

SEMINAR

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EMSL/Auditorium



Frontiers in Chemical Physics & Analysis Seminar Series

Presents...

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Select Adsorption of Ions to Aqueous Interfaces

Motivated by observations in atmospheric chemistry of otherwise inexplicable chemical reactions of sea salt aerosols, recent computer simulations predict a dramatically different behavior for “soft” ions, finding the concentrations of some anions to be significantly enhanced at the liquid-vapor interface, and attributing this to the preference of highly polarizable ions for the surface, with its unbalanced electric fields. Others have questioned this proposed mechanism, and suggested relative dehydration energy as the most crucial factor influencing surface activity.

We have recently verified predicted surface affinities for a number of small ions in a series of femtosecond UV second harmonic generation experiments, which demonstrated Langmuir adsorption behavior of the ions and yielded free energies of adsorption that were in agreement with predicted values.

A related and controversial phenomenon is known as the Jones-Ray Effect. In the 1930's, experiments revealed that some salts did not produce the monotonic increase in surface tension that had become the expected behavior, but actually exhibited a minimum in the surface tension at millimolar concentrations, in clear violation of the Onsager-Samaras model. This result has since been reproduced by other groups, but has never been satisfactorily explained. We have verified the Jones-Ray Effect for two solutions by UV femtosecond SHG experiments, which reveal an initial surface enhancement, followed by a depletion at higher concentrations.

A particularly interesting case is the potential existence of hydroxide and/or hydronium at the interface, thus establishing the surface pH of water, where conflicting interpretations are reached from macroscopic and molecular-scale studies. We have presented SHG results for hydroxide and hydriodic acid solutions, which support surface enhancement of hydronium, but give no indication of preferential adsorption of hydroxide at the outermost liquid layer of the interface. These results are in agreement with other molecular-scale experiments and simulations, but disagree with conclusions based on macroscopic experiments.

Given that two-thirds of the Earth is covered by aqueous solutions, these new findings could have an important influence on ocean and atmospheric chemistry, as well as electrochemistry and biology.