

Surface Segregation of Hydroniums and Chlorides in a Thick Ice Film at Higher Temperatures

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This work examines the dynamic properties of ice surfaces in vacuum for the temperature range of 140~180 K, which extends over the onset temperatures for ice sublimation and the phase transition from amorphous to crystallization ice. In particular, the study focuses on the transport processes of excess protons and chloride ions in ice and their segregative behavior to the ice surface. These phenomena were studied by conducting experiments with a relatively thick (~100 BL) ice film constructed with a bottom H₂O layer and an upper D₂O layer, with excess hydronium and chloride ions trapped at the H₂O/D₂O interface as they were generated by the ionization of hydrogen chloride. The migration of protons, chloride ions, and water molecules to the ice film surface and their H/D exchange reactions were measured as a function of temperature using the methods of low energy sputtering (LES) and Cs⁺ reactive ion scattering (RIS). Temperature programmed desorption (TPD) experiments monitored the desorption of water and hydrogen chloride from the surface. Our observations indicated that both hydronium and chloride ions migrated from the interfacial layer to segregate to the surface at high temperature. Hydrogen chloride gas desorbs via recombination reaction of hydronium and chloride ions floating on the surface. Surface segregation of these species is driven by thermodynamic potential gradient present near the ice surface, whereas in the bulk, their transport is facilitated by thermal diffusion process. The finding suggests that chlorine activation reactions of hydrogen chloride for polar stratospheric ice particles occur at the surface of ice within a depth of at most a few molecular layers, rather than in the bulk phase.

Keywords: Ice, Hydronium, Chloride, Surface, Proton transfer, Diffusion