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Water at interfaces

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Editorial

Water at interfaces

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Proton mobility in thin ice films: a revisit

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We have examined proton transport through an ice film in the temperature range 73–140 K by initially adding hydronium ions into the interior of the film and then monitoring the build-up of hydronium ion population at the film surface. The result confirms that the proton exhibits limited mobility in the ice film at low temperature, but it becomes highly mobile at temperature above 130 K. Based on this result we suggest an explanation of the anomalous experimental observations in the literature for the proton mobility in ice films.

Proton transport in ice is an important process related to electrical conductivity1,2 and chemical reactivity of ice,3 and this subject has been studied by numerous researchers for a long time.1–13 The experimental results on the mobility of protons in ice, however, vary widely; whereas some studies claim that proton mobility in ice crystals is faster than that in liquid water,4 other studies indicate that proton transport is a thermally activated process that occurs substantially slowly in ice at low temperature5–9 or even not at all.10 Devlin and coworkers5–7 studied the H/D isotopic exchange in water molecules in ice nanocrystals at a temperature below 145 K using IR spectroscopy, and suggested that the H/D exchange occurred via proton transfer between water molecules and subsequent movement of Bjerrum defects (the “hop-and-turn” mechanism). Everest and Pursell8 examined the H/D isotopic exchange process in the first few molecular layers of ice films at similar temperatures using IR spectroscopy. Geil et al.9 conducted NMR experiments with ice crystals and revealed two types of proton transport processes in the temperature range 160–260 K: a fast process mediated by Bjerrum defect dynamics and a slow process that was attributed to interstitial diffusion of water molecules. Cowin et al.10 performed the ‘soft-landing’ experiments of hydronium ions on ice films and observed that protons were immobile across the ice film over a fairly wide temperature range (30–190 K). Park et al.11 adsorbed HCl onto an ice film and examined the H/D exchange reaction in surface water molecules. They observed that proton transfer was facile only in the lateral direction at the film surface, whereas vertical proton transfer to the film interior was almost absent at 90–140 K. The proton transport behaviors observed in these studies, i.e., mobile protons in ice5–9 and vertically immobile protons at the ice surface,10,11 seem to contradict each other. Recently, Lee et al.12,13 offered an explanation for this contradiction by showing that protons exhibit asymmetric transport behavior at the surface and interior of ice due to the thermodynamic affinity of protons for the ice surface.

The interpretation by Lee et al.12,13 agrees with the occurrence of proton transport via several different mechanisms that operate within different temperature regimes: the proton hopping relay,1,2 the hop-and-turn process,5–7 and interstitial molecular diffusion.9 Yet, an opposing evidence also exists in the literature. As part of the soft-landing experiments of hydronium ions, Cowin et al.10 prepared a ‘proton-sandwich’ ice film by depositing hydronium ions onto an ice film and then water molecules to form an ice overlayer at 165 K. Subsequent Kelvin probe measurements revealed no vertical movement of protons embedded in the ice film. The observation conflicts with the mobile character of protons observed in other works at comparable temperatures, and the proton mobility issue is considered yet unresolved. One might suspect that proton mobility in ice films is affected by specific conditions of samples, for instance, sample geometry (thin film, cluster, or bulk crystal), morphology (crystalline or amorphous phase), proton location (surface or interior doping), and the presence of counter anions. Such conditions need to be matched as closely as possible or carefully considered for the investigation of a controversial system. With this motivation we revisit the proton mobility measurement in ice films in this work. Several research groups have already reported detailed studies on this topic by using IR spectroscopy,5–8 Kelvin probe,10 and reactive ion scattering (RIS) spectroscopy,11–13 from which a unanimous conclusion can be drawn about vertical immobility of protons that are located at the ice film surfaces. In the present paper, we address only the conflicting issue of proton mobility in a ‘proton-sandwich’ ice film.

We performed the experiments in an ultrahigh vacuum chamber (base pressure $1 \times 10^{-10}$ Torr) equipped with instruments for surface analysis and a sample manipulator with a temperature-control stage.3 Ice films were grown on the (0001) surface of a Ru single crystal by a backfilling method at H2O partial pressure of $1 \times 10^{-8}$ Torr. The ice films grow in a layer-by-layer fashion under these conditions as verified by depositing alternate H2O and D2O layers and analyzing the isotopic population of surface water molecules.18 HCl gas (Aldrich, 99+% purity) was introduced into the chamber through a separate leak valve facing the Ru substrate surface. The ‘proton-sandwich’ films were made by two different procedures. In film I, water vapor was deposited onto a Ru substrate at a thickness of 4 bilayers (BL) at a temperature of 140 K to grow a crystalline ice film. Then, HCl was adsorbed onto the film surface at 140 K in a small amount (an exposure
of 0.5 L; 1 L = 1 × 10^{-6} \text{Torr s}). Finally, an overlayer of water molecules (4 BL) was added onto it at 73 K. The HCl gas provided excess hydronium ions and chloride ions to the film by spontaneous ionization at 140 K. Film II was prepared by growing the overlayer of water molecules (4 BL) at 140 K, instead of 73 K in film I, while the rest of the procedures were kept the same as those in film I. We also prepared an ice film with excess protons at the surface (film III) for a control experiment. This sample was prepared by growing an 8 BL-thick ice film at a selected temperature between 60 K (amorphous phase) and 140 K (crystalline phase), followed by HCl adsorption onto the surface for an exposure of 0.5 L. The ice film thickness was estimated from the temperature-programmed desorption (TPD) experiments.

Neutral and ionic species present at the film surfaces were analyzed by the techniques of Cs^+ reactive ion scattering (RIS) and low energy sputtering (LES), respectively, for their mass and population. The principle and instrumentation for these techniques have been described in detail elsewhere. Briefly, a low-energy Cs^+ beam is scattered from a target surface. Neutral molecules at the surface are picked up by the Cs^+ projectiles, forming Cs^+ molecule cluster ions (RIS process). Hydronium ions at the surface are ejected by the impact of low energy Cs^+ ions (LES process). These ions are detected by a quadrupole mass spectrometer with its ionizer filament switched off. The Cs^+ beam energy was 30 eV in the present experiments, unless specified otherwise. The Cs^+ impact did not cause secondary ionization of water molecules at this energy, and the probing depth into the ice film surface was estimated to be 1 BL. The beam current density was maintained below 1.0 nA cm^{-2} to avoid surface contamination by incident Cs^+ ions.

To measure the extent of proton transport in an ice film, we prepared the proton-sandwich ice films, as described above, and monitored the population of hydronium ions at the film surface. Fig. 1 shows the LES intensity for hydronium ions measured as a function of temperature for three ice films (I, II, and III). At the surface of film I for which the temperature of the ice overlayer growth was 73 K, the hydronium ion intensity was small and stayed almost constant in a temperature range of 73−120 K. The hydronium ion intensity increased considerably during the temperature increase from 130 to 140 K at a rate of 2 K s^{-1}, and there was a further intensity increase as the sample was kept at 140 K for 20 min. At a temperature above 140 K, the water desorption from the surface significantly reduced the thickness of these thin films and hampered any reliable measurement. The observed temperature-dependence of hydronium ion signals can be rationalized by the occurrence of two proton-transport mechanisms operating within different temperature regimes, as explained in a previous study. The weak hydronium ion intensity below 120 K is due to the transport of a limited portion of protons from a sandwich layer to the surface via the hopping relay process, which does not require thermal activation. The increased hydronium ion intensity above 130 K is due to the proton transport via a thermally activated, hop-and-turn mechanism.

In contrast to film I, film II showed a substantially high population of hydronium ions at the surface even at low temperature (≤120 K). The hydronium ion intensity increased somewhat further above 130 K. The high surface population of hydronium ions at T ≤ 120 K suggested that hydronium ions were already present at the surface when the film was prepared. We consider that during the growth of the ice overlayer at 140 K, protons remain aloft on the film surface due to its inherent tendency to reside at the ice surface and the activation of proton transport processes at this high temperature. There seems no other appropriate interpretation for the high abundance of hydronium ions observed from this surface, because the majority of protons trapped in a sandwich layer did not move to the surface at T ≤ 120 K in film I. These results indicate that a proton-sandwich film can be made only at a low enough temperature to suppress the proton migration during the overlayer growth, and film II must be a ‘proton-at-the-surface’ film.

Fig. 1 also shows the hydronium ion intensity measured from a sample prepared by HCl adsorption on the film surface (film III). The hydronium ion signal from this surface was very strong at low temperature (it went beyond the display scale for T < 120 K) and decreased with increasing temperature. As discussed in a previous study, the stronger intensity for hydronium ions at lower temperature can be attributed to the fact that hydronium ions are less efficiently hydrated and more weakly bonded to the ice surface at a lower temperature, and this enhances the LES yield for the hydronium ions. At high temperature, the efficiently hydrated hydronium ions with strong bonding to the surface reduces the LES yield.

After waiting for 20 min at T = 140 K, the hydronium ion intensity from film III reached a value close to those monitored from films I and II. The difference in hydronium ion intensities at this stage was within the intensity fluctuations associated with the instrumental factors. At this temperature...
the motions of protons and water molecules are activated, and the proton distribution near the ice surface will reach an equilibrated state after a sufficiently long time. The observation of approximately the same hydronium-ion intensities indicates an approach to such equilibrium, at which the majority of hydronium ions populate near the ice surface, efficiently solvated by water molecules.

The discovery made with film II brings attention to the soft-landing experiments of hydronium ions on ice films reported by Cowin et al. As part of the experiments to monitor proton mobility in ice films, they intended to prepare a proton-sandwich structure by depositing hydronium ions onto an ice film and then growing the ice overlayer at 165 K. Since hydronium ions can remain afloat on the surface of the growing layer at this temperature, one can imagine that the ice film may have protons at the surface instead of having them in the interior. In this case, the protons may persist to stay at the surface during the subsequent Kelvin probe measurement and thus appear immobile in the vertical direction.

We have changed several experimental conditions in the present work to check their effects on proton mobility. As the thickness of the ice overlayer of film I was increased from 4 to 8 BL, protons still migrated from a sandwich layer to the surface, though more slowly than for the case of the 4 BL-thick overlayer at the same temperature. In film II, increasing the overlayer thickness to 8 BL was not able to hold the excess protons in the film interior at all. To see the effects of film growth temperature and ice morphology, we varied the temperatures for HCl adsorption and the upper layer growth between 60–100 K for films I and II, and the growth temperature for film III between 60–140 K. These changes did not alter the major qualitative features of the curves shown in Fig. 1. Also, during the temperature ramp (73–140 K) at a rate of 2 K s−1 in the present experiment, the upper layer of film I would be remained in an amorphous phase for the most of the time, whereas the film morphology changed to a crystalline phase at 140 K after waiting for 20 min, if protons did not interfere with the phase change characteristics. In this respect, the result suggests that protons are mobile through the ice film in both amorphous ($T < 140$ K) and crystalline phases ($T \geq 140$ K) that form during the course of the temperature ramp. In addition, it has been observed that Cl− ions produced from HCl dissociation do not migrate to the surface of film I at $T \leq 140$ K, while protons build up a substantial population at the surface. This shows that the upward migration of proton is not caused by the presence of counter anions.

In conclusion, the present study suggests that the anomalous experimental reports on the mobility of protons in ice films can be explained by the affinity of protons for the ice surface and the facile proton transport near the surface at $T \geq 130$ K. The result verifies that protons are mobile in an ice film and can migrate from the film interior to the surface at favorable temperatures. This conclusion is unaffected by the changes in ice film morphology and thickness (2–8 BL) and by the presence of counter anions.

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