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Introduction: Structure and Chemistry at Aqueous Interfaces

Aqueous surfaces and interfaces are ubiquitous and play an important role in many natural and technological processes. 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. However, this has changed within the past decade, thanks to modern spectroscopic techniques and molecular simulations.

The goal of this issue is to cover the recent remarkable progress in our understanding of the structure of and chemistry at aqueous interfaces. The emphasis is strongly on investigations with molecular resolution, which can provide detailed and accurate information about the structure of the interface, and about the position and reactivity of host species. On one hand, results from modern, surface sensitive spectroscopic and imaging measurements of neat and doped aqueous interfaces are presented. On the other hand, we aim at covering results from state-of-the-art molecular dynamics simulations and quantum chemical calculations of the structure of molecular and ionic species at aqueous interfaces. The aim is to provide a comprehensive, up-to-date picture of this increasingly important and vigorously developing field of research.

This thematic issue is organized as follows. The first four contributions deal with the recent progress in nonlinear vibrational spectroscopy and photoemission measurements, tailored for aqueous interfaces. The next four papers map the corresponding developments in theory and molecular simulations. The following four papers deal with computational and experimental studies of atmospherically relevant processes at air/water and air/ice interfaces. The next three reviews deal with experimental results for nanoscale aqueous interfaces of small particles and thin films, while the last contribution summarizes computational results for biologically relevant water/membrane interfaces. Below, we introduce the individual contributions in more detail.

Interfaces present many challenges to quantitative characterization using spectroscopic probes. 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 and second harmonic generation are nonlinear spectroscopic techniques that are surface sensitive because the signal vanishes in centrosymmetric media. Vibrational sum frequency generation continues to emerge as a powerful approach to probing structure and dynamics at aqueous interfaces, as is evident in the first two contributions, one by Shen and Ostroverkhov and the other by Gopalakrishnan et al., which review the experimental aspects, theory, and a wide variety of applications of the technique. The paper by Winter and Faubel deals with photoemission measurements on water and aqueous solutions. Photoelectron spectroscopy is a sensitive probe of solute/solvent interactions, but for volatile liquids such as water, it was long considered technically infeasible. 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.

Recent progress in molecular level understanding of aqueous interfaces is a good example of fruitful feedback between experiments, theory, and simulations. In his review, Benjamin first lays theoretical foundations of static and dynamic electronic spectroscopy in condensed phases and at liquid interfaces. Computational and experimental results for liquid/vapor, liquid/liquid, and liquid/solid interfaces are then presented, and similarities between these interfaces and the situation in reversed micelles and microemulsions are discussed. The review by Perry et al. focuses on the theoretical background of sum frequency generation. A microscopic expression for system susceptibility is provided, and the time vs frequency domain results are compared. Several applications of theoretical sum frequency generation spectroscopy to water/vapor and other aqueous interfaces are also provided.

The contribution of Jungwirth and Tobias suggests a new view of the surfaces of aqueous electrolytes, based on molecular dynamics simulations performed in several groups over the past few years. Unlike the traditional picture of surfaces of inorganic salt solutions as being practically devoid of ions, simulations employing polarizable force fields indicate that soft ions (e.g., the heavier halides, azide, or thiocyanate), as well as hydronium, exhibit a significant affinity for the air/water interface. The computational results, supported by surface selective spectroscopic measurements, are analyzed in terms of Gibbs adsorption thermodynamics, and implications for heterogeneous tropospheric chemistry are discussed. The review by Mundy and Kuo discusses recent progress and prospects in the theoretical modeling of

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Pavel Jungwirth graduated in physics from the Charles University in Prague in 1989. He completed his doctoral thesis in computational chemistry at the Heyrovský Institute in Prague under Rudolf Zahradník in 1993. In 1994 and 1995 he was a Golda Meir Fellow at the Hebrew University in Jerusalem and a postdoc at the University of California, Irvine, working with Benny Gerber on quantum molecular dynamics of polyatomic systems. In 1995–2003 he was a research group leader at the Heyrovský Institute, and in 2004 he moved with his group to the Institute of Organic Chemistry and Biochemistry of the Academy of Sciences of the Czech Republic. Since 2000 he has also been an Associate Professor at Charles University. In 2001 he was a Lady Davis visiting professor at the Hebrew University, and in the same year he was awarded the Annual Medal of the International Academy of Quantum Molecular Science. His current research interests encompass molecular simulations of ions at aqueous interfaces, chemistry of atmospheric aerosols, structure and dynamics of solvated and dipole bound electrons, and interactions of ions with biomolecules.

Barbara J. Finlayson-Pitts was born and raised in Ottawa, Canada. She completed her B.Sc. (Hons) at Trent University in Peterborough, Canada, in 1970 and her Ph.D. at the University of California, Riverside, with Professor James N. Pitts, Jr., in 1973. After one year of postdoctoral research at UC Riverside, she joined the faculty in the Department of Chemistry at California State University, Fullerton, in 1974. In 1994, she became Professor of Chemistry at the University of California, Irvine, where she is currently located. Her research interests are elucidating reactions at interfaces and in thin films of atmospheric interest, particularly involving sea salt, oxides of nitrogen, and organics.

Doug Tobias received his B.S. and M.S. degrees in chemistry from the University of California, Riverside, and his Ph.D. in chemistry and biophysics from Carnegie Mellon University. Following appointments as a postdoctoral researcher at the University of Pennsylvania and guest researcher at the National Institute of Standards and Technology, in 1997 he joined the faculty in the Department of Chemistry at the University of California, Irvine. His research involves the application of molecular dynamics simulations to a wide variety of problems in biophysical and atmospheric chemistry, with an emphasis on structure and dynamics at interfaces.

chemical reactions at aqueous interfaces using *ab initio* molecular dynamics simulations, in which the forces used to drive the simulation are derived from the electronic structure as it evolves along the classical trajectory of the nuclei. In addition to reviewing methodological aspects of *ab initio* MD simulations that use a density functional theory description of electronic structure, Mundy and Kuo survey recent applications to heterogeneous chemical reactions at solid/vapor and liquid/vapor interfaces. Chang and Dang then in their review return us back to classical molecular dynamics simulations of the water/vapor and water/(other) liquid interfaces. They focus particularly on the problem of transferring a single ionic or molecular solute across such an interface. The concept of the potential of mean force, i.e., the free energy profile of a solute along a line perpendicular to the interface, is developed, and many examples are presented. The results stress the role of polarization interactions at aqueous interfaces.

The interaction of gases with liquids in the atmosphere, with or without chemical reaction, involves a number of coupled steps including diffusion of the gas to the surface, mass accommodation, diffusion inside the liquid, and possibly reaction in the bulk or at the gas/liquid interface. The review by Davidovits et al. describes the resistor model for decoupling these processes, as well as experimental techniques that have been applied to obtain mass accommodation and reactive uptake of gases at aqueous interfaces of atmospheric interest. Molecular dynamics simulations that have recently been used by several groups to study the molecular scale aspects of gas accommodation by liquids are the focus of the review by Garrett et al. At first glance, the predictions of the simulations appear to be at odds with the parameters extracted from experimental measurements of gas uptake using phenomenological models. The reviews of both Davidovits et al. and Garrett et al. discuss the phenomenological models and molecular dynamics and fluid dynamics simulations of mass accommodation molecular dynamics, and while they do not resolve the discrepancies, they do identify directions for future work.

The uptake of acidic gases into aqueous systems, including ice, plays an important role in acid deposition, polar stratospheric clouds, and the polar snowpacks, where unusual photochemistry generating nitrous acid has recently been observed. In addition, the interaction of these gases with ice must be understood in order to interpret appropriately the ice core data that are used to understand the composition of the atmosphere over hundreds of thousands of years. The review by Huthwelker et al. treats thermodynamic and kinetic approaches to the interaction of gases with ice, and describes the experimental techniques used to probe these interactions. Results for the solubility and diffusion, as well as for total uptake of some acid gases of atmospheric importance, including the hydrogen halides, HNO_3, HONO, and SO_2, are described, and some remaining unsolved problems in this area are highlighted.

Organic films are increasingly recognized as playing an important role in the atmosphere. These films are found on the ocean surface, on aerosol particles, and on surfaces in the tropospheric boundary layer, including buildings, vegetation, etc. The review by Donaldson and Vaida describes the nature of these organic films, laboratory techniques for studying them, and the results of field studies that show evidence for their general existence. The potential role of these films on the physical and chemical properties of systems of importance in the atmosphere is discussed, as well as their possible role in prebiotic biochemistry.

Second harmonic generation, which is one of the leading experimental tools for exploration of extended aqueous interfaces, has recently been applied also to studies of colloidal particles suspended in aqueous solutions. The paper by Eisenthal reviews the rapidly growing field of characterization of the water/nanoparticle and water/microparticle interfaces using second harmonic generation spectroscopy. Presented results show a new direction in colloid chemistry with important implications both for basic science and applications in technology and medicine.

Understanding thin water layers on surfaces is crucial for many different problems in chemistry, physics, engineering, and biology. The reviews by Verdaguer et al. and Ewing focus on the nature of the first few layers of water on well-defined surfaces such as transition metal oxides, MgO, NaCl, BaF_2, α-$A1_2O_3$, and mica, with discussion of the differences between water in these thin films and bulk liquid water. In addition, water confined in narrow spaces (e.g., between flat mica surfaces and in gaps where capillary effects are important) is treated.

The broad, chemically heterogeneous, and thermally disordered interface between aqueous solutions and model biological membranes is the subject of the review by Berkowitz et al. Biological membranes are complex mixtures of lipids in which the polar headgroups, which come in a variety of sizes, shapes, and charges, are in contact with the surrounding solution. Berkowitz et al. review both experimental and theoretical studies of the structure and physical properties of membrane/water interfaces.

It is hardly possible to cover within one issue all aspects of the vigorously developing field of molecular characterization of aqueous interfaces. Nevertheless, we are convinced that the sixteen contributions introduced above provide a thorough and timely review of modern aspects of “Structure and Chemistry at Aqueous Interfaces”. We are grateful to all the contributors and hope that this special issue will be found useful by a broad scientific audience.

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