Proton Transfer

Protons at Ice Surfaces**

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Ice surfaces play an important role in many chemical processes that occur in nature at low temperatures. Ice particles in the polar stratospheric clouds, for example, catalyze the heterogeneous reactions that lead to the seasonal depletion of the ozone layer,[1] and prebiotic molecules detected in interstellar space are believed to form in the ice mantle of interstellar dust particles.[2,3] The environmental and astrobiological importance of ice reactions has stimulated research on this subject in recent years.[4] A critical issue in the study of ice reactions is the rate of proton transfer. Proton transfer is responsible for a variety of chemical reactions in the aqueous phase, ranging from acid–base neutralization to enzymatic reactions. Proton mobility is anomalously high compared to that of other ions in liquid water. This unique behavior is attributed to a proton relay (Grotthuss) mechanism in which the effective motion of a proton involves a sequence of proton tunnelings along the hydrogen-bonded chain of water molecules.[5–8] This sequential proton transfer is promoted by the rearrangement of hydrogen-bond networks in liquid water in order to accommodate a proton in stable solvation structures.[5–8]

In ice, however, such a large structural rearrangement is impossible due to the fixed geometry of water molecules in the tetrahedral hydrogen-bond structure. Therefore, proton transfer in ice must involve a different mechanism. It is believed that at least two features are essential for this proton transfer.[9] First, the proton transfer should not significantly alter the fixed geometry of water molecules in the tetrahedral lattice. However, in an ice lattice constructed according to the "ice rules", such proton transfers can occur only up to a limited distance. Therefore, the second requirement is that an ice lattice should possess orientational (Bjerrum) defects where the ice rules are violated locally. If these defects move due to reorientation of water molecules, the passage of protons can be extended.

Proton transfer in ice has been studied using various experimental approaches. Electrical conductivity measurements of ice,[9,10] which have a long history, support the proton-transfer mechanism associated with the motion of the Bjerrum defect. The proton mobility in ice deduced from the

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conductivity measurements varies greatly, however, mainly due to the difficulty in controlling and characterizing the space-charge layer formed at the ice/electrode interfaces.[9] More recently, Devlin and co-workers[11, 12] studied the H/D isotope exchange of water molecules in ice nanocrystals doped with protons. By identifying water isotopomers by IR spectroscopy, they showed that proton transfer occurs through a combination of proton hopping between adjacent water molecules and thermal rotation of molecules (hop-and-turn process) at temperatures above 125 K.

Cowin et al.[13] have deposited hydronium ions on ice films from low-energy beams and observed that the surface protons are immobile across the films over a fairly wide temperature range (30–190 K), and Park et al.[14] have studied H/D exchange reactions on ice films adsorbed with HCl and have shown that the H/D exchange is facile only at the film surface, while its propagation into the interior is absent or very slow at 90–140 K. These incongruous observations suggest that further study is necessary to understand proton transfer in ice. In particular, these results raise the possibility that protons might behave quite differently at the ice surface and in the interior. The current study examines this puzzling issue.

We carried out experiments with ice films deposited on a Ru(0001) single crystal in an ultrahigh-vacuum chamber by a backfilling method at a water vapor pressure of $(1–5) \times 10^{-8}$ Torr.[15] The temperature of the Ru substrate was varied between 40 and 1500 K by a liquid He cryostat and resistive heating. H_2O, D_2O, and HCl gases were introduced into the chamber through separate leak valves. The ice films were prepared in the form of two different structures.

In structure I, the excess protons were sandwiched between the underlying D_2O layer and the upper H_2O layer. In order to prepare this film, D_2O was deposited on the Ru substrate at a thickness of 2 bilayers (BLs) at 140 K. A small amount of HCl was then deposited on top of the D_2O layer [approx. 0.1 monolayer (ML) by the exposure of 0.1 L; 1 L = 1×10^{-6} Torr s] at 140 K. Finally, an H_2O overlayer was deposited to a thickness of 4–12 BLs at temperatures below 100 K. The HCl gas provides excess protons to the film by spontaneous ionization at 140 K,[16, 17] and the underlying D_2O layer serves as a spacer to remove any effects of the Ru substrate on the upper layer, since D_2O forms a well-ordered film on Ru(0001) at 140 K without dissociation.[18] It was essential to deposit the upper H_2O layer at low temperature; otherwise the protons remained afloat on the surface during the deposition instead of being buried within the sandwiched layer, as explained below. Diffusional mixing of the H_2O and D_2O layers did not occur during the deposition.[15]

In structure II, the excess protons were placed on the surface of an ice film. To prepare this film, we deposited a 2-BL-thick layer of D_2O on Ru at 140 K, followed by H_2O for a 4- to 12-BL thickness at below 100 K, and finally a small amount (approx. 0.1 ML) of HCl. The thickness of the ice film was estimated from temperature-programmed desorption experiments.

The surface of the ice films was analyzed by reactive-ion scattering (RIS) and low-energy sputtering (LES) using a low-energy Cs^+ beam (10–30 eV). It has been shown[4] that RIS and LES can detect neutral molecules and ions, respectively, at the surface of ice films with a depth resolution of 1 BL. Water isotopomers (H_2O, HDO, and D_2O) and their isotopomeric abundance were measured by RIS, and the proton population was measured by detecting hydronium ions (H_3O^+, H_2DO^+, HD_2O^+, and D_3O^+) by LES.

The results of the RIS and LES measurements with the ice films of structure I (proton-sandwich films) are shown in Figure 1. Apart from reflected Cs^+ primaries at m/z 133, the
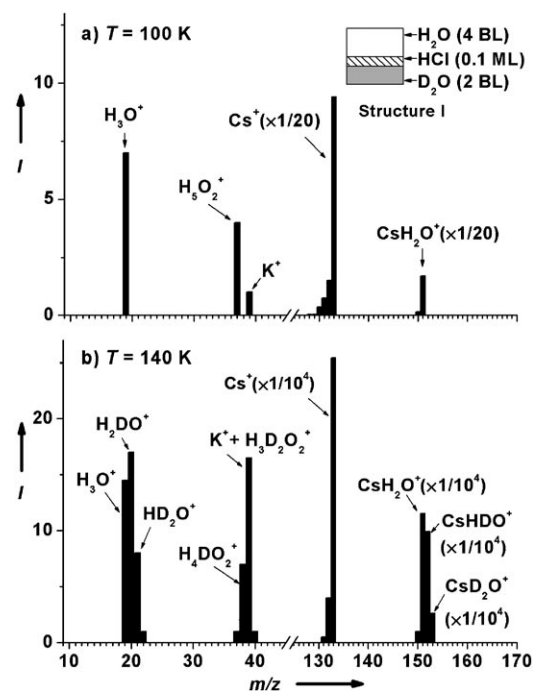

Figure 1. Positive-ion mass spectra measured at the surface of ice films of structure I. The film structure is depicted on the top right. In spectrum (a), the sample temperature was maintained at 100 K during the measurement. In spectrum (b), the temperature was raised to, and maintained at, 140 K for 20 min before the measurement. The Cs^+ and Cs^+–water peak intensities are reduced by the factors indicated. The energy of the incident Cs^+ beam was 30 eV.

mass spectra are characterized by two kinds of peaks. The peaks above m/z 133 are due to RIS, that is, pick-up of surface molecules by the incoming Cs^+. The LES peaks, which are due to the ejection of pre-existing ions at the surface, appear at masses lower than m/z 133. In spectrum (a), the RIS peak at m/z 151 (CsH_2O^+) is due to H_2O molecules at the surface. The LES peaks at m/z 19 and 37 represent the ejection of H_3O^+ and its hydrated cluster ($H_5O_2^+$), respectively. The peak at m/z 39 is due to the reflection of a K^+ impurity in the Cs^+ beam. The H_3O^+ peak indicates that the protons have migrated from the HCl sandwich layer to the surface. This peak is not due to the deposition of residual HCl vapor inside the chamber because it did not appear in the control experiments on pure ice films.

In spectrum (b), the film temperature was raised to 140 K for the measurement. The hydronium ion intensity increased substantially from that measured at 100 K. This indicates enhanced proton transfer to the surface at 140 K. Further, D-

substituted species appear for hydronium ions (*m/z* 19–22) and Cs⁺–water clusters (*m/z* 151–153). These deuterated species indicate that the H/D exchange starts at the D_2O/H_2O interface and propagates to the surface. The film becomes crystalline after annealing at 140 K, and this surface morphology change increases the intensity of scattered ions (Cs⁺, K⁺, and Cs⁺–water) by three orders of magnitude in spectrum (b).[15] It has been shown[14] that this morphology change does not significantly alter the LES efficiency for hydronium ions.

Figure 2 shows the variation of LES intensity for hydronium ions as a function of temperature for films of structures I
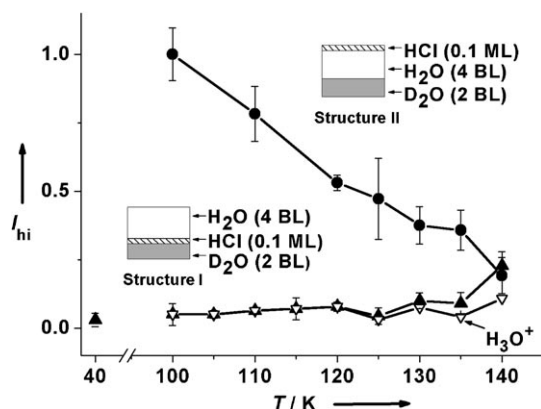

Figure 2. Variation of hydronium ion intensity, I_{hi}, as a function of temperature from films of structures I (▲) and II (●). The hydronium ion intensity is the summation of the intensities of all the isotopomers (H_3O^+, H_2DO^+, HD_2O^+, and D_3O^+). The H_3O^+ intensity of the structure-I film is plotted separately (▽). The scale on the ordinate is normalized against I_{hi} of structure II at 100 K. For measurements between 100 and 140 K, the ice film temperature was increased at the rate of 2 K min⁻¹.

and II. For structure I, the hydronium ion intensity is small and constant in the temperature range 40–125 K, but it then increases noticeably. Below 125 K, the hydronium ion signal contains only H_3O^+ without the D-substituted species. The H_3O^+ signal appears immediately after film deposition and does not increase in intensity with time. Above 125 K, the increase in the hydronium ion signal is mainly due to the D-substituted species ($H_{3-x}D_xO^+$, $x = 1$–3), which suggests a common origin for the proton-transfer enhancement and the H/D exchange process at higher temperatures. At 140 K, the hydronium ion intensity is approximately the same from the surfaces of structures I and II. The same proton population at the two surfaces independent of the initial proton locations suggests that the spatial distribution of protons has reached an equilibrium state as a result of active proton transfer through the films. Above 140 K, water desorption from the surface becomes significant, and this hampers any reliable measurements above this temperature.

For the structure-II film, the hydronium ion intensity decreases with an increase in temperature. This suggests two possibilities: 1) proton migration from the film surface to the interior at an elevated temperature, or 2) increased hydration of protons at the surface. Desorption of HCl does not occur

from the ice surfaces below 140 K.[17] In order to check possibility (1), we performed control experiments that measured the hydronium ion intensity from structure-II films of different thicknesses (4–10 BL) at 140 K. We observed that the surface proton population does not change with film thickness. Further, we continuously exposed these films to a large amount of HCl gas at 140 K in order to measure their HCl uptake curves. The surface proton population became saturated at an HCl exposure of around 2 L; this was independent of film thickness. The results of the control experiments rule out the possibility of continuous proton migration to the film interior. Next, we considered possibility (2). If a proton is fully hydrated at the surface it will occupy a slightly subsurface position relative to the surrounding water molecules. In this situation, the ejection of hydronium ions will be effectively blocked because the LES is a soft-sputtering method that ejects only top-layer species.[4] The stronger bonding between hydronium ions and the ice surface due to hydration will also reduce the LES yield. Thus, we can conclude that protons reside mostly at the film surfaces in hydrated forms.

The Cl⁻ population was measured at the surface of structure-I films by the LES of negative ions. Cl⁻ did not appear at the surface until the film temperature reached 140 K, although the proton population at the surface was substantial. This result indicates that the observed proton transfer to the surface is not driven by the electrostatic forces from Cl⁻.

The rationale for the propensity of protons to reside at the surface seems straightforward. The excess protons in liquid water prefer to form three-coordinate, planar water structures (commonly called Zundal and Eigen structures).[5–8] In ice, however, all water molecules, including those attached to the excess protons, must be four-coordinate. This bonding requirement destabilizes the protonated molecules and generates a thermodynamic repulsive force that transfers the protons to the surface where water molecules are less coordinated. This thermodynamic tendency for surface residence clearly explains the previous observations[13,14] that protons at ice surfaces are immobile towards the interior.

We further examined the kinetics of vertical proton transfer from the ice interior to the surface by measuring the temporal change in proton population and water isotopomeric distribution at the surface of the structure-I film. Figure 3 shows the results obtained at 130 K. The proton population at the surface rapidly increases to reach a limiting value after 5 min. The H/D exchange of surface water molecules was determined from the $Cs(H_xD_{2-x}O)^+$ ($x = 0$–2) isotopomeric intensities. It occurs more slowly than the proton transfer. The D-enrichment factor of water, defined as $f_{DE} = ((\text{[HDO]}/2) + \text{[D}_2\text{O]})/(\text{[H}_2\text{O]} + \text{[HDO]} + \text{[D}_2\text{O]})$, increased up to 0.2, thus indicating the complete isotopic mixing between 4 BLs of H_2O and 1 BL of D_2O. Figure 3 also shows f_{DE} measured in the absence of HCl for an ice film consisting of H_2O and D_2O layers. In this film, the isotopic mixing occurs more slowly than in the structure-I film because it is mostly due to the self-diffusion of water. This shows that the H/D exchange in the structure-I film occurs due to the excess protons.
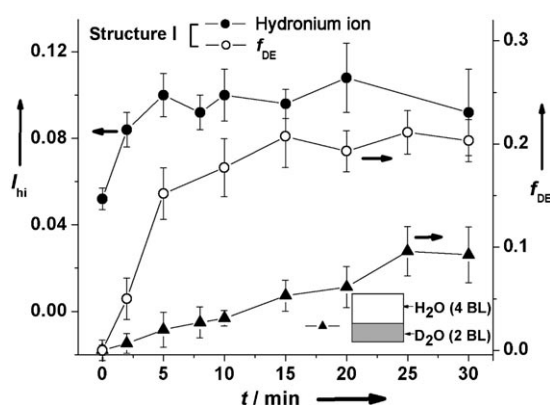
Figure 3. Change in hydronium ion intensity (I_{hi}; ●) and D-enrichment factor in water (f_{DE}; ○) as a function of time for a structure-I film at 130 K. The film structure was the same as that in Figure 2. The hydronium ion intensity includes all isotopomers, and the scale for I_{hi} is the same as that in Figure 2. The scale for f_{DE} is shown along the right ordinate. f_{DE} measured with a pure ice film (its structure is depicted) is also shown (▲). The films were deposited at 100 K and heated to 130 K; the kinetic measurements were then initiated.

Figure 3 shows that the relative speeds of three kinetic processes are in the following order: proton transfer > H/D exchange > self-diffusion. In addition, an extra channel exists for proton transfer that rapidly generates surface H_3O^+ at low temperatures (< 125 K). In the following we will discuss a molecular-level interpretation for these observations using the proton-transfer model depicted in Figure 4. Although this model is configured for a crystalline ice film, key mechanistic features should be applicable to noncrystalline films as well.

The rapid appearance of surface H_3O^+ at 40–125 K suggests the occurrence of sequential proton hopping through the hydrogen-bonded chain, as illustrated in Figure 4b. Such a proton relay does not require molecular reorientation and is
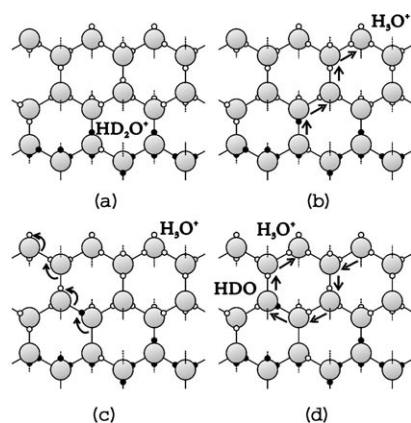
therefore feasible even at low temperatures. This mechanism cannot be responsible for proton transfer through bulk ice, however, because the length of a successful proton transfer is limited. Nevertheless, some successful routes may be found across a very thin ice film (only one successful route exists in Figure 4b), through which a specific fraction of protons can be transported.

When an ice film is warmed to a temperature above 125 K water molecules gain thermal energy and rotate.[11,12] This creates additional paths for proton hopping (Figure 4c) and therefore more protons can be transferred to the surface. A combined process of molecular reorientation and proton hopping generates an HDO isotopomer (Figure 4d). It should be noted that more D-enriched isotopomers are formed and transported by the recurrence of the hop-and-turn processes. Therefore, the build-up of D-enriched surface species will lag behind the build-up of surface protons, as observed in Figure 3.

To summarize, the detection of hydronium ions at the surface by LES and the asymmetric transport behavior of protons through ice films reveal that protons mainly reside at the ice surface. The surface affinity of a proton is a thermodynamic consequence of the difficulty of embedding protons in the ice lattice with regard to energy. A proton can transfer over a short distance by a hopping relay even at low temperatures (< 125 K) at which the molecular motions are frozen. At higher temperatures, the rate and distance of proton transfer increase due to the hop-and-turn mechanism. This also produces the D-enriched isotopomers. We stress that the present work explicitly demonstrates the occurrence of two types of proton-transfer mechanisms and differentiates their operating ranges and temperatures.

As shown in this study, protons are a unique mobile species in ice films at temperatures at which the motions of molecules and ions are virtually frozen. Proton mobility at the ice surface in the lateral direction is shown to be even higher.[14] With such high mobility and surface affinity, protons can efficiently migrate and protonate molecules on ice surfaces, and are therefore available to catalyze reactions that would otherwise not occur at low temperatures. Indeed, proton-catalyzed reactions have been observed on frozen alcohol films at 100 K.[4] Since hydrogen is the most abundant element in interstellar space, either in neutral or ionized forms, it can be imagined that protons accumulate at the ice surfaces of interstellar dust particles to build up a significant population. Under such circumstances, proton-catalyzed reactions might occur at the surface to form prebiotic organic molecules.[2,3] It is noteworthy that proton-catalyzed reactions are essential for the synthesis of many organic molecules.

Figure 4. a) A cross-sectional view of a model ice surface with an H_2O layer (2 BLs) on top of a D_2O layer. The small white circles indicate H atoms, and the small black circles indicate D atoms. A hydronium isotopomer ion (HD_2O^+) is initially located at the H_2O/D_2O interface. b) A proton is transferred to the surface by a hopping relay (the arrows) without reorientation of the water molecules. c) Thermally activated rotation of water molecules produces new paths for proton transfer. d) HDO is transported by the recurrence of hop-and-turn processes.

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