

4.026 Phase transition in salt solutions at the bulk and interface with core level spectroscopy.

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Abstract:

Sea salt, and in particular chloride, is an important reactant in the atmosphere. Chloride in sea salt aerosol is – once chemically converted to molecular halogens (Cl₂, BrCl) and released to the atmosphere – well known as important atmospheric reactant. A crucial factor determining the overall reactivity of this halogen release is the local physical environment of the chloride ion. For example, the reactivity of liquid aerosols decreases significantly upon crystallization. Surprisingly, the phases of NaCl-water systems are still under debate. Using core electron spectroscopy of the oxygen atoms in water, we previously showed that these systems follow the phase rules at the air-ice interface. This finding contrasts some earlier observations, where the presence of liquid below the eutectic point of bulk solutions was postulated.

In the present study, we present new electron yield near-edge X-ray absorption fine structure spectroscopy (NEXAFS) data obtained at near-ambient pressures up to 20 mbar of NaCl frozen solutions. The method is sensitive to small changes in the local environment of the chlorine atom and can either probe the surface or the bulk of the sample. The study indicates significant differences in the phases of NaCl - water mixtures at temperatures below the freezing point for the surface of the ice vs. the bulk. This has significant impact on modelling chemical reactions in snow or ice and its environmental consequences. Further, this study reveals more general and new insight into the fundamental question of how the local environment of dopants change upon freezing at the air-ice interface. In this presentation I will thus also focus on presenting our new set-up to allow to precisely control temperature and pressure for sub-freezing core electron spectroscopy studies.