of a large excess of hydroxide anions at the air–water interface.[6, 2] The same mechanism has been used to explain the repulsive thin film disjoining pressure of water[7] and the surface relaxation of water.[8] Electrospray ionization mass spectrometry has also been used[88] to examine RCOOH

dissociation at the interface to find evidence that hydroxide is present. Indeed hydroxide adsorption would nicely explain these phenomena, particularly the pH dependence.

An adsorption energy of  $\approx -20 k_B T$  for the hydroxide ion at the air–water interface is required for these explanations to make sense. The fluctuation–suppression model, discussed above, was developed to explain this large attraction.[40] This hydroxide adsorption appears to contradict the positive surface tension increment of NaOH at moderate concentration. A common explanation is to assert that this adsorption force only acts at very low salt concentration. This argument has been made[2, 89] in response to evidence from molecular dynamics simulation that hydroxide is repelled from the air–water interface, because these simulations must necessarily be performed at high–concentration due to system size limitations. In contrast the calculations we have performed here are valid at the infinite dilution limit, so this criticism does not apply. Additionally there is no physically plausible mechanism and no evidence for such a large concentration dependence in the interaction potential. If anything the interaction should become less repulsive as the Debye length decreases and the image charge repulsion is screened.

In addition, surface tensions have also been measured as the  $\text{OH}^-$  concentration is increased from  $10^{-7}$  M to moderate levels.[90] No decrease in surface tensions is observed. This is inconsistent with a large hydroxide adsorption.[40, 91, 92, 93] A Poisson Boltzmann model combined with the Gibbs adsorption isotherm predicts this enhancement would cause a very large decrease in surface tension in this regime (pH 7  $\rightarrow$  10) where the zeta potential is still measurable and so the hydroxide anions must still be enhanced.

The fact that there is strong theoretical evidence to refute this supposed dramatic attraction, that spectroscopic experiments show no conclusive evidence for this massive enhancement and that surface tension measurements are essentially impossible to reconcile with such a large effect strongly indicates that there is no large adsorption of hydroxide anions to the air–water interface, and that the explanation of these properties probably lies elsewhere. The calculations presented here provide no real alternative explanations for these effects, but unexplained phenomena are hardly unusual in the area of interfacial science. For example, the presumably related Jones–Ray effect is still not satisfactorily explained[94] nor are many similar dynamic behaviors such as the astonishing systematic ion–pair dependent bubble coalescence inhibition phenomenon,[95] which remains inexplicable in terms of conventional notions of equilibrium colloid science.[96] The failure of Stokes law for the rise of bubbles in a column when bubbles are beyond a certain size is another simple example of the complexity of this type of measurement.[97]

Contamination is obviously a devilish problem for measurements involving interfacial systems and has been put forward as a potential explanation[98, 99, 100] for the zeta potential measurements. It is commonly argued that it

is too implausible for this effect to arise from the presence of contaminants due to the reproducibility of the result.[89, 11, 101] Indeed, it would be surprising if contaminants are the explanation, but similarly such a large hydroxide adsorption would be equally surprising given the above arguments. In addition, hydrophobic interfaces with no zeta potential have been observed.[102]

A promising explanation comes from Joly et al.[100], who calculate the zeta potential of a hydrophobic interface as the contaminant concentration goes to zero. Intriguingly, the zeta potential goes to -75 mV rather than 0. This nicely explains electrophoretic mobility experiments. This is caused by an increase in slip length which compensates for the decrease in surface charge. Ref. 103 and 104 also point out the importance of changes in the slip length in zeta potential measurements. This explanation is consistent with experimental results indicating that the presence of surfactant impurities in supposedly purified water are sufficient to alter the slip condition of bubbles significantly.[105, 106, 107]

Other potential explanations may be charge transfer effects,[73] or dynamic effects combined with an enhancement of autolysis at the interface.[89]

### 3.7. Future Outlook

In Ref. 30 we performed essentially the same procedure of generalizing the ionic solvation model, but it was applied to calculating ion–ion interactions instead of ion–surface interactions. Although there are some additional complications, it should in principle be possible to do this for hydronium and hydroxide as well. This should then allow us to gain a better understanding of the dependence of pH on background salt. A problem of crucial importance.[108]

We can also apply the model to other anisotropic ions with unusual behaviors such as iodate,[63] perchlorate,[109] nitrate, and acetate;[110] to multivalent ions where water structure may be more important; to other surfaces where water’s self ions may play an important role;[111] and to see if it can explain the negative adsorption entropy of ions to the air–water interface.[37] It is also obviously important to combine the model with a more sophisticated statistical mechanical description of ion–ion interactions.[112]

## 4. Conclusion

To summarize, we have applied the model developed in Ref. 26 and 29 to calculate the solvation energies and interaction free energies with the air–water interface of the hydronium and hydroxide ions. Hydronium is enhanced at the air–water interface (2 Å inwards from the sharp interface) with a potential minima of  $-2.2k_B T$ , whereas the hydroxide anion is repelled with very similar behavior to the fluoride anion.

If the cavity sizes are adjusted to reproduce experimental solvation energies, the resulting interaction potentials adequately reproduce surface excesses calculated from experimental surface tensions. To the best of our knowledge

Table 7: Theoretical surface excesses in units of ( $\text{\AA}$ ) for all salts. Theoretical values calculated at a concentration of  $\rho = 0.05$  M as in Ref. 29.

Electrolyte	$\Gamma_{\text{theory}}/\rho(\infty)$ <sup>a</sup>	$\Gamma_{\text{theoryA}}/\rho(\infty)$ <sup>b</sup>
HF	13.1	0.3
HCl	13.1	0.5
HBr	13.4	1.2
HI	17.8	4.8
LiOH	-7.8	-7.9
LiF	-7.8	-7.8
LiCl	-7.8	-7.7
LiBr	-7.7	-7.3
LiI	-5.7	-4.8
NaOH	-7.8	-7.8
NaF	-7.8	-7.7
NaCl	-7.8	-7.6
NaBr	-7.7	-7.2
NaI	-5.7	-4.7
KOH	-7.7	-7.7
KF	-7.7	-7.7
KCl	-7.7	-7.6
KBr	-7.6	-7.2
KI	-5.6	-4.7
RbOH	-7.9	-7.7
RbF	-7.9	-7.7
RbCl	-7.9	-7.6
RbBr	-7.8	-7.1
RbI	-5.8	-4.7
CsOH	-7.9	-7.5
CsF	-7.8	-7.5
CsCl	-7.8	-7.4
CsBr	-7.7	-6.9
CsI	-5.8	-4.5

<sup>a</sup> Calculated with  $R_{\text{cav}}$ .

<sup>b</sup> Calculated with  $R_{\text{cavA}}$ .

this constitutes the most accurate theoretical estimation of these key experimental properties. This is remarkable considering the simple nature of the model, which uses the continuum solvent approximation. This indicates that even if water structure is important in determining these properties, it can be accounted for within a relatively simple model. This work also provides additional theoretical evidence that hydroxide is not strongly adsorbed to the air–water interface.

## 5. Appendix

Table 7 gives the theoretical surface excesses for all 29 salts modelled so far. The alkali halide values are the same as in Ref. 29. For many of these salts there are no experimental values and for others there is large experimental error.

## 6. Acknowledgement

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