

Coverage-dependent desorption kinetics of ice on a well-ordered alumina thin film surface

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Water's ubiquitous nature and the critical importance of understanding the growth of ice films on surfaces from both a fundamental and applied perspective have led to extensive investigations into the structure and properties of ice on surfaces [1]. Water molecules on surfaces engage in uniquely anisotropic electrostatic interactions, namely hydrogen bonds, between molecules, and simultaneously they also experience electrostatic and, in some cases, covalent interactions with the surface [2]. These interactions are critical to fundamental aspects of ice on surfaces, including its crystal growth, structure, wetting behavior, phase transitions, and proton ordering.

Among the experimental methods, thermal desorption (TD) spectroscopy (TDS) is widely used, and TD spectra of ice are highly sensitive to these water-related interactions. For example, the TD spectra of ice on Pt (111) (a hydrophilic surface) and Cu (111) (a hydrophobic surface) demonstrate distinct differences, indicating that the nature of water-surface and water-water interactions and the corresponding ice structure have a significant impact on the TD spectra [1]. These variations in the spectra are due to the fact that the desorption kinetic parameters, such as desorption energy (E_d) and pre-exponential factor (ν), are influenced by molecular interactions and are, therefore, functions of the coverage, ϑ . Therefore, to evaluate the molecular interactions in an ice film on a surface by means of TDS, it is essential to quantitatively measure the coverage-dependent desorption kinetic parameters. However, the typical analytical methods (Redhead [3], threshold [4], and inversion analysis [5]) used in thermal desorption spectroscopy (TDS) do not satisfactorily quantify the coverage dependence of E_d and ν for ice films.

In this study, we employ King's "complete analysis" method [6], which allows the complete determination of coverage-dependent E_d and ν , to obtain fully coverage-dependent E_d and ν ranging from sub-monolayer to 2 ML ice. We use the crystalline two-layer (2L) thin alumina film epitaxially grown on NiAl (110) [7] as a substrate for ice growth. The choice of alumina as a substrate is based on its wide range of applications in various fields, from heat exchange plates to catalyst supports, and the well-defined surface structure of 2L-alumina thin film makes it an ideal substrate for our investigation. We found that the desorption activation energy (E_d) decreases with increasing coverage in the sub-ML region, indicating a non-attractive interaction between water molecules in the first layer on the surface, which is different from typical hydrogen bonding and is likely due to a perturbation presented by the alumina substrate. In addition, we found that the pre-exponential factor (ν) in the second layer of ice is one order of magnitude larger than that in the first layer, highlighting the critical role of entropic effects in the desorption kinetics of water molecules from ice films.

[1] For example: M. A. Henderson, *Surf. Sci. Rep.* **46**, 1 (2002), A. Hodgson and S. Haq, *Surf. Sci. Rep.* **64**, 381 (2009). [2] J. Carrasco et al., *J. Chem. Phys.* **130**, 184707 (2009). [3] P. A. Redhead, *Vacuum* **12**, 203 (1962). [4] E. Habenschaden and J. Küppers, *Surf. Sci. Lett.* **138**, L147 (1984). [5] S. L. Tait et al., *J. Chem. Phys.* **122**, 164707 (2005). [6] D. A. King, *Surf. Sci.* **47**, 384 (1975). [7] R. M. Jaeger et al., *Surf. Sci.* **259**, 235 (1991), G. Kresse et al., *Science* **308**, 1440 (2005).