Sublimation dynamics and isotope fractionation of crystalline- and amorphous-ice thin films

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Ice sublimation is one of the most fundamental processes associated with growth of ice particles and snow on earth and in the universe [1, 2]. In spite of the fundamental importance of molecular level understanding of the sublimation process, little is known about mechanistic details including isotope effects. It was recently reported that not only the translational degree of freedom but also the rotational degree of freedom play key roles in the desorption process of water molecules, based on the comparison of sublimation rates of pure H_2O, D_2O and $H_2^{18}O$ ice [3]. However, the effects of neighboring water molecules on desorption process have not been investigated, although water molecules at ice surfaces are strongly interacted each other through hydrogen bonds.

Here, using temperature-programmed desorption (TPD) under ultra-high vacuum condition, we have investigated the sublimation dynamics of H_2O, HDO, and D_2O from isotope mixed crystalline-ice (CI) and amorphous-ice (AI) thin films, whose D to H ratio x_D was systematically controlled. For both CI and AI, desorption rate of each isotope becomes smaller as the x_D become increased (Fig. 1). This result indicates that desorption of water molecules from ice surface is not a unimolecular process; neighboring water molecules indeed affect the desorption rate. Based on the Arrhenius plots, we found that many-body cooperative isotope effects appear at larger x_D, especially in the pre-exponential factor of the desorption rate rather than the activation energy of desorption. Additionally, we found the extraordinary isotope fractionation of AI under and after the crystallization process at ~155 K. We will discuss these results in details.
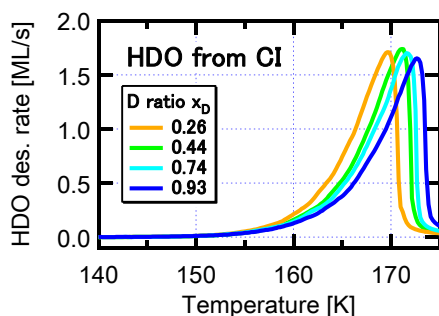

Figure 1: D to H ratio dependence of the desorption rate of HDO molecules from isotope mixed CI.

References
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