



Akademie věd České republiky

Teze disertace  
k získání vědeckého titulu "doktor věd"  
ve skupině věd chemických

## **Ions at the Air/Water Interface**

Komise pro obhajoby doktorských disertací v oboru fyzikální chemie

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Pracoviště uchazeče: Ústav organické chemie a biochemie AV ČR

Místo a datum: Praha, 16. 10. 2007

## Resumé

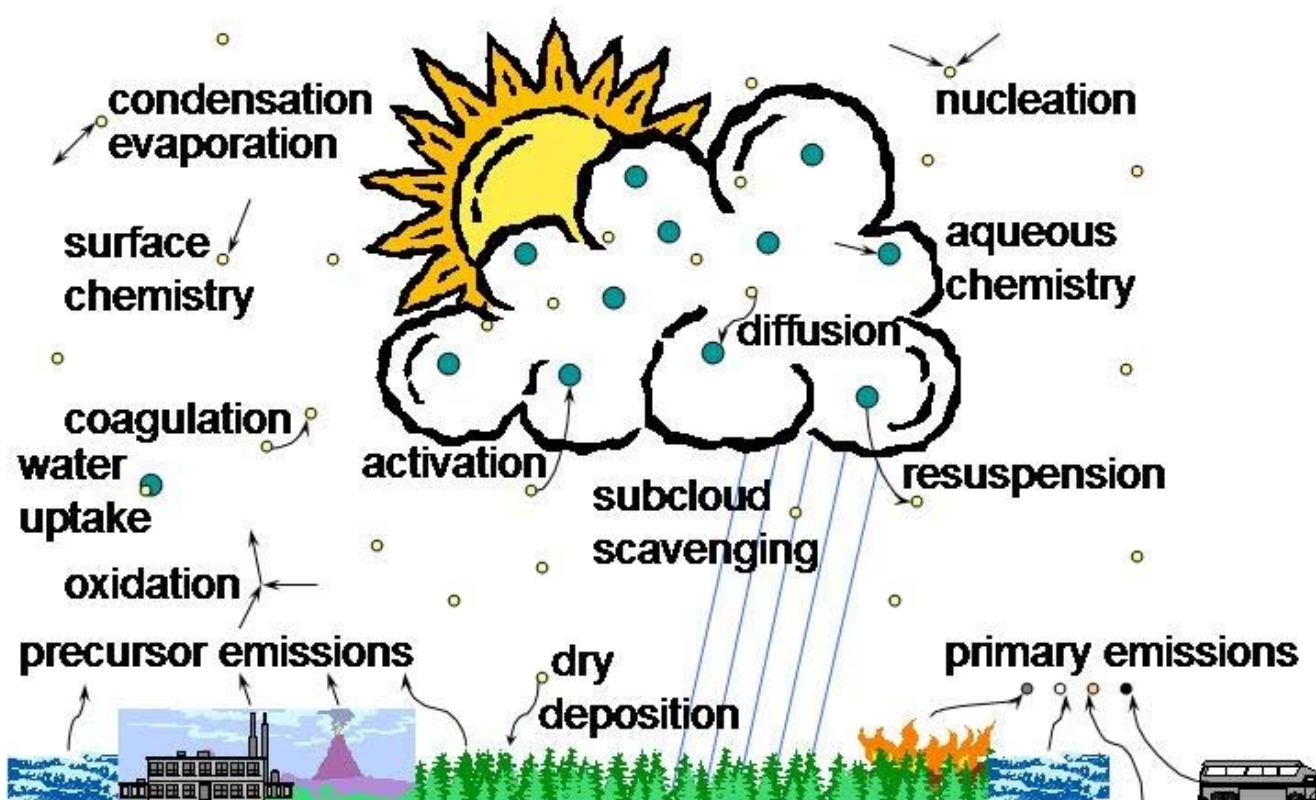
Předkládaná disertace shrnuje autorovy výpočetní studie chování iontů na vodných površích. Původní inspirace k této práci vzešla z měření reaktivity aerosolů mořské vody ve znečištěné přímořské atmosféře. Tento jev se podařilo vysvětlit pomocí povrchových reakcí na těchto aerosolech, což nás ale zároveň přivedlo do rozporu s Onsagerovou teorií povrchů elektrolytů. Podle ní jsou inorganické ionty z povrchu solných roztoků odpuzovány a svrchní monomolekulární vrstva se skládá z čisté vody. Naše molekulově dynamické výpočty ukázaly, že situace je složitější. Tvrdé (nepolarizovatelné) ionty, jako např. alkalické kationty či flór se skutečně chovají podle Onsagerova modelu. Měkké (polarizovatelné) ionty se ale na povrchu vody vyskytují a mohou se tak účastnit povrchových chemických reakcí. Některé ionty (např. bromid, iodid, či hydroxoniový kation) se dokonce na vodním povrchu akumulují. Naše teoretické předpovědi, poprvé zveřejněné v r. 2000, jsou v posledních pěti letech potvrzovány řadou povrchově citlivých spektroskopických měření.

Disertace se skládá z 40 původních, 2 zvaných a 2 přehledných článků a 3 knižních kapitol, týkajících se problematiky iontů na rozhraní voda/vzduch. Tyto práce lze rozdělit do pěti podskupin. První zahrnuje články zaměřené na atmosférické aplikace iontů na slaných kapkách. Druhá skupina podává moderní fyzikálně-chemický obraz povrchu elektrolytů, založený na molekulově dynamických simulacích. Třetí skupina publikací rozšiřuje problematiku na povrchovou hydrataci organických iontů. Fázových přeměn (krystalizace, mrznutí) v slaných roztocích a vlivu povrchu se věnují články ve čtvrté skupině. Konečně pátá skupina zahrnuje studie vodných klastrů s ionty, které slouží zejména jako modelové systémy.

Soubor publikací je doplněn úvodem, které podává autorův subjektivní pohled na problematiku s cílem „vtáhnout čtenáře do děje“, krátkým komentářem k jednotlivým publikacím, shrnujícím závěrem a krátkým seznamem literatury.

## Introduction

The original inspiration for our molecular dynamics studies of ions at the air/water interface came from experimental investigations of atmospheric aerosols. Aerosols are natural or anthropogenic particles suspended in the atmosphere. These particles are either solid (e.g., soot, dust, salt, and ice particles) or liquid (water droplets and aqueous sea-salt aerosols), with typical sizes ranging from 100 nm to several millimeters<sup>1</sup>. Figure 1 schematically depicts processes involving atmospheric aerosols.



**Fig. 1:** Schematic picture of processes involving atmospheric aerosols (courtesy of D.

Dabdub from UC Irvine).

The role of aerosols in the physics of cloud formation is relatively well recognized and appreciated<sup>2</sup>. In a nutshell, solid microparticles of soluble salts, such as sulfates, nitrates, or chlorides, serve as cloud condensation nuclei, on which droplets are formed, while ice

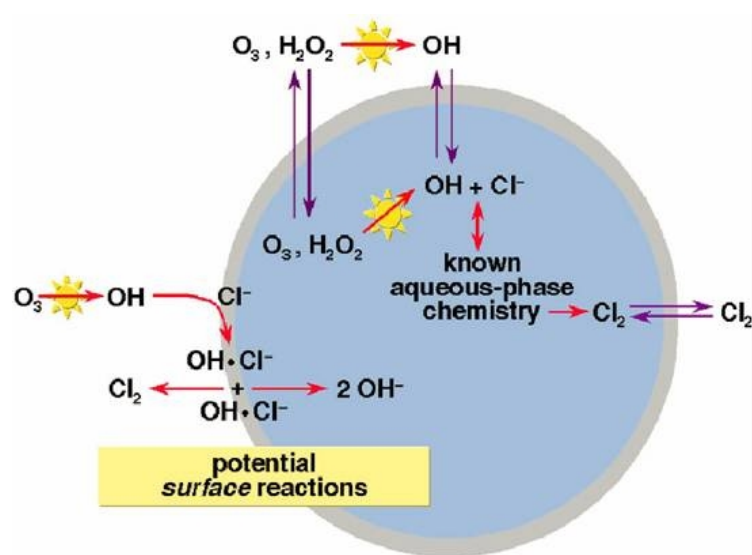
particles grow on mineral dust (clay) aerosols. Aerosols also play an important role in the global radiative balance<sup>1</sup>. In a direct way, they reflect and scatter the incoming solar radiation. Indirectly, their amount and composition influences the cloud coverage and, consequently the Earth albedo. Quantitatively, these effects are not very well established, however, current estimates show that aerosols can reduce by up to 50 % the global warming effect of the greenhouse gases<sup>3</sup>. In polluted areas aerosols represent a considerable health risk and as such are being closely monitored via the so called PM10 and PM2.5 indices, reflecting integral concentration of particles of average sizes of 10 and 2.5 microns<sup>1</sup>. Finally, atmospheric aerosols serve as “reactors” for important chemical processes in the atmosphere. This fact has been largely overlooked until it has been conclusively demonstrated less than two decades ago that heterogeneous halogen chemistry on particles forming polar stratospheric clouds is responsible for the creation of polar ozone holes<sup>1</sup>. Since then, increasing effort has been directed to elucidation of chemical processes occurring on or in atmospheric aerosols.

### **Chemistry on aqueous sea salt aerosols**

While gas phase chemistry can be usually satisfactorily described via rate constants and kinetic equations a much more detailed, molecular picture is required for understanding processes taking place on solid particles and in or on aqueous aerosols. Of particular importance is the surface layer of the aerosols, which comes directly into contact with the reactive gases present in the atmosphere. We cannot hope for understanding the aerosol chemistry without properly describing this interfacial layer and its ability to adsorb atmospheric gases. In this light, it is surprising how little is known at the molecular level about the surfaces of the most ubiquitous and generic atmospheric aerosols, such as aqueous sea salt particles, ice crystals, and water microdroplets.

One of the first heterogenous tropospheric reaction, which has been elucidated at a detailed molecular level, is the production of molecular chlorine from aqueous sea salt aerosols in the presence of ozone and UV radiation<sup>4,5</sup>. A combined experimental and computational study, involving also the author of this proposal, showed that this reaction, which is important for the chemistry of the marine boundary layer, takes place primarily at the air/water interface of the aqueous sea salt particles.<sup>5</sup>

Figure 2 schematically shows the interfacial formation of Cl<sub>2</sub> by a direct charge transfer from chlorides, present in the aerosols, to atmospheric hydroxyl radicals.



**Fig. 2:** Mechanisms of Cl<sub>2</sub> formation from aqueous sea salt aerosols (adopted from Ref. 5).

### Characterization of ions at aqueous surfaces

Aqueous surfaces and interfaces are ubiquitous and play an important role not only in the atmosphere but also in many technological processes (even unwanted ones such as corrosion). The anisotropic and heterogeneous interfacial region is typically only a few molecular diameters wide. While many established techniques exist for characterizing solid surfaces with atomic resolution, the situation is different for liquid aqueous interfaces. Primarily due to surface disorder, capillary waves, and volatility of liquid water, our

knowledge about the detailed molecular structure of these interfaces has been rudimentary until recently. This has changed, however, within the last decade thanks to molecular simulations and modern spectroscopic techniques.

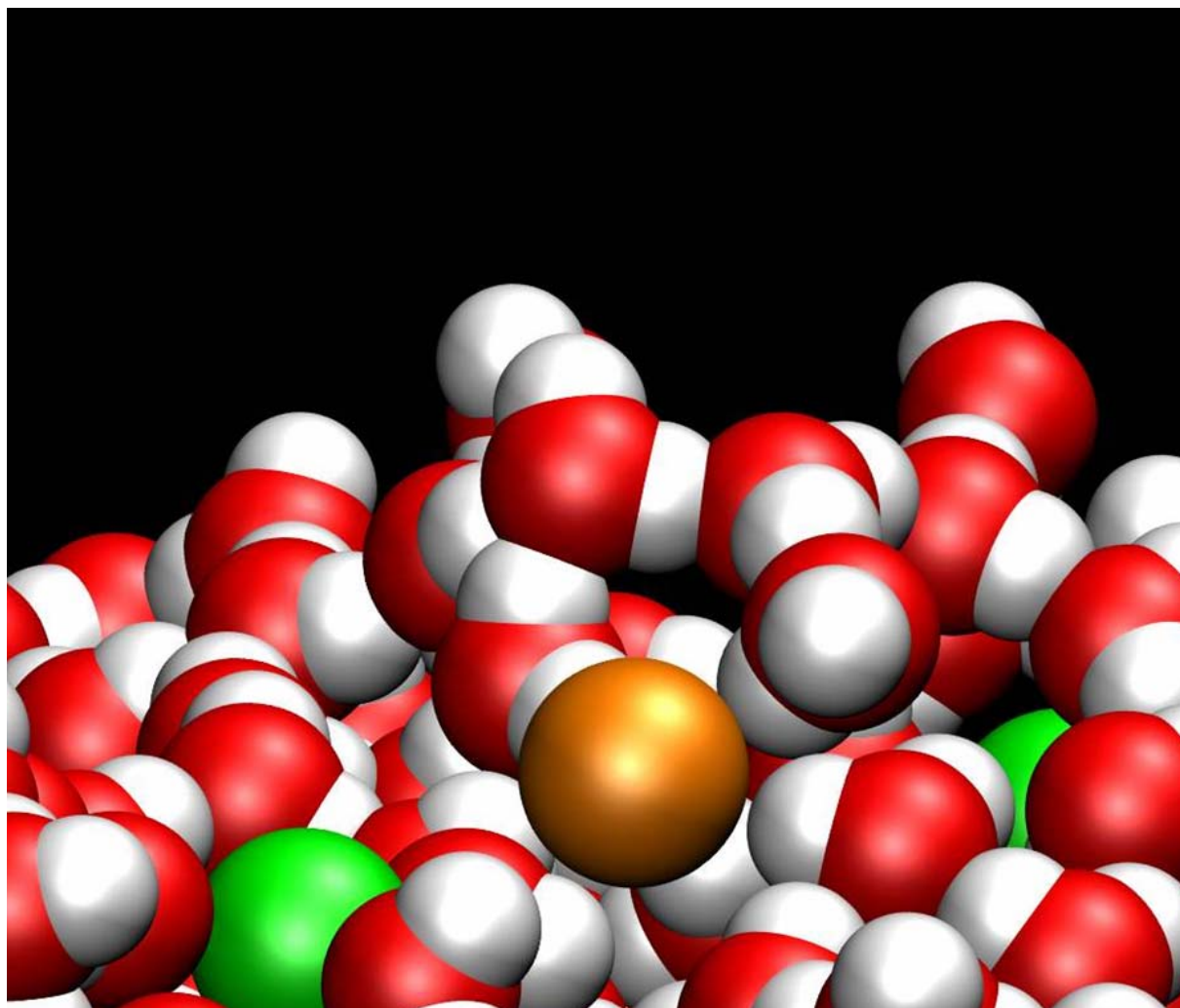
. For experiment, one of the greatest inherent challenges is the lack of sensitivity due to the relatively small number of molecules occupying the interface relative to the bulk. Sum frequency generation<sup>6</sup> and second harmonic generation<sup>7</sup> are nonlinear spectroscopic techniques that are surface sensitive because the signal vanishes in centrosymmetric media. Another method, photoelectron spectroscopy<sup>8</sup> is a sensitive probe of solute-solvent interactions but for volatile liquids such as water it was long considered technically unfeasible. However, with the recent advent of liquid microjets, which do not obscure the measurements with large amounts of water vapor, such experiments became possible. The surface selectivity comes from the finite mean free path of photoelectrons in water which can be as short as sub-nanometer for certain photon energies. The above techniques thus continue to emerge as powerful experimental approaches to probing structure and dynamics at aqueous interfaces.

Present progress in molecular level understanding of aqueous interfaces is a nice example of fruitful feedbacks between experiments on one side and theory and simulations on the other side. Based on molecular dynamics simulations we were able to suggest a new view on surfaces of aqueous electrolytes.<sup>9</sup> Unlike the traditional picture of surfaces of inorganic salt solutions being practically devoid of ions,<sup>10,11</sup> simulations employing polarizable force fields indicated that soft ions (e.g., heavier halides, azide, or thiocyanate), as well as hydronium, exhibit a significant propensity for the air/water interface.<sup>9,12</sup> The computational results, supported by surface selective spectroscopic measurements, were analyzed in terms of Gibbs adsorption thermodynamics and used for rationalizing heterogeneous tropospheric chemistry in the marine boundary layer.<sup>9</sup>

## **Molecular picture from computer simulations**

The traditional, ion-free picture of the surfaces of aqueous salt, acid, and base solutions is based on a model of a charged spheres in a dielectric continuum.<sup>13</sup> Electrostatic forces described within this model are important but they do not provide the whole picture. Such a model, e.g., does not distinguish between cation vs. anion solvation, since it lacks specific ion-water interactions in the first solvation shell, as well as polarization and dispersion effects, and it also underestimates solvation entropy effects.

Continuum models thus should not be pushed beyond their range of validity, i.e., to effects at sub-nanometer separations where the granularity of the ion-water and water-water interactions is of a key importance. This involves the first solvation shell structure, as well as the detailed behavior of ions at aqueous interfaces. Theoretical questions at the Angstrom scale can hardly be properly addressed without calculations with atomic resolution. Statistically averaged results containing all the molecular details can be obtained by Molecular Dynamics (MD) or Monte Carlo (MC) simulations.<sup>9,12</sup> These simulations employ either an empirical force field (i.e., a prescribed interatomic interaction potential of an analytical form) or the Car-Parrinello approach, where forces are evaluated by quantum chemical methods such as the different variants of the density functional theory.<sup>14</sup> MD and MC calculations do not involve any macroscopic parameters (e.g., dielectric constants) but rather derive all properties from motions of mutually interacting atoms. An ion containing aqueous interface within this picture is shown in Figure 3. This snapshot from our MD simulation demonstrates the atomic resolution one can obtain with all the details concerning ion distributions, molecular orientations, hydrogen bonding patterns, and surface corrugation accessible for analysis.



**Fig. 3:** *A cut from a snapshot from our molecular dynamics simulation of an aqueous salt solution/vapor interface demonstrating the atomic resolution of the obtained picture. The particular system shown here is NaBr(aq) with sodium in green and bromide in gold color.*

Our calculations show the importance of a detailed molecular description of the air/solution interface which accounts both for interactions within the first solvation shell and for long range effects.<sup>9</sup> In particular, ion and water polarization, solvent exclusion, and hydrogen bonding rearrangements determine whether or not a particular ion is found at the aqueous surface. A new view of inorganic ions at the air/water interface is emerging from our simulations, which is supported by surface selective spectroscopic experiments.<sup>9</sup> As mentioned above, traditionally, surfaces of aqueous electrolytes are described as inactive and



practically devoid of ions.<sup>10,11</sup> This is true for hard (non-polarizable) ions, such as fluoride and alkali cations. However, due to specific ion effects, and polarization interactions in particular, soft (polarizable) monovalent anions, such as the heavier halides and other polarizable inorganic anions exhibit a propensity for the air/water interface. Similarly, the hydronium cation shows an affinity for the aqueous surface, albeit primarily due to its specific hydrogen bonding features.<sup>9</sup> Surface propensity has also been investigated for different organic ions (e.g., carboxylate anions) where the main surface driving force is the hydrophobic effect.<sup>15</sup> Finally, differences in surface and bulk behavior of ions between liquid water and ice were studied via simulations of ice nucleation and crystallization in aqueous solutions. Unlike water, ice is an extremely bad solvent which leads to the effect of brine rejection from freezing salt solutions.<sup>16</sup>

## **Conclusions**

The presence and, in some cases, even enhancement of ions soft ions at aqueous interfaces has important consequences for heterogeneous physics and chemistry relevant both for technology and for atmospheric processes. This is true for extended aqueous surfaces and, in particular, for small droplets which have a large surface-to-bulk ratio. Probably the best known example of such a process is the production of molecular chlorine and other reactive halogen compounds at the surfaces of aqueous sea salt aerosols in the polluted marine boundary layer. Our simulations have been pioneering in the sense of predicting the existence of polarizable ions at the air/water interface which is being confirmed by experiment, in particular by surface selective spectroscopic techniques.

## References:

- (1) Finlayson-Pitts, B. J.; Pitts, J. N. *Chemistry of the Upper and Lower Atmosphere*; Academic Press: San Diego, 2000.
- (2) Prupacher, H. R.; Klett, J. D. *Microphysics of Clouds and Precipitation*; Kluwer: Dordrecht, 1997.
- (3) Ramanathan, V.; Crutzen, P. J.; Kiehl, J. T.; Rosenfeld, D. *Science* **2001**, *294*, 2119.
- (4) Oum, K. W.; Lakin, M. J.; DeHaan, D. O.; Brauers, T.; Finlayson-Pitts, B. J. *Science* **1998**, *279*, 74.
- (5) Knipping, E. M.; Lakin, M. J.; Foster, K. L.; Jungwirth, P.; Tobias, D. J.; Gerber, R. B.; Dabdub, D.; Finlayson-Pitts, B. J. *Science* **2000**, *288*, 301.
- (6) Gopalakrishnan, S.; Liu, D.; Allen, H. C.; Kuo, M.; Shultz, M. J. *Chem. Rev.*, **2006**, *106*, 1155.
- (7) Eisenenthal, K. B. *Chem. Rev.*, **2006**, *106*, 1462.
- (8) Winter, B.; Faubel, M. *Chem. Rev.*, **2006**, *106*, 1176.
- (9) Jungwirth, P.; Tobias, D. J. *Chem. Rev.*, **2006**, *106*, 1259.
- (10) Onsager, L.; Samaras, N. N. T. *Journal of Chemical Physics* **1934**, *2*, 528.
- (11) Randles, J. E. B. *Phys. Chem. Liq.* **1977**, *7*, 107.
- (12) Chang, T.-M.; Dang, L. X. *Chem. Rev.*, **2006**, *106*, 1305.
- (13) Markin, V. S.; Volkov, A. G. *Journal of Physical Chemistry B* **2002**, *106*, 11810.
- (14) Mundy, C. J.; Kuo, I.-F. W. *Chem. Rev.*, **2006**, *106*, 1282.
- (15) Minofar, B.; Mucha, M.; Jungwirth, P.; Yang, X.; Fu, Y.-J.; Wang, X.-B.; Wang, L.-S. *J. Am. Chem. Soc.*, **2004**, *126*, 11691.
- (16) Vrbka, L.; Jungwirth, P. *Phys. Rev. Lett.*, **2005**, *95*, 148501.

## Abstracts of publications included in the dissertation

1.

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# Experiments and Simulations of Ion-Enhanced Interfacial Chemistry on Aqueous NaCl Aerosols

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A combination of experimental, molecular dynamics, and kinetics modeling studies is applied to a system of concentrated aqueous sodium chloride particles suspended in air at room temperature with ozone, irradiated at 254 nanometers to generate hydroxyl radicals. Measurements of the observed gaseous molecular chlorine product are explainable only if reactions at the air-water interface are dominant. Molecular dynamics simulations show the availability of substantial amounts of chloride ions for reaction at the interface, and quantum chemical calculations predict that in the gas phase chloride ions will strongly attract hydroxyl radicals. Model extrapolation to the marine boundary layer yields daytime chlorine atom concentrations that are in good agreement with estimates based on field measurements of the decay of selected organics over the Southern Ocean and the North Atlantic. Thus, ion-enhanced interactions with gases at aqueous interfaces may play a more generalized and important role in the chemistry of concentrated inorganic salt solutions than was previously recognized.

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## Surface Effects on Aqueous Ionic Solvation: A Molecular Dynamics Simulation Study of NaCl at the Air/Water Interface from Infinite Dilution to Saturation

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The concentration dependence of the behavior of the Na<sup>+</sup> and Cl<sup>-</sup> ions solvated in a water slab has been investigated using molecular dynamics simulations employing a polarizable potential model. At all concentrations, the sodium ions are almost exclusively located in the interior, while the chloride anions occupy also a significant portion of the surface of the slab. This difference, which has important consequences for the atmospheric reactivity of aqueous sea-salt microparticles (microbrines), is discussed in terms of the relative sizes and polarizabilities of the two ions. The salt concentration, which has been varied from infinite dilution to saturation, has a strong effect on many physical properties, such as the ion solvation numbers and the degree of ion pairing, which are quantified separately for the interior and surface regions of the water slab.

### How Many Waters Are Necessary To Dissolve a Rock Salt Molecule?

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It is textbook knowledge that in order to dissolve rock salt in liquid water at ambient conditions at least nine water molecules per salt molecule are needed. An obvious but until now unsolved question arises: How many water molecules are necessary to solvate a single sodium chloride molecule? In other words, what is the smallest water cluster in which a solvent separated  $\text{Na}^+/\text{Cl}^-$  ion pair becomes stabilized? The answer, based on accurate quantum chemical calculations, is that simple extrapolation from the liquid is quantitatively wrong and that the *hexamer* represents the smallest water species that dissolves the NaCl molecule.

### Surface solvation of halogen anions in water clusters: An *ab initio* molecular dynamics study of the $\text{Cl}^-(\text{H}_2\text{O})_6$ complex

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The structure and dynamics of  $\text{Cl}^-(\text{H}_2\text{O})_6$  has been studied by *ab initio* molecular dynamics using the Car–Parrinello approach, and compared to results of *ab initio* quantum chemical calculations, molecular dynamics based on both polarizable and nonpolarizable empirical potentials, and vibrational spectroscopy. The electronic structure methodology (density functional theory with the gradient-corrected BLYP exchange–correlation functional) used in the Car–Parrinello dynamics has been shown to give good agreement with second-order Møller–Plesset results for the structures and energies of  $\text{Cl}^-(\text{H}_2\text{O})_n$ ,  $n = 1–4$ , clusters. The configurational sampling during the 5 ps *ab initio* molecular dynamics simulation at 250 K was sufficient to demonstrate that the chloride anion preferred a location on the surface of the cluster which was significantly extended compared to the minimum energy geometry. The structure of the cluster predicted by the polarizable force field simulation is in agreement with the *ab initio* simulation, while the nonpolarizable force field calculation was in qualitative disagreement, predicting an interior location for the anion. The time evolution of the electronic structure during the *ab initio* simulation was analyzed in terms of maximally localized orbitals (Wannier functions). Calculation of the dipole moments from the centers of the Wannier orbitals revealed that the chloride anion is significantly polarized, and that the extent of water polarization depends on location in the cluster, thus underscoring the importance of electronic polarization in halogen ion solvation. The infrared absorption spectrum was computed from the dipole–dipole correlation function, including both nuclear and electronic contributions. Aside from a systematic redshift by 3%–5% in the frequencies, the computed spectrum was in quantitative agreement with vibrational predissociation data on  $\text{Cl}^-(\text{H}_2\text{O})_5$ . Our analysis suggests that accounting for anharmonicity and couplings between modes is more important than the fine tuning of the electronic structure method for the quantitative prediction of hydrogen bond dynamics in aqueous clusters at elevated temperatures. © 2001 American Institute of Physics.

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### Molecular Structure of Salt Solutions: A New View of the Interface with Implications for Heterogeneous Atmospheric Chemistry

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Most salts raise the surface tension of water. Interpretation of this phenomenon via the Gibbs adsorption equation has led to the commonly held belief that the ions are repelled from the air/solution interface. Here, we report results from molecular dynamics simulations of a series of sodium halide solution/air interfaces. The simulations reproduce the experimentally measured increases in surface tension relative to pure water. Analysis of the structure reveals that the small, nonpolarizable fluoride anion is excluded from the interface, in accord with the traditional picture. However, all of the larger, polarizable halide anions are present at the interface, and bromide and iodide actually have higher concentrations in the interfacial region than in the bulk. On the basis of the simulations we develop a molecular picture of hydrogen bonding in the interfacial region that might be tested by surface sensitive spectroscopic experiments. The novel, microscopic view of the interfacial structure of aqueous salt solutions presented in this paper has implications for the reactivity of sea salt aerosols in the marine boundary layer, and bromine chemistry in the remote Arctic at polar sunrise.

6.

*J. Phys. Chem. A* **2002**, *106*, 379–383

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### Chloride Anion on Aqueous Clusters, at the Air–Water Interface, and in Liquid Water: Solvent Effects on $\text{Cl}^-$ Polarizability

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The effect of asymmetric aqueous solvation on the polarizability of the chloride anion is investigated by accurate ab initio calculations on structures obtained from classical molecular dynamics and Car–Parrinello molecular dynamics simulations. It is shown that a water environment significantly reduces the halide polarizability on clusters, at interfaces, and in the bulk. In the relatively rigid cluster environment, the amount of this reduction strongly depends on the particular geometry of the complex, while in more disordered, extended liquid systems, the geometric effect is much weaker. Therefore, a single effective value around  $4 \text{ \AA}^3$  may be employed for the chloride anion polarizability in aqueous environments.

### Excited States of Iodide Anions in Water: A Comparison of the Electronic Structure in Clusters and in Bulk Solution

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A new computational approach for calculating charger-transfer-to-solvent (CTTS) states of anions in polar solvents is presented. This is applied to the prototypical aqueous iodide system when the anion is placed in the interior or at the gas–liquid interface of a bulk water solution or hydrated in small gas phase clusters. The experimental vertical detachment energies and CTTS transition energies are quantitatively reproduced without any adjustable parameters. The representative shapes of bulk CTTS wave functions are shown for the first time and compared with cluster excited states. The calculations start with an equilibrium classical molecular dynamics simulation of the solvated anion, allowing for an extended sampling of initial configurations. In the next step, *ab initio* calculations at the MP2 level employing an extended diffuse basis set are performed for the anionic ground and lowest triplet state, as well as for the corresponding neutral system. It is argued that due to the small singlet–triplet splitting, the triplet state is a good model for the experimental CTTS state. The present calculations on aqueous iodide ion are made computationally feasible by replacing all water molecules (or all waters except for the first solvation shell) by fractional point charges. It is concluded that the bulk wave function is mainly defined by the instantaneous location of voids in the first solvation shell, which arise due to thermal disorder in liquid water. The key ingredient to CTTS binding in the bulk is the long-range electrostatic field due to the preexisting polarization of water molecules by the ground state iodide ion. This is very different from the situation in small water clusters, where the CTTS state is an order of magnitude more fragile due to the lack of long-range polarization. Therefore, it is argued that the electronic structure of small halide clusters cannot be directly extrapolated to the bulk.

## FEATURE ARTICLE

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### Ions at the Air/Water Interface

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We present results from theoretical studies of aqueous ionic solvation of alkali halides aimed at developing a microscopic description of structure and dynamics at the interface between air and salt solutions. The traditional view has depicted the air/solution interface of simple electrolytes as being devoid of ions. However, it is now firmly established that polarizable anions, such as the heavier halides, occupy the surface of small to medium sized water clusters. Using a combination of theoretical calculations, including *ab initio* quantum chemistry, Car–Parrinello molecular dynamics simulations, and primarily molecular dynamics simulations based on polarizable force fields, we present a unified view of the interfacial structure of aqueous ionic clusters and bulk solutions. Indeed, we demonstrate that the heavier halogen anions have a propensity for the interface that is proportional to their polarizability. The cluster results are directly supported by existing experimental and theoretical studies, and the bulk solution results are indirectly supported by several recent experiments. The novel view of the ionic solution/air interface presented here has also implications for dynamics following photoexcitation and electron photodetachment of ions. Moreover, the present results provide insight into heterogeneous atmospheric chemistry leading to halogen release from sea salt aerosols in the lower marine troposphere and from the Arctic snowpack during polar sunrise.

## Quantum Dynamics and Spectroscopy of Electron Photodetachment in $\text{Cl}^- \cdots \text{H}_2\text{O}$ and $\text{Cl}^- \cdots \text{D}_2\text{O}$ Complexes

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We have modeled electron photodetachment spectra of  $\text{Cl}^- \cdots \text{H}_2\text{O}$  and  $\text{Cl}^- \cdots \text{D}_2\text{O}$  complexes using 3D quantum dynamical simulations on the three low-lying electronic states of the nascent neutral systems. Time-dependent quantum simulations combined with anionic and neutral stationary-state calculations by imaginary time propagation allowed for a detailed interpretation of the spectral features in terms of the underlying dynamics. Because of large differences between the anionic and neutral potential surfaces, the systems are found after electron photodetachment primarily high above the dissociation threshold. Nevertheless, pronounced long-lived resonances are observed, particularly for the lowest neutral state, reflecting the fact that a significant portion of the excess energy is initially deposited into nondissociative modes, that is, to (hindered) water rotation. These resonances form bands corresponding to water rotational states with a fine structure due to intermolecular stretch progressions. Comparison is made to experimental zero electron kinetic energy (ZEKE) spectra of the  $\text{I}^- \cdots \text{H}_2\text{O}$  complex, where analogous anharmonic vibrational progressions have been observed.



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## Polarizability and aqueous solvation of the sulfate dianion

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### Abstract

Polarizability of the sulfate dianion solvated in water clusters and in an extended water slab is investigated by a combination of ab initio calculations and classical and Car–Parrinello molecular dynamics. Quantum chemistry calculations at the MP2/aug-cc-pvdz level are performed for structures obtained from molecular dynamics simulations replacing water oxygens and hydrogens by fractional point charges. Sulfate polarizability in bulk water amounts to roughly  $7 \text{ \AA}^3$ . Despite this large value  $\text{SO}_4^{2-}$  clearly prefers interior over surface solvation, in accord with previous experimental evidence for large aqueous clusters.

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## 12 Physical Properties and Atmospheric Reactivity of Aqueous Sea Salt Micro-Aerosols

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**Summary.** Aqueous sea salt micro-aerosols play an important role in the heterogeneous chemistry of the lower marine troposphere both in polluted and in remote areas. In particular, reactions with gases such as ozone or OH radicals leading to the release of molecular chlorine have been intensely studied, both experimentally and theoretically. Moreover, thin layers of sea water deposited on Arctic ice packs have been discovered to be a major source of reactive bromine species which destroy the surface ozone layer during polar sunrise. There is increasing evidence that the air-water interface is of a key importance in these chemical processes. Despite this, little has been known about the structure and physical properties of aqueous sea salt aerosols at a detailed, molecular level. Here, we summarize results of classical molecular dynamics, Car-Parrinello molecular dynamics and *ab initio* quantum chemistry calculations on concentrated aqueous sodium chloride and bromide solutions confined to cluster and slab geometries. The main questions addressed by the simulations concern the onset of NaCl ionic solvation in water clusters, transition from clusters to slabs, structure of solvation layers and degree of ion pairing in concentrated solutions with confined geometries. A key result of the simulations is the observation that polarizable halogen anions (chloride and bromide) are present at the air-water interface of bulk solutions in amounts sufficient for the heterogeneous atmospheric chemistry to take place. The calculations also reveal that bromide actually exhibits surfactant activity, i.e. its concentration at the interface is higher than in the bulk. This is in accord with the observed enhanced atmospheric reactivity of aqueous bromide compared to chloride and with SEM experiments on wetting and re-drying of NaCl/NaBr co-crystals.

V. Buch J. P. Devlin (Eds.)

## Water in Confining Geometries



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## LETTERS

### Salt Crystallization from an Evaporating Aqueous Solution by Molecular Dynamics Simulations

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Molecular simulations of crystal nucleation and growth from an evaporating salt solution are presented. Despite the fact that crystallization from solution is the most common way of producing crystals in nature, it has not been simulated on a computer with molecular resolution. We show that such calculations are feasible both for clusters and for extended systems, containing initially an almost saturated solution of sodium chloride. Moreover, we demonstrate that, within a broad range of external conditions, the nanosecond time scale computer simulations robustly and reproducibly display the onset of salt crystallization from solution. We also provide analysis at an atomic resolution and establish the role of water molecules in the process. The present simulations provide unique information about the mechanism and dynamics of nucleation and crystal growth from an evaporating solution. Such information can be used for predictions of morphologies and growth rates of macroscopic crystals from first principles.

Aqueous Salt Nanodroplets

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### VAN DER WAALS ATTRACTION AND COALESCENCE OF AQUEOUS SALT NANODROPLETS

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Collisions of aqueous salt nanodroplets at zero initial relative velocity are investigated by means of molecular dynamics simulations. The character of the van der Waals interactions, which bring the droplets together and cause coalescence, is described in detail, and the parameters of the droplet–droplet potential are extracted from the collisional trajectories. Concentration and size effects, together with implications for cloud and precipitation modeling are discussed.

14.

12690

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### Impact, Trapping, and Accommodation of Hydroxyl Radical and Ozone at Aqueous Salt Aerosol Surfaces. A Molecular Dynamics Study

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Collisions of the gaseous hydroxyl (OH) radical and ozone (O<sub>3</sub>) with the surfaces of sodium chloride or iodide solutions, as well as with the surface of neat water, were investigated by molecular dynamics simulations. The principal intent was to answer atmospherically relevant questions concerning the trapping and accommodation of the OH and O<sub>3</sub> species at the surface and their uptake into the bulk solution. Although trapping is substantial for both species, OH adsorbs and absorbs significantly better than O<sub>3</sub>. Most of the trapped O<sub>3</sub> molecules desorb from the surface within 50 ps, whereas a significant fraction of OH radicals remains at the interface for time intervals exceeding 100 ps. The aqueous surface has also an orientational effect on the OH species, favoring geometries with the H atom pointing toward the aqueous bulk. The effect of the dissolved salt on the trapping efficiency is minor; therefore, most likely, atomic ions solvated in aqueous aerosols do not act as strong scavengers of reactive gases in the atmosphere. However, frequent and relatively long contacts between the adsorbed molecules and halide anions do occur, allowing for heterogeneous atmospheric chemistry in the interfacial layer.

15.

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### Polarizability of the nitrate anion and its solvation at the air/water interface

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The anisotropic molecular polarizability of the nitrate anion and its decomposition into atomic contributions is studied using *ab initio* quantum chemistry and the Atoms in Molecules theory. Aqueous solvation of NO<sub>3</sub><sup>-</sup> in interfacial environments is investigated by a Car–Parrinello molecular dynamics simulation of a cluster, and classical molecular dynamics of an extended slab system with bulk interfaces using a polarizable force field based on the Atoms in Molecules analysis. Both in aqueous clusters and in systems with extended interfaces the nitrate anion clearly prefers interfacial over bulk solvation. This is primarily due to its large value of molecular polarizability, the gas phase value of which is reduced by only 5–10% in the aqueous environment. For polarizable force field simulations of ionic solvation, we recommend to cast the NO<sub>3</sub><sup>-</sup> polarizability into three equal contributions of roughly 1.3 Å<sup>3</sup> placed on the oxygen atoms of the anion.

PCCP

### Adsorption of Atmospherically Relevant Gases at the Air/Water Interface: Free Energy Profiles of Aqueous Solvation of N<sub>2</sub>, O<sub>2</sub>, O<sub>3</sub>, OH, H<sub>2</sub>O, HO<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub>

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Free energy profiles associated with moving atmospheric gases or radicals across the air/water interface were calculated as potentials of mean force by classical molecular dynamics simulations. With the employed force field, the experimental hydration free energies are satisfactorily reproduced. The main finding is that both hydrophobic gases (nitrogen, oxygen, and ozone) and hydrophilic species (hydroxyl radical, hydroperoxy radical, or hydrogen peroxide) have a free energy minimum at the air/water interface. As a consequence, it is inferred that atmospheric gases, with the exception of water vapor, exhibit enhanced concentrations at surfaces of aqueous aerosols. This has important implications for understanding heterogeneous chemical processes in the troposphere.

## J|A|C|S ARTICLES

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### Solvent-Mediated Folding of a Doubly Charged Anion

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**Abstract:** The microsolvation of the suberate dianion,  $^{-}O_2C(CH_2)_6CO_2^{-}$ , with two separate charge centers was studied by photoelectron spectroscopy and molecular dynamics simulation one solvent molecule at a time for up to 20 waters. It is shown that the two negative charges are solvated in the linear suberate alternately. As the solvent number increases, the negative charges are screened and a conformation change occurs at 16 waters, where the cooperative hydrogen bonding of water is large enough to overcome the Coulomb repulsion and pull the two negative charges closer through a water bridge. This conformation change, revealed both from the experiment and from the simulation, is a manifestation of the hydrophilic and hydrophobic forces at the molecular level.

## Solvation of the Azide Anion ( $\text{N}_3^-$ ) in Water Clusters and Aqueous Interfaces: A Combined Investigation by Photoelectron Spectroscopy, Density Functional Calculations, and Molecular Dynamics Simulations<sup>†</sup>

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We report a photoelectron spectroscopy and computational study of hydrated  $\text{N}_3^-$  anion clusters,  $\text{N}_3^-(\text{H}_2\text{O})_n$  ( $n = 0-16$ ), in the gas phase. Photoelectron spectra of the solvated azide anions were observed to consist of a single peak, similar to that of the bare  $\text{N}_3^-$ , but the spectral width was observed to broaden as a function of cluster size due to solvent relaxation upon electron detachment. The adiabatic and vertical electron detachment energies were measured as a function of solvent number. The measured electron binding energies indicate that the first four solvent molecules have much stronger interactions with the solute anion, forming the first solvation shell. The spectral width levels off at  $n = 7$ , suggesting that three waters in the second solvation shell are sufficient to capture the second shell effect in the solvent relaxation. Density functional calculations were carried out for  $\text{N}_3^-$  solvated by one to five waters and showed that the first four waters interact directly with  $\text{N}_3^-$  and form the first solvation shell on one side of the solute. The fifth water does not directly solvate  $\text{N}_3^-$  and begins the second solvation shell, consistent with the observed photoelectron data. Molecular dynamics simulations on both solvated clusters and bulk interface revealed that the asymmetric solvation state in small clusters persists for larger systems and that  $\text{N}_3^-$  prefers interfacial solvation on water clusters and at the extended vacuum/water interface.



## Propensity of soft ions for the air/water interface

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### Abstract

*Major recent advances:* Results of molecular dynamics simulations with polarizable force fields, supported by surface sensitive experiments, indicate that the propensity of atomic and hydrophilic molecular ions for the air/water interface exhibits strong ion specificity. While hard, non-polarizable ions are repelled from the interface, soft, polarizable ions exhibit surface affinity.

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**Keywords:** Propensity; Soft ions; Air/water interface

## Molecular Structure of Surface-Active Salt Solutions: Photoelectron Spectroscopy and Molecular Dynamics Simulations of Aqueous Tetrabutylammonium Iodide<sup>†</sup>

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*Received: February 12, 2004; In Final Form: July 13, 2004*

We report photoelectron measurements and molecular dynamics (MD) simulations with a polarizable force field of surface-active tetrabutylammonium iodide (TBAI) in aqueous solution. Photoemission is studied for a photon energy of 100 eV, using a 6- $\mu\text{m}$ -diameter liquid jet. Surfactant activity of the TBAI salt at the solution surface is proved by a dramatic ( $\times 70$ ) increase of the  $\text{I}^-$ (4d) signal, as compared to that of a NaI aqueous solution for identical salt concentrations. Completion of the segregation monolayer is suggested through the growth of the iodide photoelectron emission signal, as a function of the salt concentration. Our experiments reveal identical electron binding energies of iodide in TBAI and NaI aqueous solutions, which are independent of the salt concentration. Zero or very small spectral shifts of any feature, including the low-energy cutoff, suggest that no dipole is formed by  $\text{TBA}^+$  and  $\text{I}^-$  ion pairs perpendicular to the surface, which is in accord with the simulated ionic density profiles. Both cations and anions exhibit strong surfactant activity, thus failing to form a strong electric double layer. While the cations are surface-bound due to hydrophobic interactions, iodide is driven to the vacuum/water interface by its large polarizability. MD simulations also allow characterization of the thermally averaged geometries of the surface-active cations, in particular the orientations of the butyl chains with respect to the water surface.

## Counter-Ion Effects and Interfacial Properties of Aqueous Tetrabutylammonium Halide Solutions

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Aqueous solvation of tetrabutylammonium fluoride and iodide was investigated by means of molecular dynamics simulations in extended slab geometry. The varying propensities of the individual ions for the air/water interface were quantified and analyzed in terms of hydrophobic, polarization, and ion–ion interactions. While the cations behave as standard ionic surfactants, the surface behaviour of the halide counter ions strongly depends on the ionic size and polarizability—iodide is surface active, while fluoride is repelled from the interface. The counter-ion effects at different concentrations on the density and charge profiles across the aqueous slab are discussed in detail.

# J|A|C|S

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## A R T I C L E S

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### Bulk versus Interfacial Aqueous Solvation of Dicarboxylate Dianions

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**Abstract:** Solvation of dicarboxylate dianions of varying length of the aliphatic chain in water clusters and in extended aqueous slabs was investigated using photoelectron spectroscopy and molecular dynamics simulations. Photoelectron spectra of hydrated succinate, adipate, and tetradecandioic dianions with up to 20 water molecules were obtained. Even–odd effects were observed as a result of the alternate solvation mode of the two negative charges with increasing solvent numbers. The competition between hydrophilic interactions of the charged carboxylate groups and hydrophobic interactions of the aliphatic chain leads to conformation changes in large water clusters containing dicarboxylates bigger than adipate. It also leads to a transition from bulk aqueous solvation of small dicarboxylates to solvation at the water/vapor interface of the larger ones. Whereas oxalate and adipate solvate in the inner parts of the aqueous slab, suberate and longer dicarboxylate dianions have a strong propensity to the surface. This transition also has consequences for the folding of the flexible aliphatic chain and for the structure of aqueous solvation shells around the dianions.

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## A possible new molecular mechanism of thundercloud electrification

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### Abstract

Thunderclouds are electrified when charge is transferred between small and large ice particles colliding in a cloud that contains strong updrafts. The small ice particles rise with one type of charge and the large ice particles fall and carry with them downward the other type of charge, which is most often negative, so that normally lightning lowers negative charge from cloud to the ground. While the collisional mechanism of thundercloud charging is well established, the nature of the charge transfer between the colliding ice particles is not very well understood on the atomic level, and no present theory can explain it in full detail. Here we propose a new charge separation mechanism that is based on molecular dynamics simulations of particle surfaces and collisions, keeping track of the individual charges as they move in the form of salt ions from one ice particle to another. Under normal conditions, when sulfates dominate as cloud condensation nuclei, this ionic mechanism is consistent with the prevailing negative charging of graupels in thunderclouds. Moreover, with dearth of sulfate anions, the present mechanism predicts a shift towards positive charging. This fits well to a large range of observations of enhanced positive lightning, connected with smoke rich in chlorides and nitrates, that could not be explained satisfactorily previously.

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## Structure and Vibrational Spectroscopy of Salt Water/Air Interfaces: Predictions from Classical Molecular Dynamics Simulations

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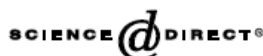
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We report the sum frequency generation (SFG) spectra of aqueous sodium iodide interfaces computed with the methodology outlined by Morita and Hynes (*J. Phys. Chem. B* 2002, 106, 673), which is based on molecular dynamics simulations. The calculated spectra are in qualitative agreement with experiment. Our simulations show that the addition of sodium iodide to water leads to an increase in SFG intensity in the region of 3400  $\text{cm}^{-1}$ , which is correlated with an increase in ordering of hydrogen-bonded water molecules. Depth-resolved orientational distribution functions suggest that the ion double layer orders water molecules that are approximately one water layer below the Gibbs dividing surface. We attribute the increase in SFG intensity to these ordered subsurface water molecules that are present in the aqueous sodium iodide/air interfaces but are absent in the neat water/air interface.



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Chemical Physics Letters 410 (2005) 222–227

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## Effect of bromide on the interfacial structure of aqueous tetrabutylammonium iodide: Photoelectron spectroscopy and molecular dynamics simulations

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### Abstract

Solvation of surface-active tetrabutylammonium iodide (TBAI) in liquid water and in sodium bromide aqueous solution was investigated by VUV photoelectron spectroscopy and by molecular dynamics simulations. The observed signal intensity changes in the photoemission spectra are consistent with the varying propensities of the different ions for the solution interface. While the cations are surface-bound due to hydrophobic interactions, the anions are driven to the vacuum/solution interface by their large polarizability and size. Iodide is more polarizable, and hence more surface-active than bromide, which explains the relatively small decrease of the iodide photoemission signal when TBAI is dissolved in bromide solution.

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## Electron Binding Energies of Aqueous Alkali and Halide Ions: EUV Photoelectron Spectroscopy of Liquid Solutions and Combined Ab Initio and Molecular Dynamics Calculations

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**Abstract:** Photoelectron spectroscopy combined with the liquid microjet technique enables the direct probing of the electronic structure of aqueous solutions. We report measured and calculated lowest vertical electron binding energies of aqueous alkali cations and halide anions. In some cases, ejection from deeper electronic levels of the solute could be observed. Electron binding energies of a given aqueous ion are found to be independent of the counterion and the salt concentration. The experimental results are complemented by ab initio calculations, at the MP2 and CCSD(T) level, of the ionization energies of these prototype ions in the aqueous phase. The solvent effect was accounted for in the electronic structure calculations in two ways. An explicit inclusion of discrete water molecules using a set of snapshots from an equilibrium classical molecular dynamics simulations and a fractional charge representation of solvent molecules give good results for halide ions. The electron binding energies of alkali cations computed with this approach tend to be overestimated. On the other hand, the polarizable continuum model, which strictly provides adiabatic binding energies, performs well for the alkali cations but fails for the halides. Photon energies in the experiment were in the EUV region (typically 100 eV) for which the technique is probing the top layers of the liquid sample. Hence, the reported energies of aqueous ions are closely connected with both structures and chemical reactivity at the liquid interface, for example, in atmospheric aerosol particles, as well as fundamental bulk solvation properties.

## Air–Liquid Interfaces of Aqueous Solutions Containing Ammonium and Sulfate: Spectroscopic and Molecular Dynamics Studies

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Investigations of the air–liquid interface of aqueous salt solutions containing ammonium ( $\text{NH}_4^+$ ) and sulfate ( $\text{SO}_4^{2-}$ ) ions were carried out using molecular dynamics simulations and vibrational sum frequency generation spectroscopy. The molecular dynamics simulations show that the predominant effect of  $\text{SO}_4^{2-}$  ions, which are strongly repelled from the surface, is to increase the thickness of the interfacial region. The vibrational spectra reported are in the O–H stretching region of liquid water. Isotropic Raman and ATR-FTIR (attenuated total reflection Fourier transform infrared) spectroscopies were used to study the effect of ammonium and sulfate ions on the bulk structure of water, whereas surface sum frequency generation spectroscopy was used to study the effect of these ions on the interfacial structure of water. Analysis of the interfacial and bulk vibrational spectra reveal that aqueous solutions containing  $\text{SO}_4^{2-}$  perturb the interfacial water structure differently than the bulk and, consistent with the molecular dynamics simulations, reveal an increase in the thickness of the interfacial region.

### Enhanced Concentration of Polarizable Anions at the Liquid Water Surface: SHG Spectroscopy and MD Simulations of Sodium Thiocyanide

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Contrasting current textbook descriptions, a consistent picture of substantial concentration enhancement of highly polarizable anions at the surface of aqueous electrolyte solutions is emerging. Such enhancement may have important implications for chemistry occurring on aqueous aerosols and ocean surfaces. Here we present a combined experimental and theoretical investigation of the liquid/air interface of aqueous sodium thiocyanide at varying salt concentrations. Normalized second harmonic generation intensities fitted to Langmuir isotherms yield a Gibbs free energy of adsorption of  $-1.80$  kcal/mol. These results are in accord with molecular dynamics simulations in slab geometry, which predict an appreciable surface enhancement of  $\text{SCN}^-$ .

### Interior and Interfacial Aqueous Solvation of Benzene Dicarboxylate Dianions and Their Methylated Analogues: A Combined Molecular Dynamics and Photoelectron Spectroscopy Study

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Aqueous solvation of benzene dicarboxylate dianions ( $\text{BCD}^{2-}$ ) was studied by means of photoelectron spectroscopy and molecular dynamics simulations. Photoelectron spectra of hydrated *o*- and *p*- $\text{BCD}^{2-}$  with up to 25 water molecules were obtained. An even–odd effect was observed for the *p*- $\text{BCD}^{2-}$  system as a result of the alternate solvation of the two negative charges. However, the high polarizability of the benzene ring makes the two carboxylate groups interact with each other in *p*- $\text{BCD}^{2-}$ , suppressing the strength of this even–odd effect compared with the linear dicarboxylate dianions linked by an aliphatic chain. No even–odd effect was observed for the *o*- $\text{BCD}^{2-}$  system, because each solvent molecule can interact with the two carboxylate groups at the same time due to their proximity. For large solvated clusters, the spectral features of the solute decreased while the solvent features became dominant, suggesting that both *o*- and *p*- $\text{BCD}^{2-}$  are situated in the center of the solvated clusters. Molecular dynamics simulations with both nonpolarizable and polarizable force fields confirmed that all three isomers (*o*-, *m*-, and *p*- $\text{BCD}^{2-}$ ) solvate in the aqueous bulk. However, upon methylation the hydrophobic forces overwhelm electrostatic interactions and, as a result, the calculations predict that the tetramethyl-*o*- $\text{BCD}^{2-}$  is located at the water surface with the carboxylate groups anchored in the liquid and the methylated benzene ring tilted away from the aqueous phase.

## FEATURE ARTICLE

## Unified Molecular Picture of the Surfaces of Aqueous Acid, Base, and Salt Solutions

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The molecular structure of the interfacial regions of aqueous electrolytes is poorly understood, despite its crucial importance in many biological, technological, and atmospheric processes. A long-term controversy pertains between the standard picture of an ion-free surface layer and the strongly ion specific behavior indicating in many cases significant propensities of simple inorganic ions for the interface. Here, we present a unified and consistent view of the structure of the air/solution interface of aqueous electrolytes containing monovalent inorganic ions. Molecular dynamics calculations show that in salt solutions and bases the positively charged ions, such as alkali cations, are repelled from the interface, whereas the anions, such as halides or hydroxide, exhibit a varying surface propensity, correlated primarily with the ion polarizability and size. The behavior of acids is different due to a significant propensity of hydronium cations for the air/solution interface. Therefore, both cations and anions exhibit enhanced concentrations at the surface and, consequently, these acids (unlike bases and salts) reduce the surface tension of water. The results of the simulations are supported by surface selective nonlinear vibrational spectroscopy, which reveals among other things that the hydronium cations are present at the air/solution interface. The ion specific propensities for the air/solution interface have important implications for a whole range of heterogeneous physical and chemical processes, including atmospheric chemistry of aerosols, corrosion processes, and bubble coalescence.

Ultrasonic Velocities, Densities, Viscosities, Electrical Conductivities, Raman Spectra, and Molecular Dynamics Simulations of Aqueous Solutions of Mg(OAc)<sub>2</sub> and Mg(NO<sub>3</sub>)<sub>2</sub>: Hofmeister Effects and Ion Pair Formation

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The ultrasonic velocities, densities, viscosities, and electrical conductivities of aqueous solutions of magnesium nitrate and magnesium acetate have been measured from dilute to saturation concentrations at  $0 \leq t/^{\circ}\text{C} \leq 50$ . The temperature derivative of the isentropic compressibility,  $\kappa_s$ , became zero at 2.28 and 2.90 mol kg<sup>-1</sup> for Mg(OAc)<sub>2</sub> and Mg(NO<sub>3</sub>)<sub>2</sub> solutions, respectively, at 25 °C. The total hydration numbers of the dissolved ions were estimated to be, respectively, 24.3 and 19.2 at these concentrations. Differences in  $\kappa_s$  for various M<sup>2+</sup> salts, using the present and literature data, correlated with reported M<sup>2+</sup>–OH<sub>2</sub> bond lengths and to a lesser extent with cationic charge densities (ionic radii). The influence of anions on  $\kappa_s$  appears to follow the Hofmeister series and also correlates approximately with the anionic charge density. Substantial differences between Mg(OAc)<sub>2</sub>(aq) and Mg(NO<sub>3</sub>)<sub>2</sub>(aq) occur with respect to their structural relaxation times (derived from compressibility and viscosity data) and their electrical conductivities. These differences were attributed to a much greater ion association in Mg(OAc)<sub>2</sub> solutions. Raman spectra recorded at 28 °C confirmed the presence of various types of contact ion pairs including mono- and bidentate complexes in Mg(OAc)<sub>2</sub>(aq). In Mg(NO<sub>3</sub>)<sub>2</sub>(aq), only noncontact ion pairs appear to be formed even at high concentrations. The experimental results are supported by molecular dynamics simulations, which also reveal the much stronger tendency of OAc<sup>-</sup> compared to NO<sub>3</sub><sup>-</sup> to associate with Mg<sup>2+</sup> in aqueous solutions. The simulations also allow an evaluation of the ion–ion and ion–water radial distribution functions and cumulative sums and provide a molecular picture of ion hydration in Mg(OAc)<sub>2</sub>(aq) and Mg(NO<sub>3</sub>)<sub>2</sub>(aq) at varying concentrations.

**Brine Rejection from Freezing Salt Solutions: A Molecular Dynamics Study**

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The atmospherically and technologically very important process of brine rejection from freezing salt solutions is investigated with atomic resolution using molecular dynamics simulations. The present calculations allow us to follow the motion of each water molecule and salt ion and to propose a microscopic mechanism of brine rejection, in which a fluctuation (reduction) of the ion density in the vicinity of the ice front is followed by the growth of a new ice layer. The presence of salt slows down the freezing process, which leads to the formation of an almost neat ice next to a disordered brine layer.

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**Specific Ion Effects at the Air/Water Interface**Pavel Jungwirth\*<sup>†</sup> and Douglas J. Tobias\*<sup>‡</sup>*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, and Center for Biomolecules and Complex Molecular Systems, Flemingovo nám. 2, 16610 Prague 6, Czech Republic, and Department of Chemistry and Institute for Surface and Interface Science, University of California, Irvine, California 92697-2025*

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To cover specific ion effects at all possible aqueous interfaces would be an almost heroic endeavor. Our goal is more modest: we aim to focus on the simplest one, i.e., the air/water interface. The general atmospheric and technological importance of this interface alone justifies our selection. Moreover, interactions between ions and air or vapor are sufficiently weak so that the nonaqueous phase can often be viewed as a vacuum. Thus, all that remains to be explored are the structural and dynamical consequences of specific interactions between ions and water molecules within the inhomogeneous interfacial region. In the subsequent sections we attempt to review the rapidly expanding body of computer simulations of ions at the air/water interface. We focus on relatively small inorganic ions (which, according to the traditional, purely electrostatic picture, should actually always be repelled from the aqueous surface), leaving aside the huge body of literature concerning technologically very important organic ionic surfactants. We present the computational results in light of continuum models and, in particular, experimental observations, ranging from traditional surface tension measurements to modern surface selective photo-

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### Electron Binding Energies of Hydrated $\text{H}_3\text{O}^+$ and $\text{OH}^-$ : Photoelectron Spectroscopy of Aqueous Acid and Base Solutions Combined with Electronic Structure Calculations

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35.



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### Selected biologically relevant ions at the air/water interface: A comparative molecular dynamics study

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#### Abstract

Interfacial behavior of selected biologically and technologically relevant ions is studied using molecular dynamics simulations employing polarizable potentials. Propensities of choline, tetraalkylammonium (TAA), and sodium cations, and sulfate and chloride anions for the air/water interface are analyzed by means of density profiles. Affinity of TAA ions for the interface increases with their increasing hydrophobicity. Tetramethylammonium favors bulk solvation, whereas cations with propyl and butyl chains behave as surfactants. The choice of counter-anions has only a weak effect on the behavior of these cations. For choline, sodium, chloride and sulfate, the behavior at the air/water interface was compared to the results of our recent study on the segregation of these ions at protein surfaces. No analogy between these two interfaces in terms of ion segregation is found.

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*Keywords:* Tetraalkylammonium; Polarizable potential; Surfactant; Molecular dynamics

## Aqueous Ionic and Complementary Zwitterionic Soluble Surfactants: Molecular Dynamics Simulations and Sum Frequency Generation Spectroscopy of the Surfaces

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An aqueous ionic surfactant, 1-dodecyl-4-(dimethylamino)pyridinium (DMP) bromide, and the corresponding zwitterion 2-[4-(dimethylamino)pyridinio]dodecanoate (DPN) were explored by means of molecular dynamics (MD) simulations and, for the ionic system, by infrared–visible sum frequency generation (IR–vis SFG). The molecular structure of the interfacial layer was investigated for the ionic and zwitterionic systems as a function of surfactant concentration, both in water and in salt (KF or KBr) solutions, by MD simulations in a slab geometry. The buildup of the surface monolayer and a sublayer was monitored, and density and orientational profiles of the surfactants were evaluated. The difference between the ionic and zwitterionic systems and the effect of the added salt were analyzed at the molecular level. The results of MD simulations were compared to those of nonlinear optical spectroscopy measurements. IR–vis SFG was employed to study the DMP ionic surfactant in water and upon addition of simple salts. The influence of added salts on the different molecular moieties at the interface was quantified in detail experimentally.

## Determination of the Electron Affinity of the Acetyloxyl Radical (CH<sub>3</sub>COO) by Low-Temperature Anion Photoelectron Spectroscopy and ab Initio Calculations

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The electronic structure and electron affinity of the acetyloxyl radical (CH<sub>3</sub>COO) were investigated by low-temperature anion photoelectron spectroscopy and ab initio calculations. Photoelectron spectra of the acetate anion (CH<sub>3</sub>COO<sup>-</sup>) were obtained at two photon energies (355 and 266 nm) and under three different temperatures (300, 70, and 20 K) with use of a new low-temperature ion-trap photoelectron spectroscopy apparatus. In contrast to a featureless spectrum at 300 K, a well-resolved vibrational progression corresponding to the OCO bending mode was observed at low temperatures in the 355 nm spectrum, yielding an accurate electron affinity for the acetyloxyl radical as 3.250 ± 0.010 eV. This experimental result is supported by ab initio calculations, which also indicate three low-lying electronic states observed in the 266 nm spectrum. The calculations suggest a 19° decrease of the OCO angle upon detaching an electron from acetate, consistent with the vibrational progression observed experimentally.

### Propensity for the Air/Water Interface and Ion Pairing in Magnesium Acetate vs Magnesium Nitrate Solutions: Molecular Dynamics Simulations and Surface Tension Measurements

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Molecular dynamics simulations in slab geometry and surface tension measurements were performed for aqueous solutions of magnesium acetate and magnesium nitrate at various concentrations. The simulations reveal a strong affinity of acetate anions for the surface, while nitrate exhibits only a very weak surface propensity, and magnesium is per se strongly repelled from the air/water interface.  $\text{CH}_3\text{COO}^-$  also exhibits a much stronger tendency than  $\text{NO}_3^-$  for ion pairing with  $\text{Mg}^{2+}$  in the bulk and particularly in the interfacial layer. The different interfacial behavior of the two anions is reflected by the opposite concentration dependence (beyond 0.5 M) of surface tension of the corresponding magnesium salts. Measurements, supported by simulations, show that the surface tension of  $\text{Mg}(\text{NO}_3)_2(\text{aq})$  increases with concentration as for other inorganic salts. However, in the case of  $\text{Mg}(\text{OAc})_2(\text{aq})$  the surface tension isotherm exhibits a turnover around 0.5 M, after which it starts to decrease, indicating a positive net solute excess in the interfacial layer at higher concentrations.

### Surface Segregation of Dissolved Salt Ions

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Surface segregation of iodide, but not of fluoride or cesium ions, is observed by a combination of metastable impact electron spectroscopy (MIES) and ultraviolet photoelectron spectroscopy (UPS(HeI)) of amorphous solid water exposed to CsI or CsF vapor. The same surface ionic behavior is also derived from molecular dynamics (MD) simulations of the corresponding aqueous salt solutions. The MIES results show the propensity of iodide, but not fluoride, for the surface of the amorphous solid water film, providing thus strong evidence for the suggested presence of heavier halides (iodide, bromide, and to a lesser extent chloride) at the topmost layer of aqueous surfaces. In contrast, no appreciable surface segregation of ions is observed in methanol, neither in the experiment nor in the simulation. Furthermore, the present results indicate that, as far as the thermodynamic aspects of solvation of alkali halides are concerned, amorphous solid water and methanol surfaces behave similarly as surfaces of the corresponding liquids.

## First steps towards dissolution of $\text{NaSO}_4^-$ by water†

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and Lai-Sheng Wang<sup>\*ab</sup>

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$\text{NaSO}_4^-(\text{H}_2\text{O})_n$  ( $n = 0-4$ ) clusters have been generated in the gas phase as model systems to simulate the first dissolution steps of sulfate salts in water; photoelectron spectroscopy and theoretical calculations indicate that the first three water molecules strongly interact with both  $\text{Na}^+$  and  $\text{SO}_4^{2-}$ , forming a three-water solvation ring to start to pry apart the  $\text{Na}^+\text{SO}_4^{2-}$  contact ion pair.

We produced  $\text{NaSO}_4^-(\text{H}_2\text{O})_n$  clusters from a  $10^{-3}$  M  $\text{Na}_2\text{SO}_4$  solution in a  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  mixed solvent using electrospray ionization and studied their structures and energetics by photoelectron spectroscopy (PES) and *ab initio* calculations. The electrospray ionization-PES apparatus has been described in detail before.<sup>18</sup> Our previous studies<sup>13,19,20</sup> showed that  $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$  clusters were the dominating species

## Simulated surface potentials at the vapor-water interface for the KCl aqueous electrolyte solution

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Classical molecular dynamics simulations with polarizable potential models were carried out to quantitatively determine the effects of KCl salt concentrations on the electrostatic surface potentials of the vapor-liquid interface of water. To the best of our knowledge, the present work is the first calculation of the aqueous electrolyte surface potentials. Results showed that increased salt concentration enhanced the electrostatic surface potentials, in agreement with the corresponding experimental measurements. Furthermore, the decomposition of the potential drop into contributions due to static charges and induced dipoles showed a very strong effect (an increase of  $\sim 1$  V per  $1M$ ) due to the double layers formed by KCl. However, this was mostly negated by the negative contribution from induced dipoles, resulting in a relatively small overall increase ( $\sim 0.05$  V per  $1M$ ) with increased salt concentration. © 2006 American Institute of Physics. [DOI: 10.1063/1.2218840]



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## Molecular dynamics simulations of freezing of water and salt solutions

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Available online 12 January 2007

### Abstract

Results of extensive molecular dynamics simulations of freezing of neat water and aqueous sodium chloride solutions are reported. The process of water freezing in contact with an ice patch is analyzed at a molecular level and a robust simulation protocol within the employed force field is established. Upon addition of a small amount of NaCl brine rejection from the freezing salt solution is observed and the anti-freeze effect of the added salt is described.

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*Keywords:* Ice freezing; Brine rejection; Molecular dynamics

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### Propensity of Formate, Acetate, Benzoate, and Phenolate for the Aqueous Solution/Vapor Interface: Surface Tension Measurements and Molecular Dynamics Simulations

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The properties of a series of aliphatic and aromatic carboxylates and phenolate-mimicking functional groups of humic acid are discussed with regard to their behavior in aqueous solutions close to the surface. Both surface tension measurements and MD simulations confirm that sodium formate behaves in accord with the classical theory of surfaces of electrolytes, whereas sodium acetate and, much more pronounced, sodium benzoate and sodium phenolate show a more hydrotropic behavior with surface active anions. Further to the surface tension data, the MD results suggest that these hydrotropes are highly oriented at the solution–vapor interface.

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## Physics and Chemistry of Ice

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SEGREGATION OF SALT IONS AT AMORPHOUS SOLID AND LIQUID SURFACES

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45.

MOLECULAR SIMULATIONS OF WATER FREEZING: BRINE REJECTION AND HOMOGENEOUS NUCLEATION

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## Autoionization at the surface of neat water: is the top layer pH neutral, basic, or acidic?

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Autoionization of water which gives rise to its pH is one of the key properties of aqueous systems. Surfaces of water and aqueous electrolyte solutions are traditionally viewed as devoid of inorganic ions; however, recent molecular simulations and spectroscopic experiments show the presence of certain ions including hydronium in the topmost layer. This raises the question of what is the pH (defined using proton concentration in the topmost layer) of the surface of neat water. Microscopic simulations and measurements with atomistic resolution show that the water surface is acidic due to a strong propensity of hydronium (but not of hydroxide) for the surface. In contrast, macroscopic experiments, such as zeta potential and titration measurements, indicate a negatively charged water surface interpreted in terms of preferential adsorption of OH<sup>-</sup>. Here we review recent simulations and experiments characterizing autoionization at the surface of liquid water and ice crystals in an attempt to present and discuss in detail, if not fully resolve, this controversy.

## Water surface is acidic

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Water autoionization reaction  $2\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^-$  is a textbook process of basic importance, resulting in  $\text{pH} = 7$  for pure water. However, pH of pure water surface is shown to be significantly lower, the reduction being caused by proton stabilization at the surface. The evidence presented here includes *ab initio* and classical molecular dynamics simulations of water slabs with solvated  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions, density functional studies of  $(\text{H}_2\text{O})_{48}\text{H}^+$  clusters, and spectroscopic isotopic-exchange data for  $\text{D}_2\text{O}$  substitutional impurities at the surface and in the interior of ice nanocrystals. Because  $\text{H}_3\text{O}^+$  does, but  $\text{OH}^-$  does not, display preference for surface sites, the  $\text{H}_2\text{O}$  surface is predicted to be acidic with  $\text{pH} < 4.8$ . For similar reasons, the strength of some weak acids, such as carbonic acid, is expected to increase at the surface. Enhanced surface acidity can have a significant impact on aqueous surface chemistry, e.g., in the atmosphere.

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computational approaches were used. First, constant volume and temperature (NVT) *ab initio* molecular dynamics simulations were carried out for liquid water with a pair of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions. To assess surface effects, the simulation was carried out for both a box with 3D periodic boundaries and a slab with two open surfaces and 2D periodic boundaries. This “on-the-fly” technique enables first-principle modeling of proton transfer systems at finite temperatures; proton transfer and transitions between the different protonated-water forms are automatically included in the computational scheme. However, the high computational cost limits the dimensionality of the model system, the duration of the trajectories, and the accuracy of the electronic structure method used to evaluate the forces and the energies.

Direct simulation of autoionization is not easily feasible because of the activation barrier (see, however, a pioneering study of bulk autoionization in ref. 13). On the other hand, recombination between  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  can be readily observed in on-the-fly simulations, on a feasible time scale, enabling

