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

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We studied the H/D exchange kinetics of pure and acid dopped 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= H2O, HDO, D2O). Ionic species, like H3O+, DH2O+, D2HO+, D3O+, adsorbed on the surface were ejected via LES process. Those techniques allowed us to trace the isotopometric 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 H2O was adsorbed on HCl (0.1 ML) dopped D2O (8 BL) film. In film 2, similar amount of H2O used in film 1 was adsorbed on pure D2O 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, H3O+ 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