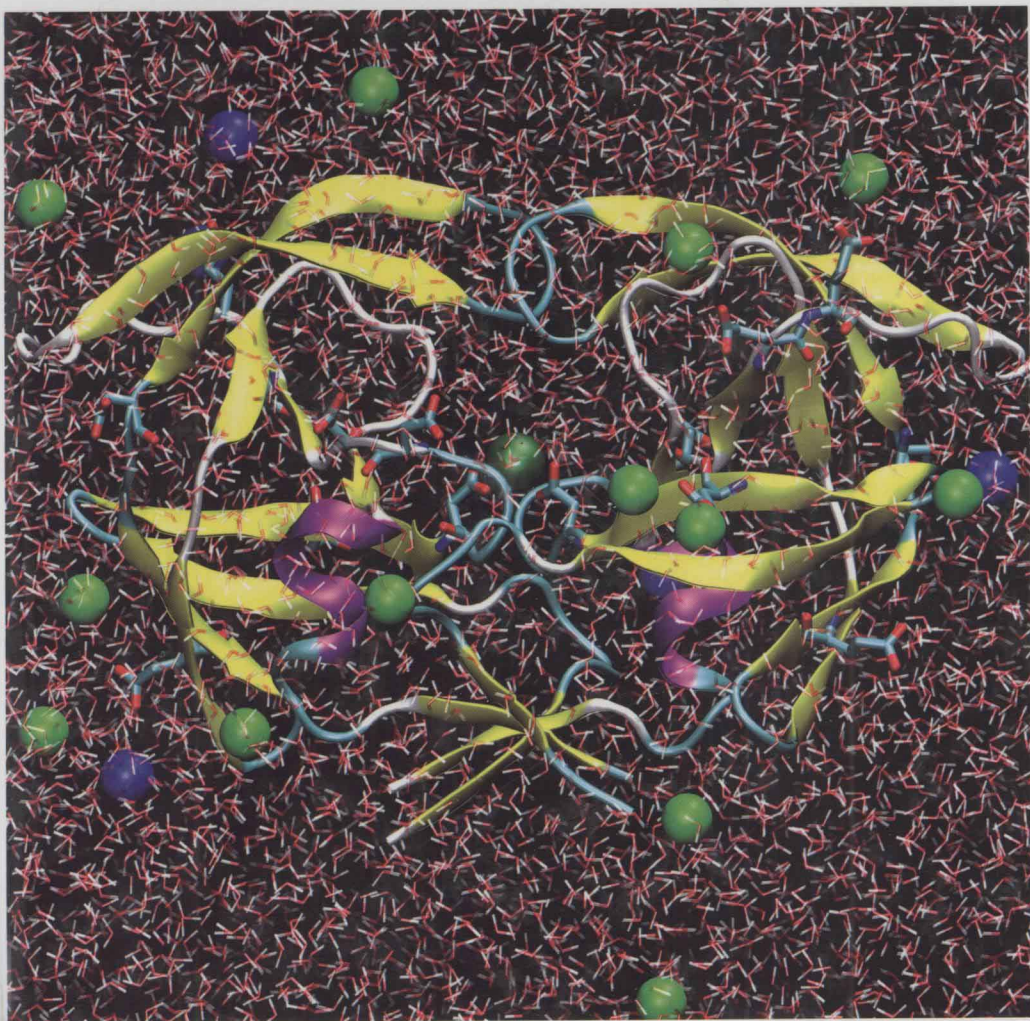
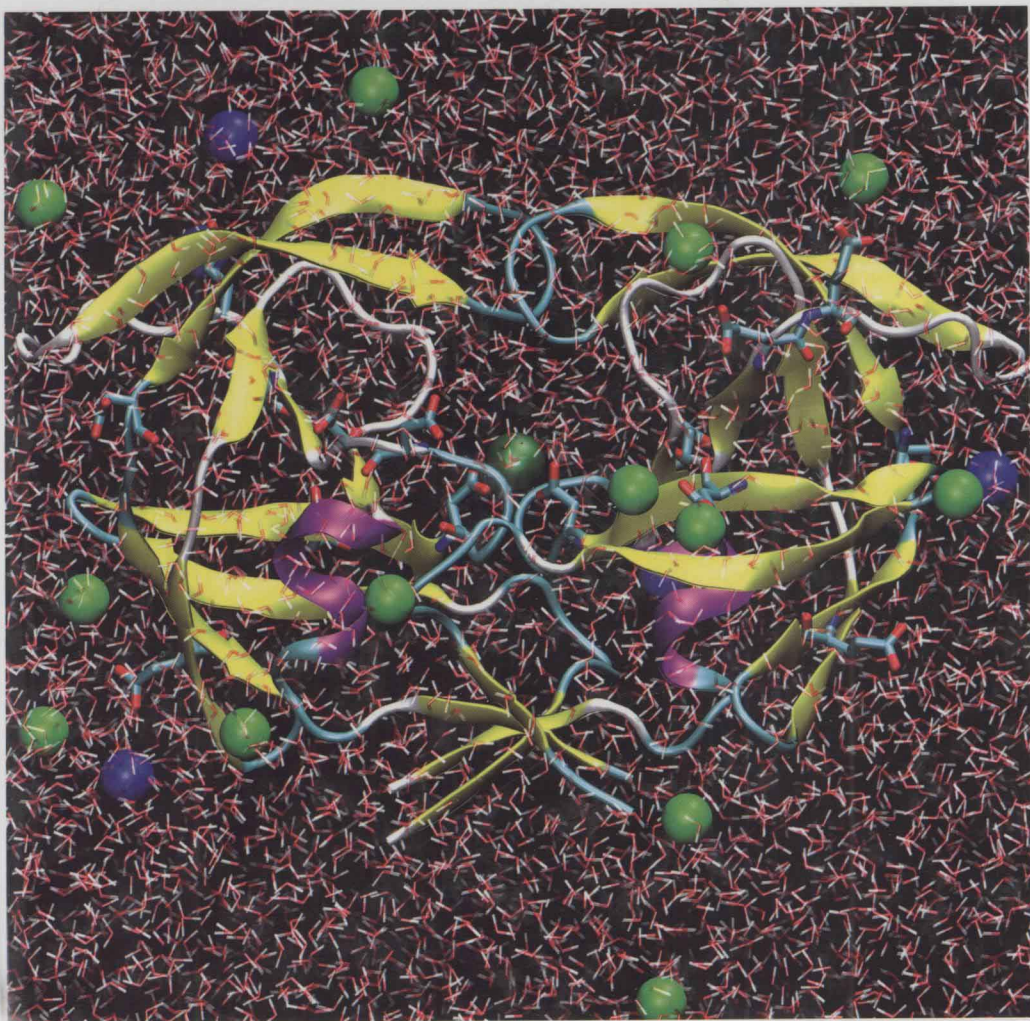


Water – From Interfaces to the Bulk



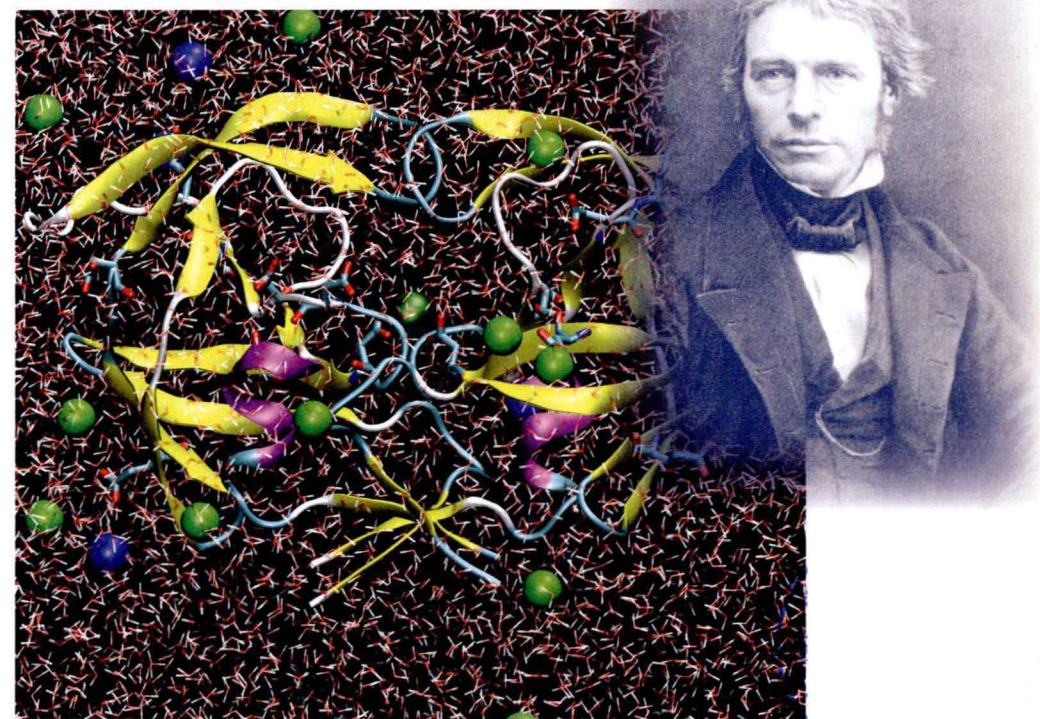
Water – From Interfaces to the Bulk



Water – From Interfaces to the Bulk

Heriot-Watt University, UK

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Water - From Interfaces to the Bulk

Faraday Discussions

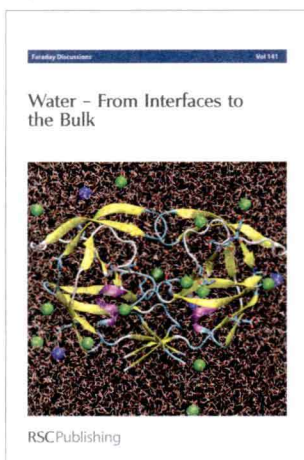
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See Pavel Jungwirth, *Faraday Discuss.*, 2009, **141**, 9–30. Snapshot from a molecular dynamics simulation showing the distribution of sodium (green) and potassium (blue) ions at the water/protein (HIV protease) interface.

Image reproduced by permission of Professor Pavel Jungwirth, from *Faraday Discuss.*, 2009, **141**, 9.

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Spiers Memorial Lecture

Ions at aqueous interfaces

Pavel Jungwirth*

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Studies of aqueous interfaces and of the behavior of ions therein have been profiting from a recent remarkable progress in surface selective spectroscopies, as well as from developments in molecular simulations. Here, we summarize and place in context our investigations of ions at aqueous interfaces employing molecular dynamics simulations and electronic structure methods, performed in close contact with experiment. For the simplest of these interfaces, *i.e.* the open water surface, we demonstrate that the traditional picture of an ion-free surface is not valid for large, soft (polarizable) ions such as the heavier halides. Both simulations and spectroscopic measurements indicate that these ions can be present and even enhanced at surface of water. In addition we show that the ionic product of water exhibits a peculiar surface behavior with hydronium but not hydroxide accumulating at the air/water and alkane/water interfaces. This result is supported by surface-selective spectroscopic experiments and surface tension measurements. However, it contradicts the interpretation of electrophoretic and titration experiments in terms of strong surface adsorption of hydroxide; an issue which is further discussed here. The applicability of the observed behavior of ions at the water surface to investigations of their affinity for the interface between proteins and aqueous solutions is explored. Simulations show that for alkali cations the dominant mechanism of specific interactions with the surface of hydrated proteins is *via* ion pairing with negatively charged amino acid residues and with the backbone amide groups. As far as halide anions are concerned, the lighter ones tend to pair with positively charged amino acid residues, while heavier halides exhibit affinity to the amide group and to non-polar protein patches, the latter resembling their behavior at the air/water interface. These findings, together with results for more complex molecular ions, allow us to formulate a local model of interactions of ions with proteins with the aim to rationalize at the molecular level ion-specific Hofmeister effects, *e.g.* the salting out of proteins.

1. Introduction

The structure, dynamics and chemistry of aqueous interfaces have attracted considerable attention in recent years, as also reflected in the theme of the 141st Faraday Discussion. The present Discussion focuses on a range of important areas concerning interfacial behavior of aqueous systems; from the surface charge of liquid water, over ice interfaces, to confined (nanoscale) systems, and to electrochemical and biological interfaces. Overviews of latest scientific problems concerning interfacial

Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic and Center for Complex Molecular Systems and Biomolecules, Flemingovo nám. 2, 16610 Prague 6, Czech Republic. E-mail: pavel.jungwirth@uochb.cas.cz

water including many of these topics can also be found in the April 2006 special issue of *Chemical Reviews* and in dedicated monographs.^{1,2} Within the present contribution we narrow the focus to issues connected with our studies of ions at aqueous interfaces.

Aqueous electrolytes including their interfaces emerged as subjects of intensive scientific scrutiny already in the nineteen-hundreds with the basic theory thereof being built up by the first half of the 20th century.^{3,4} More recently, studies of aqueous electrolytes and specific ion effects have been undergoing a remarkable renaissance with a particular emphasis on interfacial systems.⁵ The reason for the renewed interest in aqueous interfaces is at least twofold. First, processes at aqueous interfaces have been shown to play a prominent role in widely studied problems in a variety of fields ranging from chemistry of atmospheric aerosols and heterogeneous catalysis^{6–8} to biophysics and biochemistry.⁹ Second, new surface-selective spectroscopic techniques and computational methods have allowed for investigations of aqueous interfaces with atomistic detail revealing how incompletely they have been understood so far.¹⁰

The present paper focuses on our recent attempts to characterize ions at aqueous interfaces at a molecular level. Since it is not supposed to be a review but rather an account of our limited contributions, it does not aim at providing a complete overview of the present state of matters within this ever broadening field. Solely due to our particular choice of systems under investigation several exciting areas concerning *e.g.* ions at water/non-polar liquid or water/solid (insulator or metal) interfaces will be omitted or only briefly touched upon here. This paper thus provides a limited and necessarily personally-biased account on the development of our understanding of interfacial behavior of aqueous ions based on molecular simulations, which we performed in close contact with surface-selective spectroscopic experiments.

Other researchers in the field might tell the story of ions at aqueous interfaces differently (and better); however, we hope that useful general patterns will emerge from this somewhat personal narrative. Chronologically, we started about a decade ago with investigations of inorganic ions at the air/water interface, being motivated by unresolved issues concerning heterogeneous chemistry of atmospheric aqueous sea-salt aerosols.^{11,12} Having collected a “database” of computational results which allowed us to unravel certain general patterns of ionic surface affinities, our interest has shifted lately toward the behavior of ions at the interface between a biomolecule and the surrounding aqueous solution, focusing on specific ion effects on proteins.^{13–15} This path has lead us (somewhat accidentally) from the simplest aqueous interface to arguably the most complex ones. Since the reader may find it pedagogically helpful to move from simple to complex interfaces, we stick to this route also in this paper. In the following chapters we thus discuss first the behavior of ions at the air/water interface, proceeding later to issues concerning ions at hydrated proteins. Doing this, we present also the latest (mostly unpublished) computational results, putting special emphasis on controversial and not completely resolved issues.

2. Inorganic ions at the air/water interface

2.1 Simulations of surfaces of aqueous salt solutions

At the simplest aqueous interface, *i.e.* that between water and air or vapor, the behavior of salt ions should be according to the textbook knowledge rather straightforward.^{4,16–18} Namely, viewing this interface as a plane between a high and low dielectric constant media, ions should be repelled from it into the water phase by the electrostatic image force (see Fig. 1). This situation is pertinent to inorganic ions. Large organic ions, *e.g.* containing long alkyl chains, are also subject to the image force; however, they are attracted to the surface due their hydrophobicity.¹⁹ But even for inorganic ions the picture turns out to be more complicated than Fig. 1 suggests. These ions are indeed repelled from the surface by the image force;

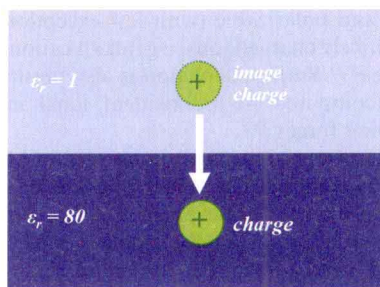


Fig. 1 A schematic picture of the water surface as a flat, sharp interface between two dielectric continua with $\epsilon_r = 80$ (water) and $\epsilon_r = 1$ (air or vapor).²¹ A model spherical ion is repelled from this surface by the electrostatic image force.

however, the free energy penalty for bringing a monovalent ion from the aqueous phase right to the interface is only of the order of several kT (the rest of the free energy penalty being paid only when the ion is fully desolvated in the air).²⁰ Such a relatively weak electrostatic repulsion from the water surface can in principle be overwhelmed by other forces connected with ion-specific interaction with water, *e.g.* due to ion cavitation and polarization.²¹ Ion-specific dispersion forces can also come into play,²² but are likely of secondary importance at the surface of strongly polar solvents.

Consequently, large and polarizable (soft) inorganic ions, such as heavier halides, can be found in the topmost water layer and can even exhibit surface enhancement, followed by subsurface depletion.^{12,23–26} This is demonstrated in Fig. 2, which shows density profiles of surface-attracted bromide and surface-repelled sodium in a slab of roughly molar aqueous solution of NaBr.¹² As a matter of fact, the surface affinity of iodide, bromide, and to a lesser extent also of chloride, was first observed in pioneering polarizable molecular dynamics (MD) simulations of water clusters,^{27–30} computationally only being found later for extended aqueous slabs.^{12,23–26} We should stress here, that even for the largest and softest investigated halide, *i.e.* iodide, the interfacial enhancement is rather modest, the peak surface concentration exceeding that of the bulk by no more than a factor of 2–3.¹² Inorganic ions thus do not behave as typical surfactants with many orders of magnitude of surface enhancement; nevertheless, some of them can act as surface active species. This concerns particularly

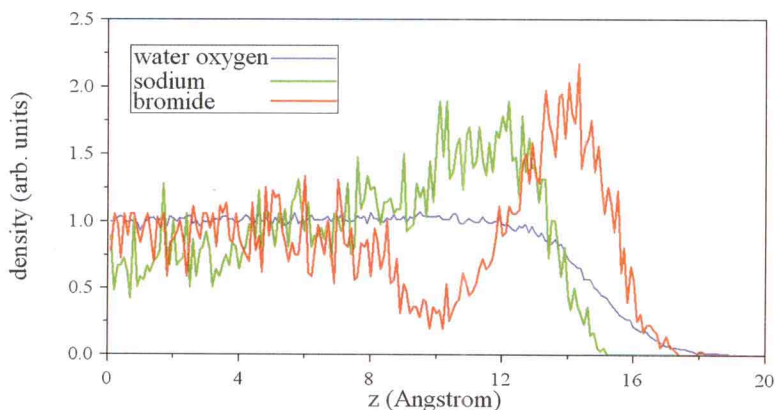


Fig. 2 Density profiles of bromide, sodium, and water oxygens in a slab of 1.2 M aqueous NaBr.¹² Distributions of ions and water are plotted in layers parallel to the surface; from the center of the slab across the interface into the vapor (only half of the slab is depicted).

anions, which are large and polarizable (with few exceptions such as fluoride). In contrast, small hard positively charged ions, *e.g.* alkali cations or fluoride are always repelled from the surface.^{21,31} Surface depletion is also pertinent to polyvalent ions, where much stronger (compared to monovalent ions) image charge repulsion overwhelms surface driving forces.³²

Affinity for the air/water interface was also observed in MD simulations of more complex inorganic salts containing molecular ions. There, the situation is complicated by difficulties in deriving accurate polarizable force fields for non-spherical ions possessing internal structure. Therefore, only a limited set of such ions has been investigated so far. Surface affinity has been observed, *e.g.* for azide³³ and thiocyanate.³⁴ For the latter case, the concentration dependence of the surface enhancement has been investigated in the molar range showing, similarly to heavier halides, a gradual saturation of the surface effect. A particularly difficult case has been that of nitrate anion, where first calculations indicated some surface enhancement.³⁵ Subsequent more converged simulations with a refined force field revealed that nitrate is repelled, albeit weakly from the top layer and rather prefers to reside in the immediate subsurface.^{36,37} This demonstrates the sensitivity of the results on simulation conditions, in particular on the force field. Rough estimates of ionic surface affinities can be already obtained from nanosecond simulations with relatively simple (but polarizable) potentials with several hundreds of water molecules in the unit cell of the slab. However, to be more quantitative, force fields must be refined and longer simulations with larger unit cells are needed.

2.2 Experimental considerations for surfaces of aqueous salt solutions

The above computational findings of surface affinities of large and soft inorganic ions were first met with skepticism, since they were in conflict with the textbook notion of an essentially ion-free electrolyte surface due to image charge repulsion.^{16–18} Moreover, inorganic salts in general increase the surface tension of water. It follows from the Gibbs adsorption equation³⁸

$$\partial\gamma/\partial\mu = 1/kT \times \partial\gamma/\partial(\ln f/x) = -\Gamma \quad (1)$$

that a positive change in surface tension γ with salt ion chemical potential μ means a negative surface excess Γ of the ions. (The chemical potential of the ion species is related to the logarithm of its mole fraction x times activity coefficient f , the latter being close to unity at small concentrations.) Note, however, that the surface excess is an integral quantity over the whole interfacial region. As such, it can still be negative if surface accumulation of ions is overcompensated by subsurface depletion. Qualitatively, such a situation is indeed observed, *e.g.* for heavier halides (Fig. 2), although it is difficult to obtain a converged value of the subsurface ion depletion computationally due to its slow convergence into the bulk and the necessarily finite width of the simulated slab.^{21,25}

The calculated surface enhancement (*e.g.* for bromide and iodide) or at least presence at the interface (*e.g.* for chloride) helped to rationalize atmospheric observations and laboratory experiments concerning heterogeneous chemistry on aqueous sea salt aerosols.^{6,11} Subsequently, surface selective spectroscopies, such as vibrational sum frequency generation (VSFG),^{39–42} second harmonic generation (SHG),^{43–45} photoelectron spectroscopy (PES),^{46–48} and atomic scattering techniques^{49,50} allowed for an indirect or direct observation of ions within the interfacial layer between an aqueous electrolyte solution and its vapor. All these techniques showed that inorganic salt ions can influence the interfacial layer. SHG and PES methods were, moreover, capable of directly detecting the interfacial ionic signal as a function of bulk concentration, revealing surface adsorption of anions like bromide, iodide or thiocyanate, but not of alkali cations.^{44,48,51} Although more work is needed to obtain fully quantitative results for each individual system, we

can conclude that the affinity of large, soft inorganic anions for the air/water interface is reasonably well established by now, both computationally and experimentally.

2.3 Simulations of hydronium and hydroxide at aqueous interfaces

Aqueous electrolytes encompass not only salts but also solutions of acids and bases. Strong acids and bases practically completely dissociate in water releasing into the solution two important ions which have been not discussed yet—hydronium and hydroxide. Even pure water contains these ions, albeit at a very low amounts of 10^{-7} M. The issue of surface affinity of H_3O^+ and OH^- has been subject of vigorous computational and experimental investigations recently.^{52–61} Researchers generally agree that these two ions exhibit a non-trivial surface behavior. However, as reflected also in this Faraday Discussion, there is disagreement not only on the quantitative amount of ionic surface adsorption but also on a more qualitative issue, namely which of these two ions exhibits larger surface enhancement.^{62–64}

Similarly as for salt ions, the first computational indication about an interesting surface behavior of hydronium and hydroxide came from medium-sized to large cluster studies.^{65–69} Note that one needs at least about 20 water molecules in order to start distinguishing between surface and internal ion solvation. For hydronium, calculations revealed a strong preference for cluster surfaces.^{65–69} This may come as a surprise since naively one could assume that proton as a small ion with zero polarizability should prefer internal solvation. The trick is, of course, that hydrated proton chemically reacts with water, the two limiting resulting structures being the Eigen (H_3O^+) and Zundel (H_5O_2^+) cations,^{70,71} which dramatically alters its properties and interfacial behavior (*vide infra*). For hydroxide, computational studies show a systematic shift from an affinity for the surface to delocalization over the whole cluster upon increasing the cluster size.^{69,72,73}

While cluster studies can provide useful hints, there is need for investigating extended aqueous surfaces in order to directly connect with experimentally scrutinized surfaces of bulk aqueous systems. MD simulations of hydronium in aqueous slabs employing a polarizable classical force field^{52,54} or a more sophisticated effective valence bond (EVB) scheme^{53,60} allowing for proton transfer, revealed that hydronium is attracted to or at least not repelled from the water surface. In contrast, hydroxide was found to be weakly repelled from the surface although it did occasionally penetrate all the way to the topmost water layer.⁵⁴

Most recently, we have performed a series of simulations^{58,62,74} to check the above early predictions. The principal aim of these calculations has been to establish the free energy difference connected with transferring hydronium or hydroxide from the aqueous bulk to the surface. Our approach to this problem has been a pragmatic combination of three computational methods—classical MD with polarizable potentials, *ab initio* MD based on density functional theory (DFT) methods, and accurate *ab initio* (MP2 or coupled cluster) calculations. A similar methodology has been already applied in our studies of salt ions at the air/water interface²¹ with that the combination of empirical and electronic structure techniques becomes particularly topical for the “difficult”, chemically non-trivial hydronium and hydroxide ions. In the following paragraphs we, therefore, briefly summarize the employed computational strategy.

Each of the above three computational approaches has its advantages and disadvantages. Classical MD simulations can be easily performed for relatively large systems containing hundreds to thousands of water molecules in periodic unit cells mimicking extended aqueous interfaces. We have been employing unit cells of the form of a rectangular prism where the system acquires the shape of a periodic slab with a bulk region between two air/water interfaces (Fig. 3). Depending on the actual system size, the area of each of these interfaces in the unit cell has varied between 3 and 9 nm². This computational approach is fast enough to allow collecting data for varying amounts of dissolved species from just a single ion to several moles

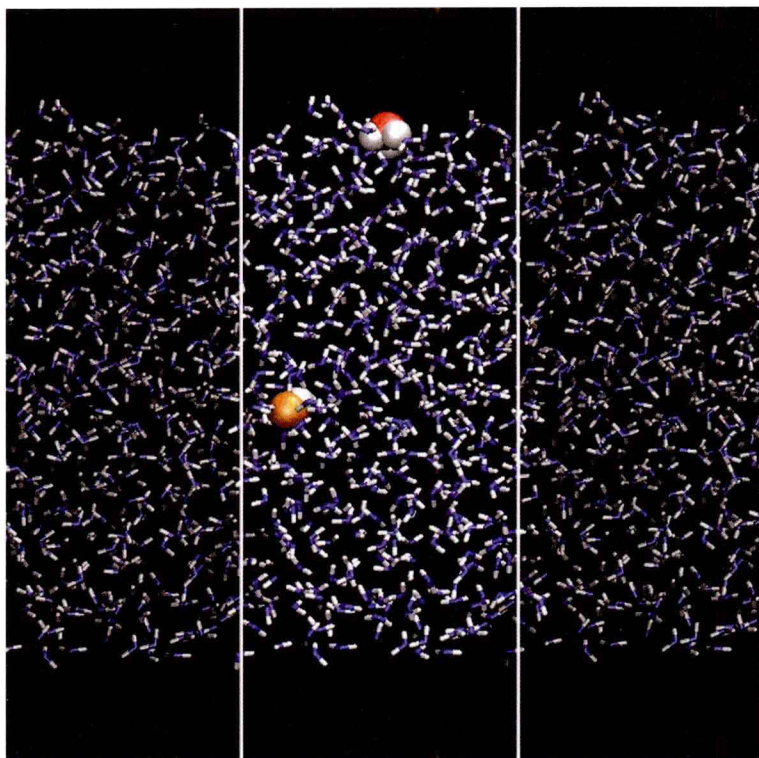


Fig. 3 Water slab containing 432 water molecules and a single hydronium and hydroxide in a unit cell of dimensions of approximately $19 \times 19 \times 237$ Å.⁵⁸ White lines define the boundary between the the central and neighboring cells.

per litre. Also, long enough (nanosecond to microsecond) runs can be performed so that thermodynamic quantities such as free energy differences can be converged either directly or using advanced simulation techniques. The basic drawback of classical MD is that the empirical potential does not allow for proton hopping unless special approaches such as the EVB are employed.^{60,75,76} Neither does it properly describe the partial charge transfer character of strong ion–water interactions, although a polarizable force field to a certain extent accounts for this effect.⁶⁴

Ab initio MD allows one to get rid of an empirical potential and to describe explicitly the electronic structure of the whole system accounting naturally for proton hopping and charge transfer effects. The price is a dramatic increase in computational load. Consequently only smaller slab systems with up to about a couple of hundred water molecules in the unit cell can be studied.⁷⁷ Also, the accessible picosecond rather than nanosecond timescales allow for studying dynamics but typically not thermodynamics. Nevertheless, a most recent “tour de force” *ab initio* MD simulation showed that free energy differences are becoming within reach of this method.⁷⁸ Another issue is that *ab initio* MD techniques are based on DFT methods, typically employing non-hybrid functionals such as BLYP or PBE.⁷⁹ These functionals are necessarily of an approximate character (*e.g.* in many cases they tend to overdelocalize the electron density) which also translates to the accuracy with which they describe aqueous systems. Currently, hybrid functionals, which provide generally a better description (*e.g.* by reducing the self-interaction error), are being introduced to *ab initio* MD. Finally, accurate *ab initio* calculations at the MP2 or even coupled cluster (CC) level can be employed for small cluster systems containing

a hydronium or hydroxide ion with several water molecules. Such calculations provide valuable information *per se* and also serve as benchmarks for developing and testing empirical potentials for the ionic product of water.⁶²

In our studies of hydronium and/or hydroxide in aqueous slabs, we have most heavily relied on classical MD simulations employing polarizable force fields.^{54,58,62,64,74} Using a thermodynamic integration method we established for the hydronium cation either in the Eigen or Zundel form a free energy surface minimum of -2 to -3 kcal mol⁻¹. This surface enhancement is in accord with results of EVB calculations, which allow for proton hopping.^{53,60} In contrast, we found that hydroxide has a very weak preference for the bulk of about 1 kcal mol⁻¹ (with the statistical error of all of our free energy estimates being ± 1 kcal mol⁻¹ with 85% confidence). In other words, simulations show that hydronium accumulates at the water surface, while hydroxide has at best the same concentration there as in the bulk. Therefore, in the topmost layer of water there shall be an excess of hydronium over hydroxide. We denote this situation as an “acidic” surface of water.⁵⁸ We use the quotation marks since pH is strictly speaking a bulk property related to proton activity, nevertheless, we operationally define as “acidic” an aqueous surface with a number excess of hydronium over hydroxide.

A simple qualitative rationalization of this effect is as follows. While H₃O⁺ makes three strong donating hydrogen bonds, its oxygen is a dysfunctional hydrogen bond acceptor due to its very low negative charge compared, *e.g.* to the O atom of a water molecule (Fig. 4). From this perspective, hydronium has been labeled as the smallest “amphiphilic” species⁵³ and as such prefers to reside at the surface with the O atom exposed into the vapor. Qualitatively, the situation for OH⁻ is the opposite with its oxygen being an excellent hydrogen-bond acceptor and hydrogen a poor donor. However, quantitatively this “amphiphilic” effect is weaker since the H atom is small and so is the reduction of its partial charge compared to hydrogen in a water molecule. Hydroxide is, therefore, able to develop also a donating hydrogen bond, albeit a weak one (Fig. 4). As a result, it does not exhibit surface enhancement although it can occasionally penetrate all the way to the surface layer.

Classical MD allows us, provided long (beyond nanosecond) simulations are performed, to obtain the free energy difference between an ion solvated in the bulk and at the surface. However, these simulations are only as good as the empirical interaction potential and without sufficient care a “garbage in, garbage out” scenario may become applicable. A dynamical approach which bypasses the use of empirical potentials is the *ab initio* MD where energies and forces are calculated using DFT-based methods.⁸⁰ We employed the BLYP functional to investigate the behavior of hydronium or hydroxide in clusters with 48 water molecules and in small aqueous slabs with 72 waters.^{58,62} Picosecond timescale trajectories revealed that hydronium

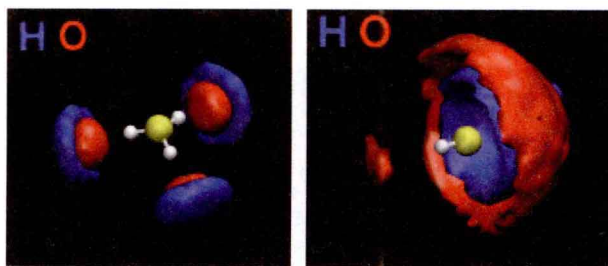


Fig. 4 Solvation shells around bulk-located aqueous hydronium (left) and hydroxide (right) from polarizable MD simulations.⁶² Color coding: ion oxygens—yellow, ion hydrogens—white, water oxygens—red, and water hydrogens—blue. While H₃O⁺ forms 3 strong and very directional donating and no accepting hydrogen bonds, OH⁻ exhibits 4–5 accepting hydrogen bonds and a weak donating one.

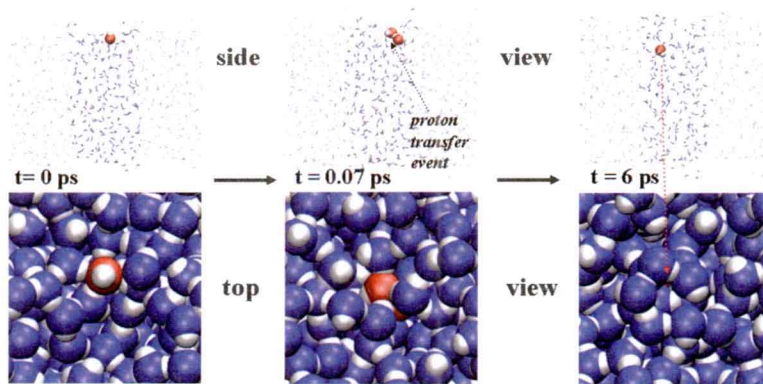


Fig. 5 Three snapshots from a *ab initio* MD trajectory of a single hydronium initially placed on the surface of an aqueous slab with 216 water molecules in a $15 \times 15 \times 70$ Å unit cell.⁸¹ OH⁻ moves swiftly from the surface to the subsurface, with proton transfer accelerating its mobility. It becomes fully hydrated with no direct exposure to the vapor phase and remains so for the rest of the 10 ps trajectory.

prefers to reside at the surface, while hydroxide tends to move from the surface to the subsurface layers. For a set of optimized cluster structures we estimated the surface preference of hydronium to be at least as strong (if not stronger) using DFT that that obtained using polarizable empirical potentials. Most recently, we have launched a larger scale *ab initio* simulation of a single OH⁻ ion in an aqueous slab containing 216 water molecules in a unit cell.⁸¹ Such size has been shown previously to be sufficient for an aqueous system to develop a well-defined bulk region between the two water/vapor interfaces.⁷⁷ In a simulation lasting ten picoseconds we see a hydroxide ion initially placed at the surface starting to “dive” into the subsurface within 50 fs and then exploring this region of the slab (Fig. 5). This indicates that there are no special “binding sites” for hydroxide at the water surface and that the free energy profile connected with the motion of OH⁻ toward the bulk lacks an appreciable surface minimum. This result is also supported by most recent massive (~ 500 ps) *ab initio* MD simulations of a very similar system which allowed to extract the free energy difference between a surface and bulk position of hydroxide.⁷⁸ The obtained value is roughly zero, this result falling within the statistical error of 1 kcal mol⁻¹ of the value obtained from MD with an empirical polarizable potential.^{58,62,78} Nevertheless, the aqueous hydroxide described within DFT has a more delocalized charge (particularly at the interface) than its counterpart modelled with a polarizable force field, which is a factor which tends to reduce its repulsion from the surface.⁷⁸

Finally, we performed accurate benchmark *ab initio* calculations at the MP2 and CCSD(T) levels employing the aug-cc-pvtz basis set for small clusters containing

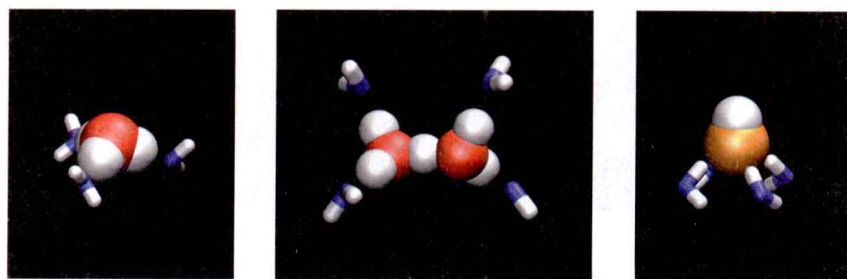


Fig. 6 *Ab initio* MP2/aug-cc-pvdz structures of H₃O⁺ with three, H₅O₂⁺ with four, and OH⁻ with four water molecules, used for benchmarking our polarizable force field.⁵⁸