

Ions at Aqueous Interfaces: From Water Surface to Hydrated Proteins

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Abstract

Surfaces of aqueous solutions are traditionally viewed as devoid of inorganic ions. Molecular simulations and surface selective spectroscopic techniques show, however, that large polarizable anions and hydronium cations can be found (and even enhanced) at the surface and are involved in chemistry at the air/water interface. Here, we review recent studies of ions at the air/water interface and compare from this perspective water to other polar solvents. For water, we focus in particular on the surface behavior of the ionic product of water, i.e., hydronium and hydroxide ions. We also investigate the feasibility of dielectric models for the description of the protein/water interface, in analogy to the air/water interface. Little correlation is found between these two interfaces in terms of ion segregation. Therefore, a local model of pairing of ions from the solution with charged and polar groups at the protein surface is suggested. Corresponding results of experimental studies on aqueous model systems are described.

1. Introduction

Structure and chemistry at aqueous interfaces is a topic of fundamental interest, with applications ranging from heterogeneous reactions in the atmosphere to technological applications, and to biochemical processes. A recent special issue of Chemical Reviews attempted to provide a comprehensive picture of the up-to-date advances in this field [1]. Several experimental [2-4] and computational [5-7] reviews in that issue focused on the behavior of ions at the simplest aqueous interface, namely the air/water interface or, in other words, the open aqueous surface. These papers serve as the point of departure for the present review, which focuses on new findings for ions at the air/water interface and on comparison of ion behavior at water surface to that at a more complex, specific aqueous interface. In particular, we elaborate on ion behavior at the protein/water interface and point out the differences from that at the free aqueous surface.

Both experimental and computational methods capable of accessing the details of ionic and molecular interactions at liquid aqueous interfaces with Angstrom resolution have matured only recently. These encompass primarily non-linear optical techniques, such as vibrational sum frequency generation (VSFG) [8-13] and second harmonic generation (SHG) [14-17], photoelectron spectroscopy (PES) in liquid jets [18-20] and on deliquesced salt crystals [21,22], and molecular dynamics (MD) simulations in slab geometry [23-30]. The basic message from the computational and experimental studies of surfaces of aqueous salt solutions, performed within the last decade, is that these surfaces are not as passive as anticipated earlier. Classical theory views the surfaces of electrolytes as essentially ion-free and, therefore, similar to the surface of neat water [31-34]. The present view is different [2,4,5,7]. It reveals strong ion specificity, with small hard ions, such as alkali cations or fluoride, being indeed repelled from the aqueous surface. However, other inorganic ions, such as soft anions (e.g., heavier halides), and also hydronium show a significant propensity for the air/water interface. In the former case, the main surface driving force is the anionic size,

solute and solvent polarizability [29,35-40], and possibly other effects [41,42], while in the latter case it is mainly the specific hydrogen bonding pattern (good donor but poor hydrogen bond acceptor properties) of H_3O^+ [9,15,28,43]. As summarized recently [2,4,5,7,30], this emerging picture of surfaces of aqueous electrolytes, based on MD simulations, is consistent with traditional surface tension and surface potential measurements and it is supported by modern surface selective spectroscopic measurements. It also provides a rationalization for surface chemistry of halides observed on aqueous atmospheric aerosols [44-46]. Nevertheless, this picture is still far from being complete and some doubts concerning the predictive power of MD simulations with empirical force fields remain both on the side of theory [27] and experiment [47].

Here, the latest studies of ions at aqueous surfaces, not covered or only partially covered in previous reviews, are summarized. We compare the behavior of inorganic ions at the water surface to that at surfaces of non-aqueous electrolyte solutions with the aim to obtain a more general picture of ion segregation at polar liquid surfaces. We also explore in detail the only ions present in pure water, i.e., hydronium and hydroxide, and discuss the consequences of their different surface propensities.

The air/water interface is but only the simplest aqueous interface. An interesting and important question arises, whether or not the more complicated interfaces (e.g., those between water and a non-polar liquid, or water and a solid or a macromolecule) resemble the simplest one in terms of interfacial ion segregation. In particular, attempts have even been made to treat ion-protein interactions in aqueous solutions as an interfacial problem [48-50]. Indeed, one can in principle view a globular protein in water as a large dielectric sphere with a smeared charge and model its surface as an interface between high (water) and low (protein) dielectric constant media. It might, therefore, be tempting to treat ions at the protein/water interface similarly to those at the air/water or non-polar medium/water interfaces, and in this review we critically explore this concept.

Interactions between ions and proteins in aqueous solutions play an important role in many biophysical and biochemical processes, such as salting-out and salting-in, protein crystallization, and enzymatic activity (for a recent review see, e.g., ref [51]). Ion specificity is traditionally rationalized in terms of the lyotropic (Hofmeister) series, which originally ordered common ions according to their ability to salt out egg white protein [52,53]. It is clear that this ion specificity is connected with ion hydration and ion-protein interactions, however, a comprehensive molecular understanding remains elusive.

Here, we review the current knowledge of ion segregation at the protein/water interface and compare it to what has been learned about the air/water interface. An important conclusion emerges from this comparison, namely that there is no direct correlation between specific ion behavior at these two interfaces. Ions that are repelled from the air/water interface, such as small alkali cations, are attracted to protein surfaces and *vice versa*, and hence a new approach should be used to understanding ion-protein interactions. Experimental and computational data indicate that pairing of ions from the aqueous solution with individual charged and polar groups at the protein surface is the dominant effect determining specific ion-protein interactions at the protein surface, while the protein shape and dielectric constant (which mainly applies to its interior, which is not easily accessible to ions) is of secondary importance [54-59].

A local ion-pairing view allows one to reduce in the first approximation the ion-protein problem to ion-amino acid or even ion-amino acid functional group one. In the present review we explore the advantages and limitations of this local interaction model by presenting and discussing recent computational and experimental results. The former concern MD simulations of proteins and amino acids in salt solutions, as well as simulations and quantum chemical calculations of pairing of charged and polar amino acid groups with salt ions in water. Regarding the experiments we discuss X-ray absorption and photoelectron spectroscopic data of amino acids in water and salt solutions, and non-linear optical

spectroscopic studies of amino acids and of structurally related surfactants at the aqueous solution interface.

The rest of the review is organized as follows. In Section 2 we start with presenting an overview of recent theoretical and experimental insight into the molecular structure of the neat liquid water surface, and then describe the molecular picture of ions at the aqueous solution interface. We also compare aqueous systems with the situation for non-aqueous liquid surfaces in order to highlight the important molecular interactions responsible for the propensity of certain ions to the solution surface. Of special interest are the surface properties of generic water ions, i.e., hydronium and hydroxide. After a brief description of the structure and dynamics of hydrated proton and hydroxide in the aqueous bulk we address the question whether or not these ions may be stabilized at the surface. Section 3 presents recent computational and experimental studies of the protein/solution interface. We discuss the behavior of ions at this interface in terms of local pairing with charged and polar groups at the protein surface. In this context we also describe our current understanding of both geometric and electronic structure of bulk and surface hydrated protein-relevant model systems. The last section then provides a short summary.

2. Air/Water Interface

2.1 General experimental and computational considerations

Our understanding of the structure and dynamics of ions at the air/water interface has changed dramatically in the last decade, thanks to advances in experimental and computational techniques, which provide detailed molecular information. It should be stressed that experimental methods that work well for the investigation of solid surfaces under ultra-high vacuum encounter problems with the mobility and the high vapor pressure of aqueous solutions. This precludes or considerably complicates the use of typical high-vacuum surface

science techniques, such as particle scattering or scanning probe methods (see, however, a recent scanning polarization force microscopy study of mobilities of aqueous ions [60]).

Another sensitive technique, well established for solid surfaces, is photoelectron spectroscopy (PES). Thanks to the fact that the mean free path of photoelectrons in water is as short as 6-10 Å near 70-200 eV kinetic energy [61], this method can achieve high surface selectivity. However, PES from liquid water has become feasible only recently, after overcoming problems with the detection of electrons above a vaporizing water surface. This has been achieved by a new technology of a stable aqueous microjet generated in a differentially pumped high-vacuum chamber [4,62-64].

An alternative way to overcome the above problems is to employ ambient pressure spectroscopic probes of the instantaneous interfacial structure, such as VSFG or SHG. The interfacial selectivity of these non-linear spectroscopic methods is ensured by the fact that the signal from the isotropic bulk region vanishes due to symmetry considerations.

On the computational side, the main tools for the description of the air/water interface have been MD simulations in slab geometry. Both the classical force field approach [5,7] and, recently, ab initio MD [65] have been employed. In the former case, the use of polarizable force fields, parameterized against experiments or quantum chemistry calculations of model systems, proved to be essential for a quantitative description of ion segregation at the aqueous surface [35,36,66]. Ab initio MD should in principle overcome problems with the empirical force fields. Unfortunately, computationally accessible system sizes and time scales are still not sufficient for obtaining a thermodynamically converged picture of ion behavior at the air/water interface. With advances in hardware and software and with improvements in the underlying density functional methods we, however, anticipate that more insight from ab initio MD will be provided in the near future.

2.2 Water versus Polar Non-Aqueous Liquid Surface

Behavior of inorganic salt ions at the air/water interface has been reviewed recently [2,4,5,7]. Molecular dynamics simulations provide a picture with atomic resolution, where ion specificity is the key issue. While hard (non-polarizable) ions are repelled from the aqueous surface, soft (polarizable) ions can penetrate all the way to the surface. If the ions are sufficiently large and polarizable as to overcome the electrostatic (image charge) repulsion from the surface they can even exhibit surface concentration enhancement followed by sub-surface depletion. This is the case for bromide, iodide, thiocyanate, and other anions [7]. This computational scenario is consistent with macroscopic surface tension [67,68] and surface potential data [34] and it is supported by surface selective spectroscopic measurements [2,4].

Is water the only polar liquid, where inorganic salt ions exhibit such an interesting surface behavior? This question has been addressed both by experiments and molecular simulations [69-73]. Ion or molecule scattering experiments, performed in high vacuum [70,72,74], take advantage of the low vapor pressure of some of the non-aqueous liquids (formamide, glycerol, etc.) avoiding thus the need to use special techniques, as in the case of more volatile water [4,21]. For volatile non-aqueous liquids, such as methanol, the surface of a cryogenic amorphous solid was studied [71,75] as a structural proxy of the corresponding liquid [76].

MD simulations and scattering experiments performed on formamide, glycerol, ethylene glycol, and liquid ammonia show that these polar liquids surface segregate polarizable anions such as iodide in a qualitatively similar way as water [70,72,74]. Figure 1 shows the density profiles, i.e., abundances of individual species in layers parallel to the surface, from the bulk across the liquid/vapor interface into the vapor phase, for different sodium iodide solutions. Note that 1 M aqueous NaI is compared to 0.5 M non-aqueous solutions. This is mainly due to technical reasons - salt solubilities in these non-aqueous polar liquids are smaller than in water, which results in significant ion pairing and clustering at

higher concentrations. Also, with this choice the molar fraction of salt ions in formamide is comparable to that in water. The interfacial ionic profiles for water, formamide, liquid ammonia, and ethylene glycol (the latter being calculated instead of the experimentally investigated glycerol [70], the large viscosity of which prevents converged MD simulations) look very similar to each other, with a surface iodide peak followed by subsurface depletion and a smaller sodium peak. Quantitatively, there are small differences between the density profiles and surface iodide peaks in the different solvents, the largest peak being observed for water and liquid ammonia.

Representative surface snapshots from the MD trajectories of the four solutions further underline the differences between the solvents (Figure 2). Already from a visual inspection of the surface it is clear that iodide is more exposed toward the vapor phase in water than in the non-aqueous polar solvents. The decrease of iodide surface exposure upon moving from water to other polar solvents is due to the fact, that in the latter cases the anion is more buried in the topmost layer. This is revealed from a local topography analysis of the solvent shell around iodide. To this end the shift z_{shift} in the direction perpendicular to the surface between the position of the anion and the center of mass of the first solvent shell around the ion was evaluated [72,73]. In the isotropic bulk environment the average value of z_{shift} is zero. However, at the anisotropic air/water interface z_{shift} deviates from zero and its value characterizes the degree of exposure of the anion, from just touching the surface from the solvent side to a more exposed ion. Note that in the investigated systems an ion that would be more than half-exposed at the solution surface was rarely observed (Figures 2 and 3).

The distribution of z_{shift} from the bulk across the interface is presented in Figure 3. For all four liquids this distribution is bimodal with a peak at $z_{\text{shift}} = 0$ for bulk solvent molecules and a secondary surface peak corresponding to anions with positions ranging between just touching the surface from the solvent side and being half-exposed. Note the pronounced minimum between these two maxima, which corresponds to subsurface depletion of iodide.

Also note that the height of the surface peak and shift toward relatively larger values of z_{shift} , which locally quantifies the protrusion of an ion into the vapor phase, is solvent-dependent, being the largest in water. From these plots it follows that water surface segregates large polarizable better than other polar solvents.

The above results indicate that water is not unique in its ability to surface segregate polarizable inorganic ions such as iodide, although the effect in other polar solvents is weaker. As a matter of fact, in some polar solvents such as methanol and other simple alcohols the surface ion effect is all but gone. For iodide in methanol this was demonstrated by MD simulations of the liquid [69,73] and metastable impact electron spectroscopy of the corresponding amorphous solid surface [71,75], which both show the disappearance of the anionic surface peak. This is primarily due to the fact that methanol molecules tend to orient at the surface with methyl groups exposed into the vapor and the OH group pointing with hydrogen into the liquid phase. Methanol surface thus has a very different structure from that of water (with dangling hydrogens and oxygens). A similar effect has also been observed in MD simulations of iodide at the surface of water/butanol mixtures [77].

2.3 Pure water and its generic ions

The remarkable ability of liquid water to spontaneously autoionize (autolyze) is behind its pH related phenomena. At ambient conditions, about one in $5.5 \cdot 10^8$ water molecules is autoionized, which yields the standard value of pH equal to 7. While this is a basic textbook knowledge, obtaining a detailed molecular picture of the bulk autoionization reaction $\text{H}_2\text{O}_{\text{aq}} \rightarrow \text{H}^+_{\text{aq}} + \text{OH}^-_{\text{aq}}$ and describing the structure and dynamics of the ionic product of water has been a major challenge [28,43,78-81].

From the dynamical point of view, the quantum mechanical structure of the hydrated proton fluctuates on the femtosecond timescale between the limiting configuration of H_9O_4^+ (Eigen cation [82] with a H_3O^+ core strongly solvated by three water molecules) and H_5O_4^+ ,

(Zundel cation [83] with the proton equally shared between two water molecules). A brief recent overview on the structural aspects of protonated and deprotonated water, from both theoretical and experimental perspective, can be found in ref [84]. This dynamical structural rearrangement is also responsible for the fast proton mobility in water (about four times larger than the self-diffusion of water) [85], which is usually described by the essentially barrierless de Grotthuss mechanism for proton hopping, involving a displacement of the protonic charge without moving the protonic mass [86]. Although the microscopic details are not yet fully understood, the interconversion between Eigen and Zundel hydration structures, constituting an important step of proton transfer in water, was directly observed recently, using femtosecond vibrational pump-probe spectroscopy [87]. Note, however, that also other structural transformations, such as Zundel-to-Zundel, have been proposed [88].

Proton transfer between acids and bases in aqueous solutions is a key chemical process [82,89], and plays an important role in biological processes in aqueous environment [90]. Ultrafast mid-infrared spectroscopic studies probing the proton transfer reactions in acid-base aqueous solution [91] suggested that the hydrated proton is the Eigen solvation core, and the role of the Zundel cation in the proton transfer dynamics is less prominent [92,93]. An up-to-date summary of the subject can be found in ref [90], and a recent review of proton transfer was presented e.g., in ref [85]. Note that the second part of the ionic product of water, OH^- , is much less studied and its bulk solution structure is still being determined. Recent results from neutron-diffraction experiments suggest that OH^- forms up to four strong hydrogen bonds between the hydroxide oxygen and the water hydrogens, depending on ion concentration [94]. An additional water molecule, identified at the hydroxide hydrogen site, is assumed to play a relevant role in the proton transfer mechanism.

Clearly, rationalization of processes involving the ionic product of water must be based on understanding hydrogen bonds in neat liquid water. Most of our knowledge on the dynamics of hydrogen-bond breaking/making, nuclear motions, and energy delocalization

comes from a number of recent infrared pump-probe experiments with sub-100 fs time resolution; see e.g., refs [95-98]. It is imperative not only to unravel the vibrational/rotational dynamical properties of an H₂O molecule in water and aqueous solutions, but also to address the electronic structure of water. In fact, electronic structure measurements of bulk liquid water, using X-ray spectroscopic techniques that exploit the high-brilliance synchrotron radiation of third-generation synchrotron light sources, have revived the very fundamental discussion of what constitutes a hydrogen bond in liquid water. With different X-ray spectroscopic techniques, including X-ray absorption spectroscopy (XAS, based on photon and electron detection modes) and X-ray Raman scattering (XRS) at the oxygen *K*-edge local structural details associated with different environments of a H₂O molecule in bulk water were revealed [99-103]. Especially notable, yet very controversial issue is the amount of broken hydrogen bonds in liquid water, with reported coordination numbers for a water molecule ranging from slightly more than two strong hydrogen bonds [100] to about four, which would be ice-like. This discrepancy has initiated a number of theoretical calculations using state-of-the-art methods [104-110] with coordination numbers converging to a value only slightly smaller than four [109,110].

In analogous XAS studies of aqueous acids also the electronic spectrum of the hydrated proton was measured [111,112] revealing a concentration-dependent structural pattern. At concentrations ≥ 1 M the strongly solvated Eigen form was concluded to dominate, whereas at lower concentrations also the Zundel form is stabilized. The former is consistent with neutron-diffraction data from concentrated HCl aqueous solutions [113]. In the following we focus on the behavior of the ionic product at the air/water interface.

2.4 Autoionization at water surface

Water molecules

The air/water interface has different properties from the aqueous bulk. Here, we briefly discuss the structure of water surface obtained from dedicated surface-sensitive measurements of neat liquid water, and from molecular dynamics studies of the liquid/vapor interface. An early infrared-visible SFG study [114] concluded that >20% of the surface molecules are orientated with one free OH bond protruding into the vapor, at about 38° relative to the surface, and the other (donor) OH extending into the bulk, participating in hydrogen bonding (this is usually termed single-donor configuration). More recent VSFG work indicates the presence of several types of species, at different depth [10,11]. The topmost one is of single-donor type already mentioned. The other type of interfacial species are assumed to be completely surrounded by other water molecules (although not necessarily fully symmetrically tetrahedrally bonded), and are located a few angstroms from the top of the surface [10,11]. The spectral assignment of surface water in VSFG has laid the groundwork for analogous measurements of aqueous solutions, allowing to explore ions at the very surface.

A slightly different picture of water surface arises from XAS studies, using total ion yield detection [99]. Here an additional interfacial water species was identified, the acceptor-only configuration, where both OH bonds stick out to vacuum, and both electron lone pairs act as a hydrogen-bond donor. The existence of more reactive states at the surface of water than in the bulk is supported by ab initio MD studies, and also the prevalence of single-donor and acceptor-only species was supported by the calculations [65]. The structural information about water surface (e.g., water orientation and density) from ab initio MD agrees well with results obtained from classical MD with polarizable force fields [115].

PES studies of the liquid-water surface, using the liquid-water microjet, were reported for valence [64] and core [116] electron emission. Ref [64] discusses the energy shifts of the

valence orbitals with respect to the gas phase when using 60-120 eV photon energies. Solvation causes a mean red shift of about 1.4 eV, yet energy shifts slightly vary for different orbitals. PES values are in good agreement with recent Monte Carlo/density functional theory calculations [117]. Hydrogen bonding interactions are also observed to affect the relative photoionization cross sections of the $\text{H}_2\text{O}_{\text{aq}}$ orbitals.

The inner-shell PES [116] uses photon energies up to 1200 eV to probe the water O1s core photoelectron emission. Depending on the photon wavelength the electrons are emitted either predominantly from H_2O molecules at the surface or in bulk water, corresponding to about 6 Å or 20 Å probing depths, respectively. O1s electron binding energies are identical for the two cases, equal to 538.1 eV (compare Figure 11, top), i.e., 1.8 eV lower than in the gas phase, but a small additional peak at 536.6 eV appears when probing at the larger depth. Ab initio calculations suggest that the overall O1s peak width of 1.67 eV results from a large class of distortions, which lead to flexible hydrogen-bond configurations found in liquid water [116]. The 536.6 eV peak was assigned to distorted tetrahedral configurations with an elongated hydrogen bond at one of the H-accepting sites.

Ionic product of water

According to the textbook knowledge inorganic ions are repelled from the aqueous surface [31-34], while recent simulations and surface selective spectroscopic experiments indicate that some inorganic ions (such as soft anions) exhibit a non-negligible surface propensity [2,4,5,7]. How about the ionic product of water? Whether or not the hydrated proton also favors bulk solvation similarly to other small cations (e.g., alkali ions) is not at all *a priori* clear. Neither is it easy to guess the surface behavior of the small, weakly polarizable hydroxide anion.

On the computational side, a considerable amount of attention has been paid recently to the behavior of the hydrated proton at the air/water interface. Already ab initio and empirical

valence bond calculations for large clusters showed a strong surface preference for hydronium [118-121]. A similar effect was observed for extended aqueous surfaces (slabs) at ambient temperatures by ab initio molecular dynamics [122,123] and MD simulations employing an empirical valence bond scheme [28], [43,78], or a classical force field [9,124]. The H_3O^+ cation is an excellent hydrogen bond donor but a very poor hydrogen bond acceptor due to its formal positive charge on oxygen (in reality, the oxygen atom bears a negative partial charge, however, much smaller than that on water oxygen). Hydronium has been, therefore, called an amphiphilic ion [28]. As demonstrated in Figure 4 it disrupts hydrogen bonding in the aqueous bulk but can be very well accommodated at the surface with three donor hydrogen bonds toward water and oxygen protruding into the vapor phase [9,15,28].

Fewer calculations than for hydronium have been performed for hydroxide concerning its behavior at the air/water interface. Classical and ab initio molecular dynamics simulations show that OH^- prefers to be solvated in the aqueous bulk [9,122,123]. Opposite to hydronium, hydroxide is an excellent hydrogen bond acceptor but a poor hydrogen bond donor. For this reason it can occasionally be found at the aqueous surface with a hydrogen bonded oxygen, while hydrogen is dangling into the vapor phase [9]. This effect seems to be stronger in clusters [125] or at the water/hydrophobic wall interface [126,127]. Nevertheless, OH^- disrupts hydrogen bonding in bulk water much less than H_3O^+ , therefore, it favors bulk solvation and does not exhibit a surface peak at the extended air/water interface [9,122,123].

Once the surface propensities of hydronium and hydroxide ions are quantified, one can attempt to evaluate the pH and pOH of the surface layer of neat water. Strictly speaking, pH expressed in terms of proton activity should be constant across a 3D sample in chemical equilibrium. In order to underline surface accumulation of hydronium (but not of hydroxide) and chemical consequences thereof, pH (or pOH) of the two-dimensional surface layer was defined and evaluated as the negative logarithm of H_3O^+ (or OH^-) surface concentration.

Using a combination of ab initio and classical molecular dynamics the topmost layer of water was shown to be acidic with pH smaller than 4.8 and pOH \sim 7.7-8.4 [122,123].

Several experimental investigations of the excess proton at the liquid water interface were reported [11,15,128]. Arguably the clearest picture has emerged from the VSFG study of HCl and NaOH aqueous solutions as a function of concentration [11]. Protons were concluded to be found throughout the interfacial region including the top water layer, and these observations are consistent with both the Eigen and Zundel form. In the Eigen form the oxygen is suggested to point towards the vapor phase. The situation for OH⁻ is not as clear. Here the changes in the VSFG spectrum compared to neat water are relatively small, indicative of some additional randomization of water molecules, with the same coordination as found in the bulk. Whether or not OH⁻ exists at the top layer remains elusive within VSFG. In an SHG study [15], which compares the surface concentration of iodide for different aqueous solutions, HI, NaI and KI, the largest interfacial iodide concentration is found in the presence of H⁺. This is suggestive of an enhanced surface concentration of hydronium compared to alkali cations. Enhanced surface concentrations of hydronium but not of hydroxide were also revealed from H-D isotopic exchange IR measurements on cryogenic ice nanocrystals with disordered (amorphous) surface and sub-surface [122,123].

In a PES study analogous to the aforementioned investigation of neat water the valence photoelectron spectra of HCl, HNO₃ and NaOH aqueous solution/vapor interfaces (in the 2-4 m concentration range) were measured at 100 eV photon energy [128]. Representative spectra are shown in Figure 6 for 3m HCl and NaOH aqueous solutions. Subtraction of the neat water spectrum reveals the experimental first ionization potential (IP) of OH⁻ at 9.2 eV, and the second lowest IP of H₃O⁺ at 20 eV; no accurate value for the first IP of hydronium could have been obtained due to strong spectral overlap with water features. From comparison with complementary electronic structure calculations, based on combined molecular dynamics and ab initio methods, it was concluded that the experimental energies are in better agreement

with calculations, which assume an Eigen rather than a Zundel core [128]. The calculated energies for the Eigen form are shown in the top-left spectrum of Figure 6. Apparently, the PES technique is specific to the structure of the hydrated proton, suggesting that the changes observed in the VSFG spectra of ref [11] are also most likely due the Eigen form. Note that the probing depth in the PES experiment of ref [128] is less than 10Å.

Unlike the above results of surface selective spectroscopies and unlike surface tension measurements, which support the computational prediction of accumulation of hydronium but not hydroxide in the topmost layer of water, there are several macroscopic measurements which seem to be at odds with the calculations. These concern zeta potential measurements of oil droplets and air bubbles in water, titration experiments for oil suspensions in water, and measurements of disjoining pressure of thin aqueous films [129-136]. For all of these systems the macroscopic measurements were interpreted in terms of accumulation of negative charge at the aqueous surface or interface. While in these experiments direct molecular characterization of the surface charge is hardly possible, the titration curves and other indications suggest OH⁻ as the negatively charged species.

It is probably too early to fully rationalize the seeming controversy about the polarity and nature of the charge at the surface of water; nevertheless, some plausible speculations can be made. The surface neutrality condition requires that any charge that accumulates at water surface must be compensated within the interfacial layer by opposite charge. As schematically displayed in Figure 7, if H₃O⁺ accumulates at the surface, there must be compensating OH⁻ in the subsurface and *vice versa*. MD simulations provide a picture with atomistic resolution of both the topmost and subsurface layers, the trade-off being the use of a finite number of water molecules in a periodically repeated cell, which interact via an approximate potential. Surface selective spectroscopies, such as VSFG and SHG probe experimentally the whole interfacial layer with bias on the most anisotropic parts. Photoelectron spectroscopy allows tuning the probing depth from about 0.5 to 1-2 nm by changing the radiation wavelength. Macroscopic

surface tension, zeta potential, and disjoining pressure measurements provide an integrated information for the whole interfacial layer the width of which is not precisely known. Moreover, many of the latter measurements involve an additional buffer or water/oil instead of water/vapor interface. It is possible that the above techniques are sensitive to different parts of the interfacial layer, hence yielding different results. More work clearly has to be done both on the side of calculations and experiments in order to resolve this issue.

3. Protein/water interface

3.1 Interfacial or local ion behavior?

Switching from the vapor/water to the protein/water interface requires a radical leap of thought since a protein molecule is anything but a vapor phase. Nevertheless, the picture of a protein as sphere of a low dielectric constant (possibly with a smeared charge) has been repeatedly invoked and is relatively common [48-50]. Within this model, depicted schematically in Figure 8a, the interface between a large globular protein and an aqueous solution should resemble that between vapor and the same solution, with the interfacial tension in the former case playing the role of surface tension in the latter case. In the following we explore this analogy by comparing data from MD simulations and experiments concerning ionic behavior at these two interfaces.

Electrostatic interactions are crucial in many processes involving proteins, a detailed discussion of which goes beyond the scope of the present review (we refer the interested reader to a very recent review on this topic [137]). The focus of the present discussion is on the behavior of ions at the protein/water interface. Ions are known to influence solubility and stability of proteins in aqueous solutions (salting-in and salting-out), the effect being highly ion specific [53]. The lyotropic (Hofmeister) series, which orders common ions according to their ability to salt-out proteins, has been traditionally rationalized in terms of interactions of ions with water [138]. According to this picture, strongly hydrated ions (kosmotropes)

organize several layers of water molecules around themselves and effectively ‘steal’ water from the protein hydration shell. In contrast, weakly hydrated ions (chaotropes) do not exhibit this effect. However, the notion of ion-induced long-range water ordering has been challenged recently both by experiments and simulations [139]. A new paradigm is emerging in which the direct ion-protein interactions are dominantly responsible for the specific ion effects (for a recent review see ref [59]).

Within the present discussion of a “generic” protein surface we leave aside ions such as polyvalent metal cations, which are functional for a given protein and are strongly bound at very specific sites. We focus rather on common monovalent ions (e.g., alkali cations or halide anions), which are usually thought of as merely defining the ionic strength of a solution. The direct ion-protein interactions in aqueous solutions of these ions have been probed computationally in the last couple decades [122,123,140-143].

Sodium and potassium are the two most abundant cations in living organisms. Almost all cells maintain at a large energetic cost a sizable concentration gradient between the cytosol, which is rich in potassium and poor in sodium, and the extracellular fluid, where the situation is reversed [144]. Do these two ions interact directly with protein surface and if so, is there any ion specificity? MD simulations performed for a set of proteins in aqueous mixtures of NaCl and KCl indeed show an affinity of alkali cations to protein surface which is about twice as strong for Na⁺ than for K⁺ [58]. In contrast, chloride exhibits very little affinity for the surfaces of the investigated proteins. Among other ions that have been investigated by MD simulations, e.g., choline and sulfate are strongly attracted to protein surface [57].

When comparing the behavior of the above ions at the protein/water and air/water interface we see a striking difference. For example, sodium, potassium, choline, and sulfate are all repelled from the open water surface but they all show (to varying degree) an affinity for the protein/water interface [145]. Moreover, calculations show that the interaction of these ions with protein surface is of a local nature. Namely, the cations are primarily attracted by

negatively charged moieties such as the COO^- groups in the side chains of glutamate and aspartate and the amide oxygens of the backbone, while sulfate exhibits an affinity to the positively charged groups in the side chains of lysine and arginine [57]. This suggests a very different picture of ion-protein interactions than proposed before [59]. This molecular picture is shown schematically in Figure 8b. The dielectric similarity between the air/water and protein/water interface is of little use here since the ion-protein behavior is dominated by local interactions with charge and polar groups at the protein surface in the presence of explicit water molecules rather than by the average dielectric properties of the protein (which are relevant mainly for the protein interior where the ions rarely penetrate) and water. The only exception might be large polarizable monovalent ions which could exhibit similar affinity to the air/water interface and to hydrophobic parts of the protein surface, primarily due to polarization effects.

If the local ion-protein interactions are of prime importance for ion segregation at surfaces of hydrated proteins then, to a first approximation, reductionism can be invoked. In particular, if we understand how different ions interact (pair) in water with individual (terminated) amino acids or even with their charged side chain groups we can obtain at least a rough picture of their segregation at a protein surface. MD simulations and ab initio calculations indeed indicate that the ion affinity to these building blocks translates semiquantitatively to the ion-protein interactions [58]. Moreover, the empirical rule of matching water affinities stating that an ion pairs most efficiently with an oppositely charged ion of roughly the same hydration enthalpy (or simply size) seems to hold very well [51,146].

3.2 Model systems suitable for experiment

Given the complexity of biologically relevant interfaces in an aqueous environment it is important to design model systems for detailed experimental investigations of interactions with ions. As argued above, in order to describe the protein/water interface at the molecular

level we must understand the local interactions among the constituent molecules themselves, and between a single constituent molecule and the surrounding water molecules. Thus, we have to understand how water molecules solvate and ions interact with amino acids or short peptides. Also, as many biological processes are driven by pH changes or are influenced by the presence of ions, these effects are important to be studied in the experiment.

Atomic structure of proteins, amino acids, and other biomolecules in bulk aqueous solution has been inferred to a large part from nuclear-magnetic-resonance (NMR) spectroscopy; see e.g., ref [147] Chemical shifts allow, e.g., to resolve most protons in many proteins, and by NMR it is possible to identify a particular chemical group under different conditions, including a particular charge or conformational state.

Only few electronic structural studies of aqueous biomolecules, in fact of any larger molecules in aqueous solution, were reported to date. Most notable are recent nitrogen K-edge XA investigations of amino acids and dipeptides in aqueous solution [148,149] as a function of pH. Thanks to the high sensitivity of the method to local hydration environment evidence was provided that for a neutral α -amino group the two hydrogen atoms do not participate strongly in H-bonding with the surrounding water molecules. Such incomplete hydration is likely to be common in various amino acids.

Experimental reports on biological or biologically relevant molecules at the aqueous solution interface are also scarce. Leucine adsorption at the air/water interface was studied as a function of concentration and pH using VSFG spectroscopy [150]. The highest surface activity was found for near-neutral solutions, i.e., for zwitterionic leucine. At the saturated surface density, the molecules take an upright position. Protonation of the carboxylic group causes changes in the overall molecular orientation. Also, the interfacial water structure can be quite significantly disordered depending on charge state. Namely, in the zwitterionic form water molecules in close proximity reorient according to the local charges. The situation is

illustrated in Figure 9, which shows all three different charge states. A similar VSFG study was reported for monolayers of various amino acids at the $\text{CCl}_4/\text{D}_2\text{O}$ interface [151].

In this context it is interesting to also mention studies on the surface behavior of two alkyl-chain surfactant molecules, octadecylamine (ODA) [152] and N-dodecylimidazolium (DIm) [153], in aqueous solution. Alkyl chains are frequent building units in biological systems, and hence their solvation behavior as a function of head-group type and pH, or in the presence of ions (Hofmeister effect) is of fundamental interest. The specific relevance of DIm from a biological point of view is described in ref [153]. Based on MD techniques the authors observe that the original balance between bulk and surface solvation forces disappear when the neutral species is being protonated and the charged surfactant is dragged into the bulk solution. Importantly, the tail segment remains in contact with the surface, preventing complete solvation.

A recent VSFS study of the surfactant ODA in water has focused on the role played by salt ions in disordering the alkyl chains [152]. The authors report on the ability of certain ions to salt-out this species from aqueous solutions, and find good agreement with the Hofmeister ranking. Specifically, the structural order/conformation of the ODA monolayer is observed to decrease in the sequences $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{Br}^- > \text{I}^- > \text{ClO}_4^- > \text{SCN}^-$, which is related to the ability of individual anions to penetrate into the alkyl chain portion of the monolayer, thereby disrupting the hydrocarbon packing.

Other studies have explored, e.g., water inside and outside of micelles. Here, a layer of surfactant molecules surrounds and confines a core of water, with the hydrophobic end protruding to the exterior solvent. In the case of ionic surfactants an important question arises whether the counter ions accommodate at the surfactant-water interface or if they penetrate deeper into the surfactant layer. A recent study, presenting mid-infrared ultrafast pump-probe spectroscopic data for such systems, highlights the issue and points to ion specificity [154].

Photoemission experiments for biologically relevant molecules and molecular ions in aqueous solution are only now being conducted. The only study so far concerns the interface of lysine in water [155], aimed at understanding local structural changes associated with protonation/deprotonation. Here, photon energies in the 400-600 eV range were applied to measure the nitrogen 1s and carbon 1s core-level photoelectron spectra of 3m lysine aqueous solutions at different pH values, i.e., as a function of charge state of the two amino groups. Figure 10 shows the N1s photoelectron spectra obtained at the pH values of 13, 9.5, and 5.5, using an excitation photon energy of 480 eV, which probes the nitrogen atoms within $<10\text{\AA}$ interfacial depth. The x-axis in the figure presents electron binding energies. The occurrence of single photoelectron peaks at pH 13 and 5.5 is consistent with the corresponding mole fractions, showing that more than 99% of all lysine molecules exist in the anionic form (both amino groups are neutral), and more than 99% of the molecules adopt the two-site protonated cationic form (both amino groups are protonated), respectively. Near pH 9.5 about 70% of all lysine molecules are in the zwitterionic form, where only the side-chain amino group is protonated. This explains the occurrence of single N1s peaks at the high and low pH (top and bottom spectra), but the appearance of two peaks for the mixed situation (middle spectrum).

Interestingly, in the anionic form a single N1s binding energy of 404.3 eV is observed, in spite of the presence of different local environments. The higher N1s energy of , 406.5 eV of the protonated amino group results from the Coulomb attraction between the photoelectron and the additional positive charge at the nitrogen site. One also observes a small N1s red shift by about 0.2 eV for the unprotonated amino group at pH 9.5 as compared to pH 13, which probably results from minor rearrangement of the solvation shell. Protonation also affects the binding energies of the carbon atoms adjacent to the amino groups. Although C1s chemical shifts are relatively small (about 0.3 eV) they can be used to identify the spectral contributions of specific carbon atoms. This provides a valuable calibration for theoretical calculations of the electronic structure of aqueous amino acids. Current systematic PES studies of a range of

amino acids, including side groups, such as aromatic imidazole [156], explore the effect of pH on the interfacial solution structure. A most recent photoemission experiment reports on the acid/base equilibria at the liquid-vapor interface of an aqueous solution of hexylamine [157]. This study exploits the high surface sensitivity PES can achieve, and demonstrates the large potential of the technique when studying surfactant monolayers at concentration as low as 0.005M [19].

We conclude with a remark on the feasibility of PES to distinguish water molecules in different environments. In section 2.4 the sensitivity of the water O1s binding energy to different $\text{H}_2\text{O}_{\text{aq}}$ hydrogen-bonding configurations was mentioned. It should be feasible to use the same O1s “chemical shift” to distinguish water in other environments, such as electrolyte solutions or water confined at pockets of a protein surface. A related issue concerns changes of the amino acids carboxylic groups ($-\text{COO}^-_{\text{aq}}$) in liquid water, e.g., in the presence of ions. This is illustrated in Figure 11, which contrasts the O1s PE spectra of a 4m Na-acetate solution, at pH 9.3 and pH 3, to the PE spectrum of pure liquid water. The three spectra were measured at 600 eV photon energy, which corresponds to high surface sensitivity (see section 2.4). The O1s signal from deprotonated acetate gives rise to a peak at 536.3 eV BE, well separated from the O1s peak of the water molecules (538.1 eV [116]). Protonation of the carboxylic group causes a 0.8 eV blue shift. Future experiments will exploit this sensitivity to examine site-specific changes.

4. Summary

Inorganic ions play a much more active role at aqueous interfaces than traditionally thought. Here, we have reviewed latest computational and experimental studies concerning ions in two interfacial environments: the open surface of water or electrolyte solution and the protein/aqueous solution interface. In the first part, behavior of ions at water surface is compared to that at surfaces of polar non-aqueous liquids. It is also demonstrated that not only

large polarizable anions but also hydronium cations segregate to the water surface. This makes the interfacial layer of neat water very special in terms of surface acidity.

In the second part, the possible analogy between the air/water and protein/water interfaces is explored. In terms of ion segregation little correspondence between these two interfaces is found. Instead, local pairing between ions from the solution with charged or polar amino acid side chains at the protein surface provides a starting model for rationalizing specific ion-protein interactions. Within such a reductionist's approach solvation of individual amino acids or functional groups and their interaction with ions in water was investigated both experimentally and computationally.

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Figure Captions

Fig. 1: Density profiles, i.e., distributions of iodide, sodium, and solvent molecules from the center of the slab across the solution/vapor interface into the vapor phase for water and the three other investigated non-aqueous polar solvents.

Fig. 2: Typical snapshots of the slab surface from molecular dynamics simulations of sodium iodide in water, formamide, liquid ammonia, and ethylene glycol.

Fig. 3: Schematic visualization of the shift z_{shift} between the position of iodide and the center of mass of its first solvent shell, and distributions of z_{shift} across the slab for the four investigated NaI solutions.

Fig. 4: Schematic hydrogen bonding patterns of H_3O^+ at the surface (a) and in the aqueous bulk (c). A tetracoordinated water molecule is also depicted (b). Reprinted with permission from ref [16] Copyright 2005, American Chemical Society.

Fig. 5: A representative snapshot of a water slab with a hydronium cation at the surface and hydroxide anion in the bulk.

Fig. 6: Photoelectron spectra of HCl and NaOH solutions, compared to that of neat water. Hydrated H_3O^+ and OH^- ions are graphically displayed. Adapted from ref [128]

Fig. 7: A schematic picture of the distribution of hydronium and hydroxide ions across the water/vapor interface.

Fig. 8: Graphical illustration of two different approaches to ion-protein interactions. a) Protein as a dielectric sphere with a smeared charge in a continuum solvent (water) with ions. b) Explicit all atom representation of the protein with charged and polar surface groups and water with dissolved ions.

Fig. 9 (left) Sum-frequency vibrational spectra of the air/water interfaces with and without adsorbed leucine. (right) Different orientations of interfacial water molecules depending on charge state of the amino acid. The circles stand for the hydrophilic

part of leucine molecules. Reprinted with permission from ref [150]. Copyright 2004, American Institute of Physics.

Fig. 10: N1s photoelectron spectra of 0.5 m aqueous lysine solution at different pH values, measured at 480 eV photon energy. Adapted from ref [155].

Fig. 11: Measured O1s photoelectron spectra and Gaussian fits for neat liquid water, as well as for 4m and 3m sodium acetate aqueous solutions at pH 9.3 and pH 3.0. The O1s binding energy of liquid water is 538.1 eV [116], while it amounts to 536.3 and 537.1 eV for the deprotonated and protonated carboxylic group, respectively.

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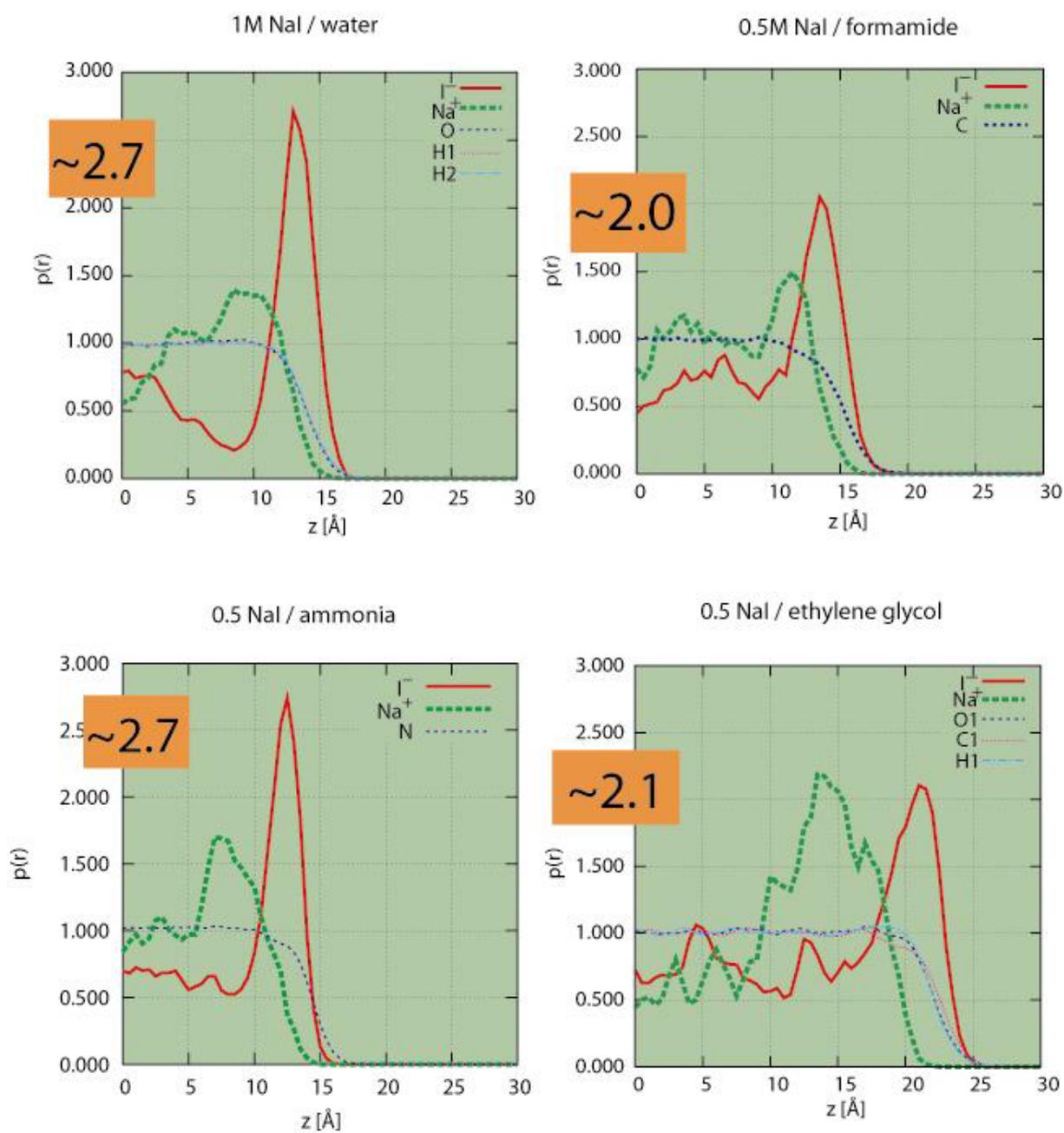


Figure 1

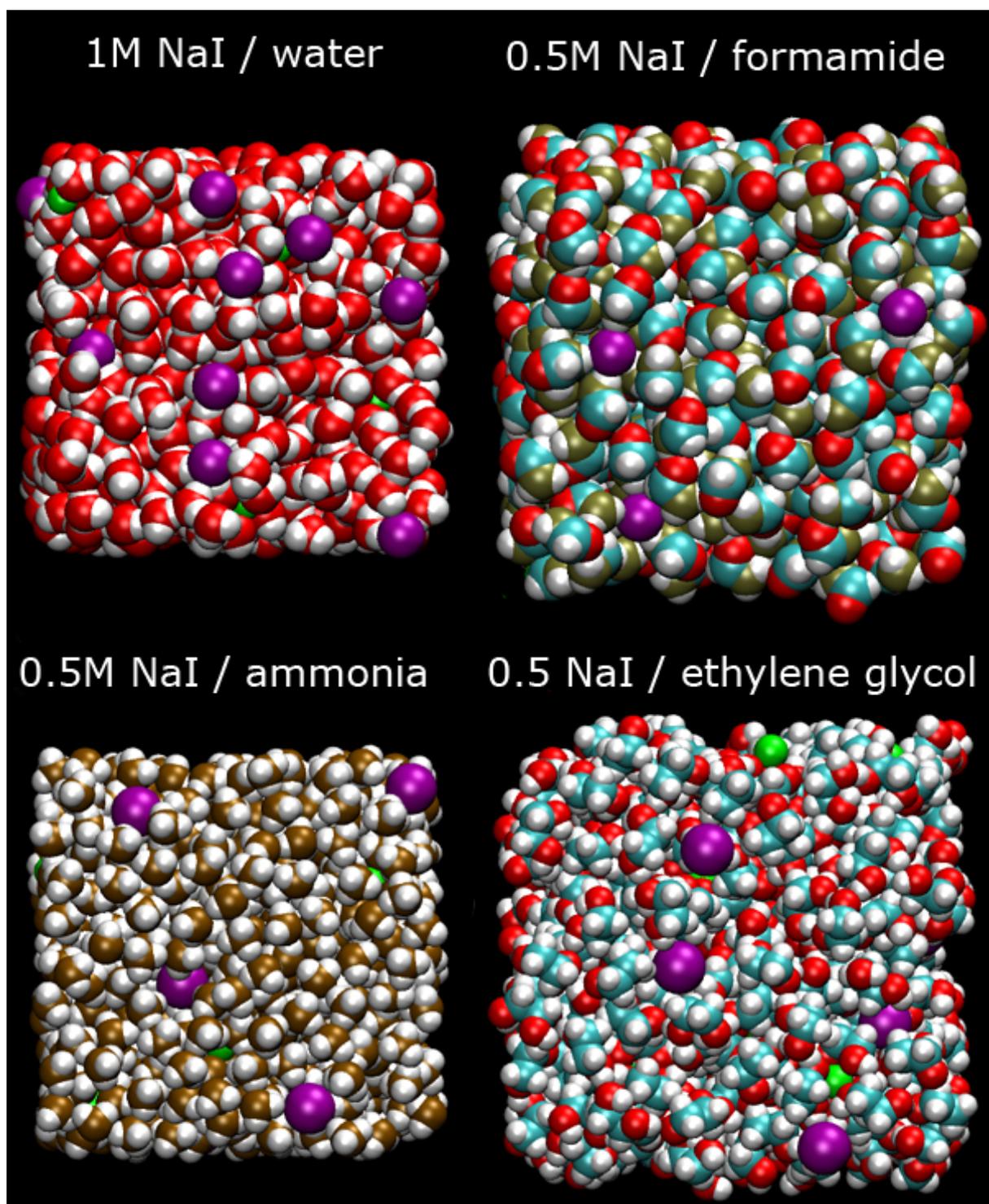


Figure 2

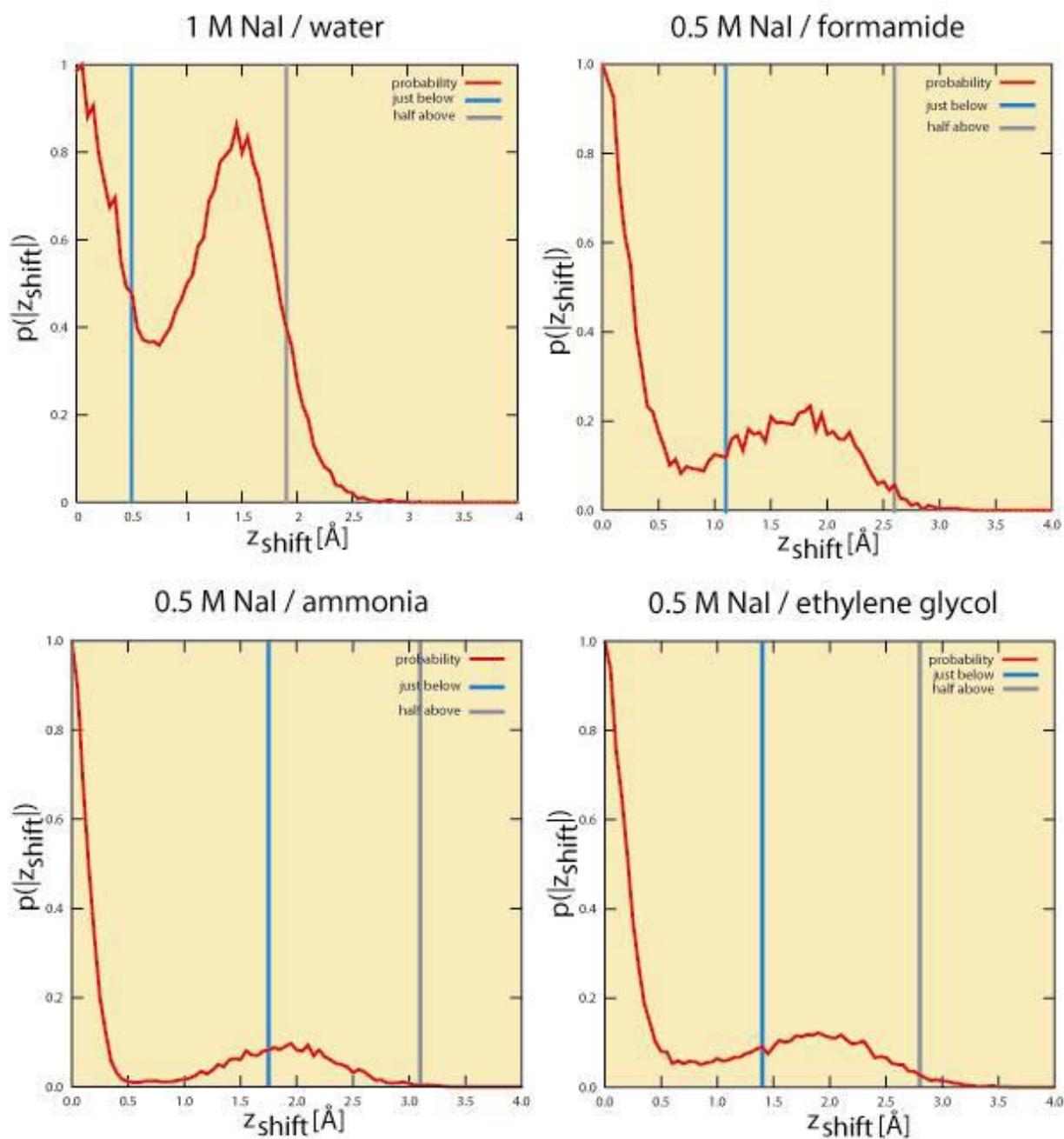
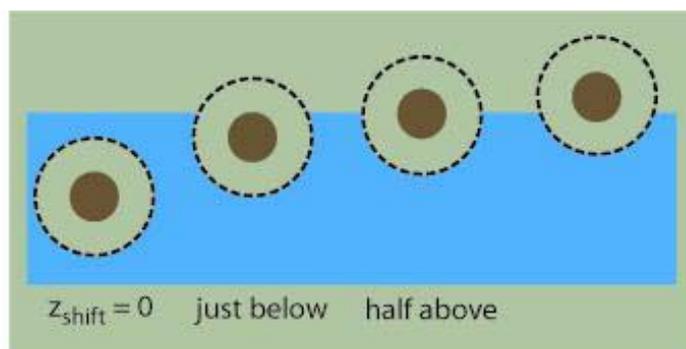


Figure 3

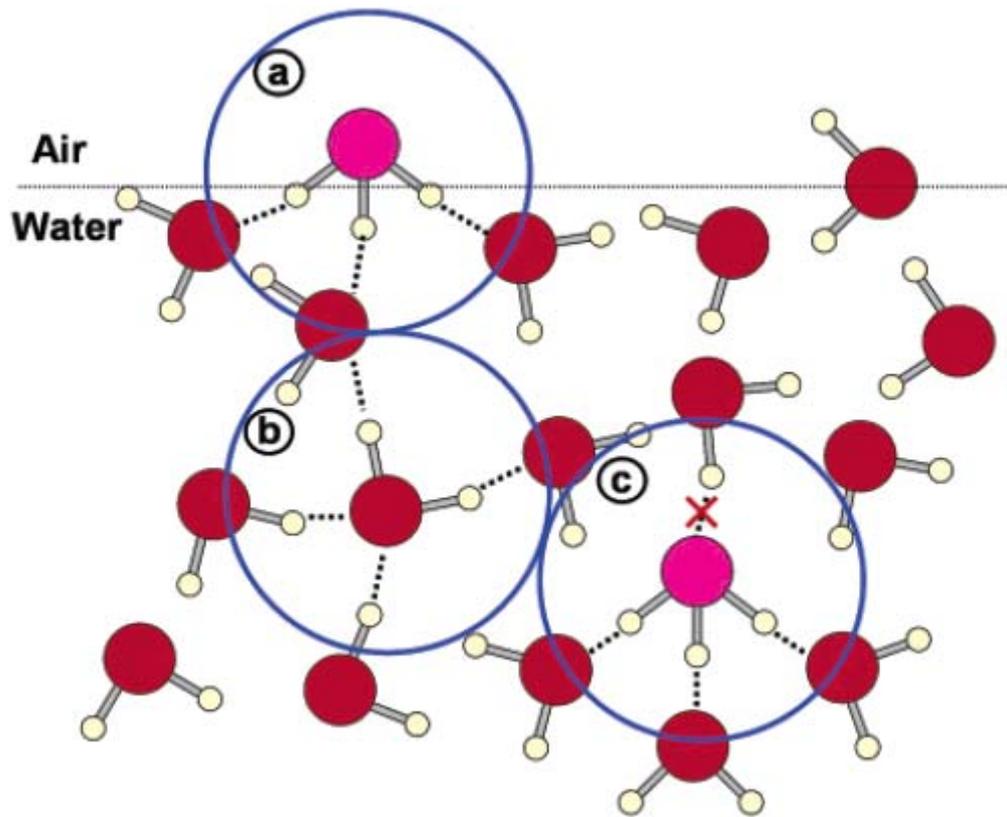


Figure 4

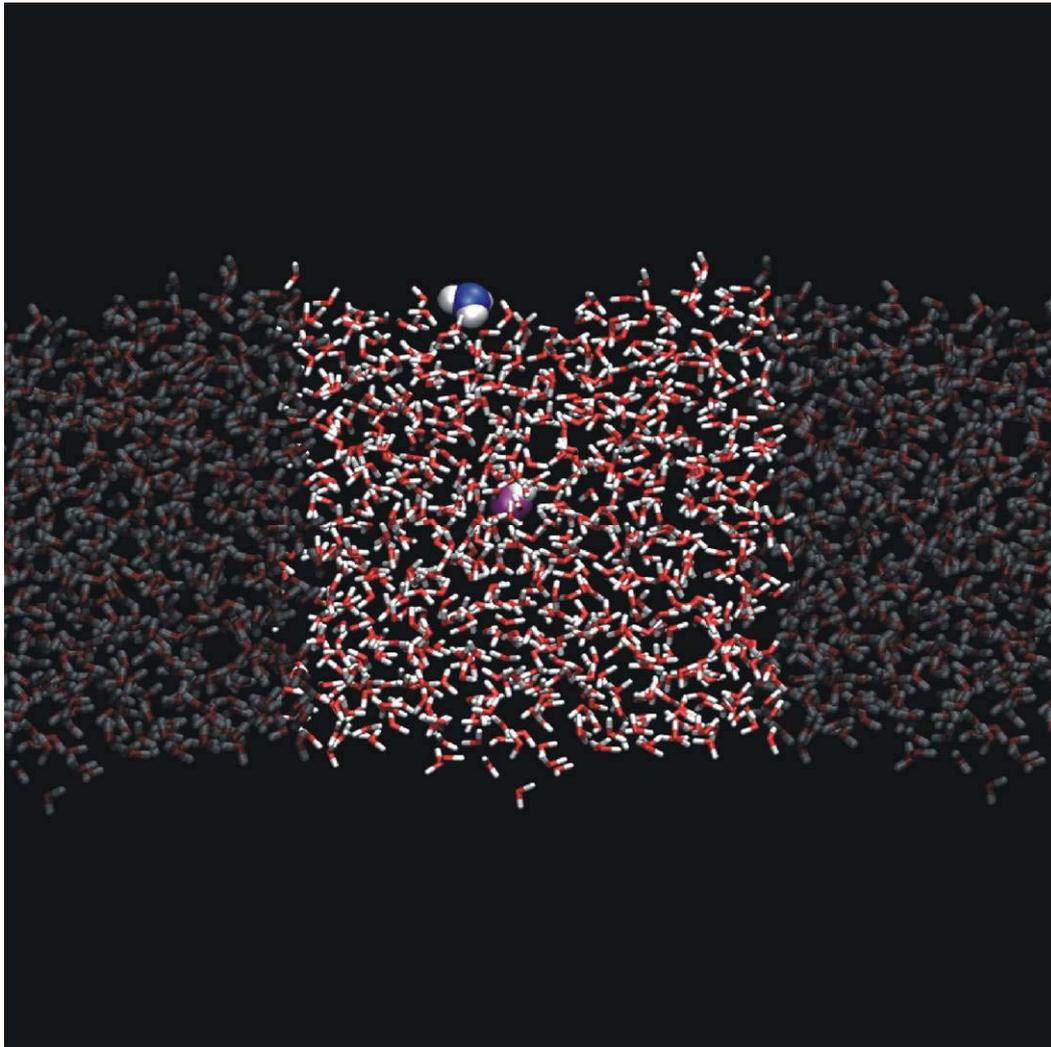


Figure 5

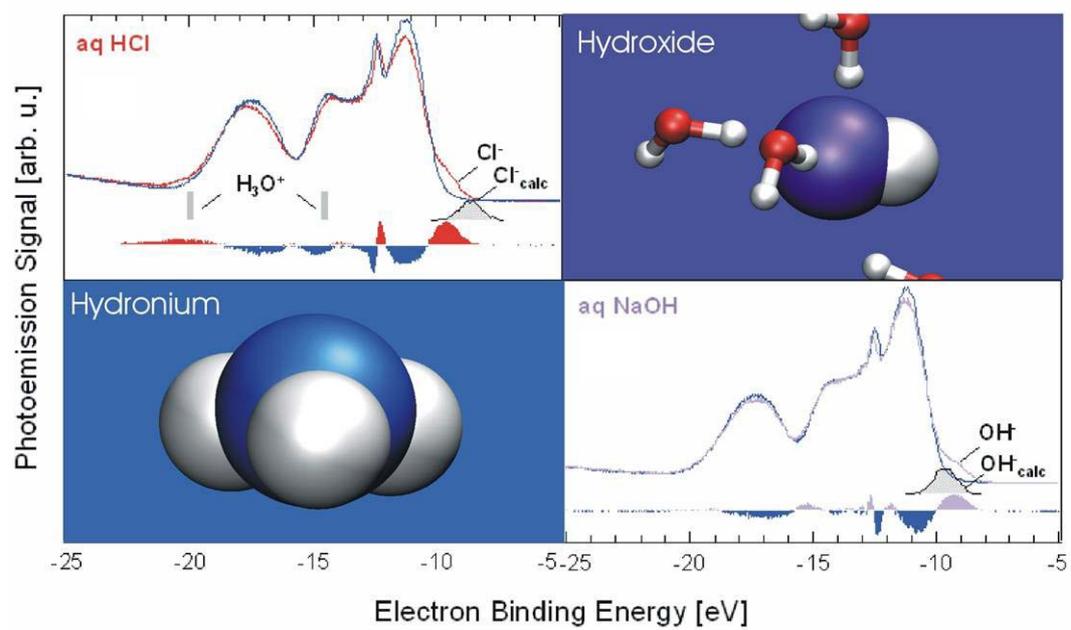


Figure 6

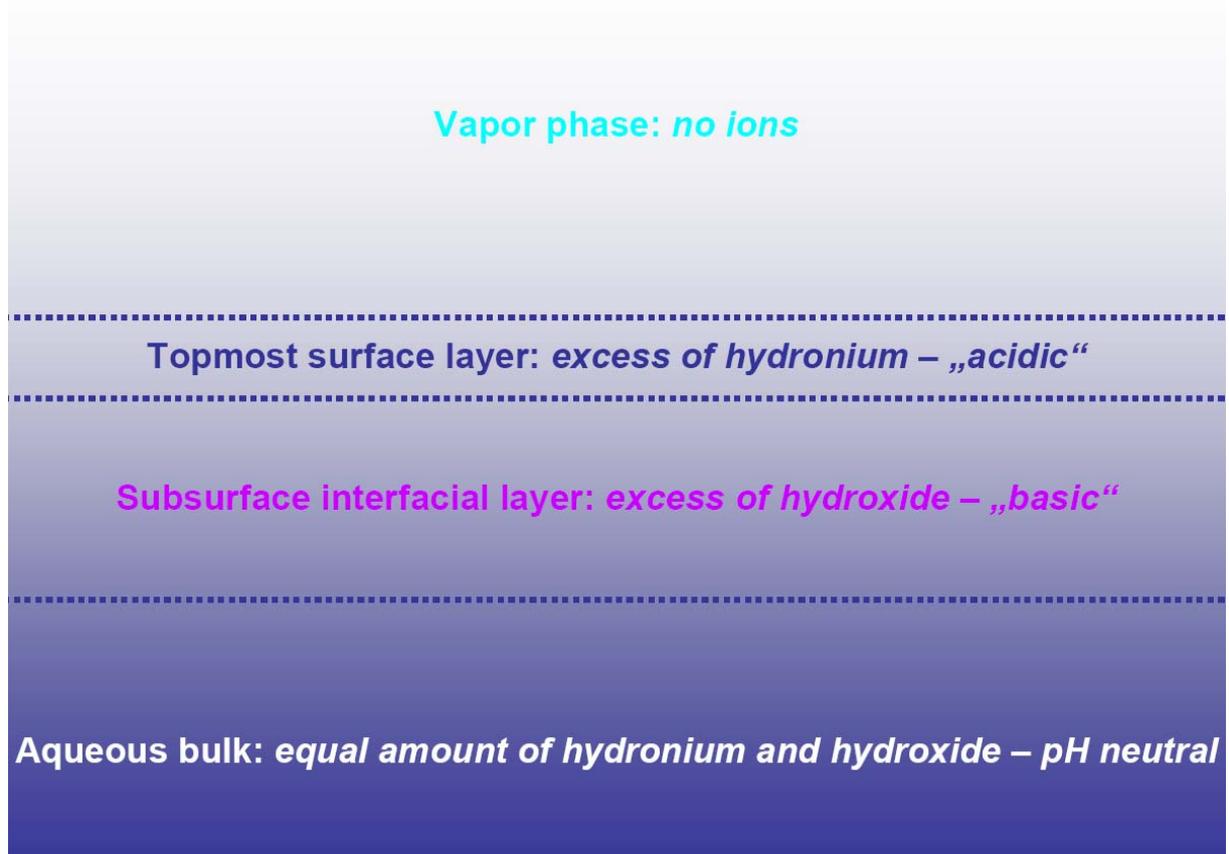


Figure 7

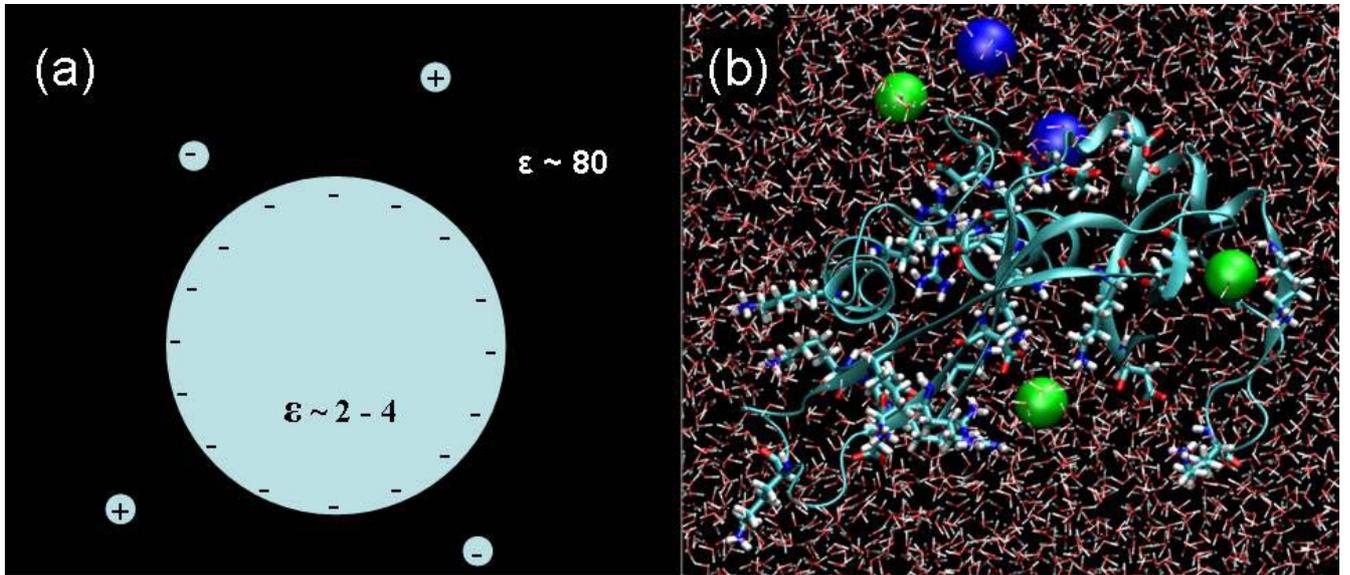


Figure 8

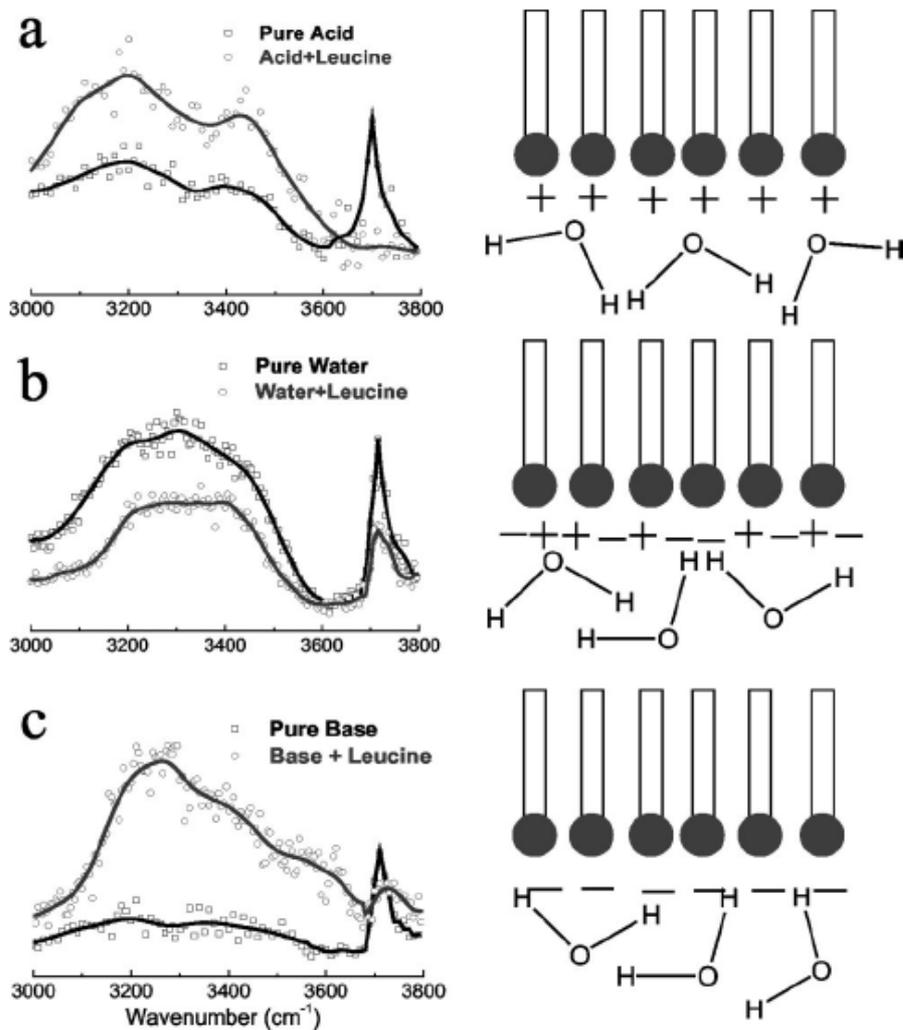


Figure 9

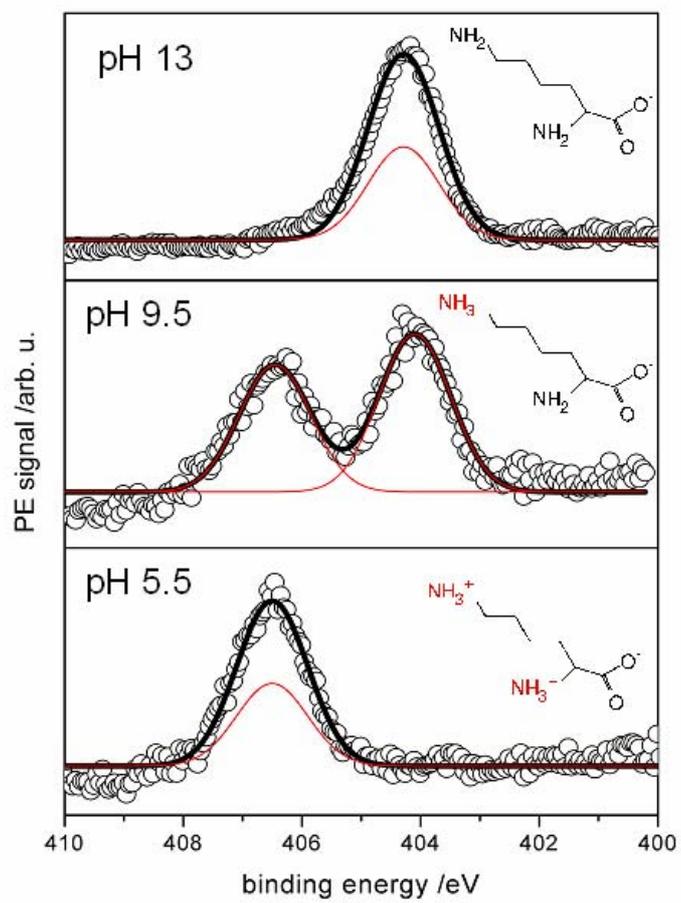


Figure 10

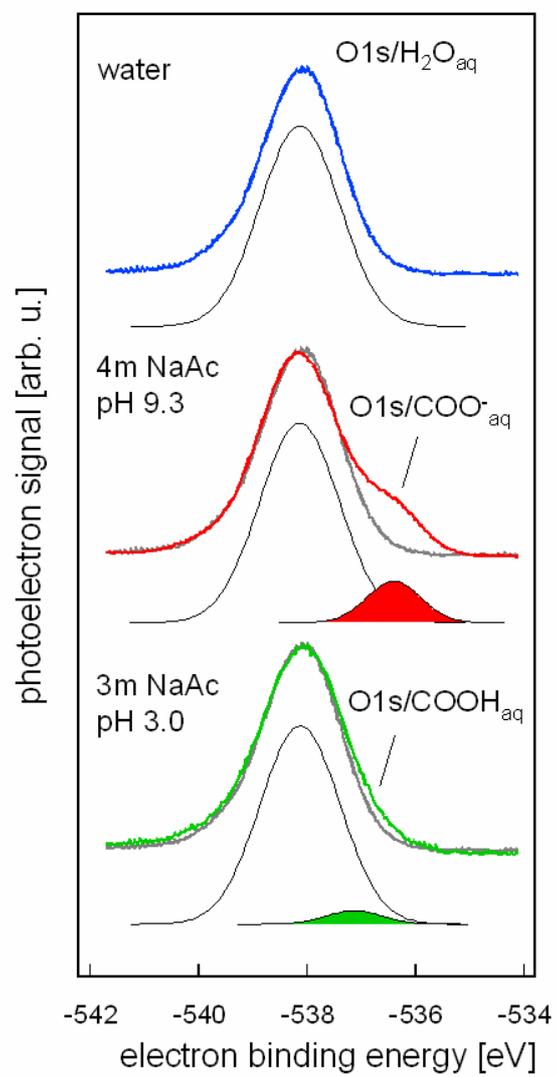


Figure 11