

Excess proton catalyzed H/D exchange reaction at the ice surface

Eui-seong Moon, Heon Kang

Department of Chemistry, Seoul National University, Gwanak-gu, Seoul 151-747, Republic of Korea

We studied the H/D exchange kinetics of pure and acid doped water-ice film by using the techniques of reactive ions scattering (RIS) and low energy sputtering (LES) with low kinetic energy cesium ion beam (<35 eV). From RIS, neutral water isotopomers were detected in the form of cesium-molecule ion clusters, CsX^+ ($X = \text{H}_2\text{O}, \text{HDO}, \text{D}_2\text{O}$). Ionic species, like H_3O^+ , DH_2O^+ , D_2HO^+ , D_3O^+ , adsorbed on the surface were ejected via LES process. Those techniques allowed us to trace the isotopomeric populations of water-ice film. To show the catalytic effect of excess proton in the H/D exchange reaction, our study was conducted with two types of water-ice films. In film 1, about 0.5 BL of H_2O was adsorbed on HCl (0.1 ML) doped D_2O (8 BL) film. In film 2, similar amount of H_2O used in film 1 was adsorbed on pure D_2O film. Kinetic data were obtained from each film type for 90-110 K (film 1) and 110-130 K (film 2) and fitted with numerically integrated lines. Through the Arrhenius plot of kinetic coefficient deduced from fitting of the H/D exchange reaction, the activation energy of film 1 and 2 were estimated to be 10 ± 3 kJ mol $^{-1}$ and 17 ± 4 kJ mol $^{-1}$. This activation barrier difference could be understood from detailed pictures of H/D exchange. In film 2, both the formation of ion pair, H_3O^+ and OH^- and proton transfer were needed for the H/D exchange. However, in film 1, only proton transfer was necessary but ion pair formation was not, so this might reduce the activation energy.

Keywords: RIS, LES, ice, H/D exchange, proton transfer, activation energy