

Proton Transport and Related Chemical Processes of Ice

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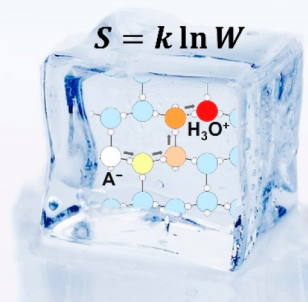


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ABSTRACT: Excess protons play a key role in the chemical reactions of ice because of their exceptional mobility, even when the diffusion of atoms and molecules is suppressed in ice at low temperatures. This article reviews the current state of knowledge on the properties of excess protons in ice, with a focus on the involvement of protons in chemical reactions. The mechanism of efficient proton transport in ice, which involves a proton-hopping relay along the hydrogen-bond ice network and the reorientation of water, is discussed and compared with the inefficient transport of hydroxide in ice. Distinctly different properties of protons residing in the ice interior and on the ice surface are emphasized. Recent observations of the spontaneous occurrence of reactions in ice at low temperatures, which include the dissociation of protic acids and the hydrolysis of acidic oxides, are discussed with regard to the kinetic and thermodynamic effects of mobile protons on the promotion of unique chemical processes of ice.



1. INTRODUCTION

Ice is ubiquitous in the cryosphere environment of Earth and in outer space and provides important media for chemical reactions that occur in nature at low temperatures. Famous examples include the heterogeneous reactions on the polar stratospheric ice particles that lead to the seasonal depletion of the ozone layer.¹ Astronomical observations using infrared (IR) telescopes and laboratory simulation experiments support the possibility that simple chemical species are transformed into more complex molecules on ice particles in interstellar space.^{2,3} In early studies on these processes, empirical observation was usually a higher priority than obtaining a basic chemical understanding of the observed phenomena. Fundamental principles that underlie these ice-related chemical processes are of interest, but the current level of understanding of the chemistry of ice is very limited, compared with the vast knowledge regarding reactions in the aqueous or gas phase, which has been accumulated for a long time.

According to a basic knowledge of chemical kinetics, cold ice can be considered an adverse environment for reactions to occur, because reagent molecules are trapped immobile in a solid ice lattice, and the rate of diffusion of the molecules is reduced by several orders of magnitude compared with that in liquid water. In addition, there is insufficient thermal energy to surmount the reaction activation barrier. However, a notable exception is the “excess” proton (also called H⁺ ion, hydronium, or positive ionic defect) in ice. Excess protons efficiently migrate in ice via the Grotthuss mechanism, which involves a proton-hopping relay along the hydrogen-bonded water chain of the ice network.^{4,5} This process makes the protons uniquely mobile species in ice at low temperatures, where the diffusion of atoms and molecules is extremely

suppressed. The general mechanism for the transport of protons in ice has been well established through extensive studies.^{4,5} However, considerable uncertainties and confusion still exist in the literature regarding the details of the proton-transport mechanism as well as the properties of excess protons in ice. The present review focuses on these issues. It discusses the current level of understanding of the static and dynamic properties of excess protons in ice, with an emphasis on the roles of protons in the chemical reactions of ice. The remainder of this paper is organized as follows. **Section 2** presents a brief history of studies on proton-transport phenomena in ice and discusses recent developments. **Section 3** highlights the different properties of protons residing in ice and on its surface. **Section 4** addresses the chemical reactions and their connection with the mobile protons of ice. **Section 5** presents a summary and concluding remarks.

Excellent reviews have been published on the chemical processes of ice surfaces. These reviews are primarily focused on the structure of ice surfaces and adsorbate–surface interactions;⁶ surface chemical properties of frozen water films and sulfuric acid films;⁷ adsorption and ionization of hydrogen chloride on ice surfaces;⁸ elementary steps of reactions on ice surfaces;⁹ theoretical studies on heterogeneous reactions related to atmospheric ozone depletion;¹⁰ structure, molecular diffusivity, and reactions on ice surfaces;¹¹ reactive

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scattering processes of low-energy ion beams on ice surfaces;^{12,13} and adsorption, diffusion, and reactions on amorphous solid water (ASW) films relevant to cosmic dust grains.^{14,15} The previous studies have mainly investigated the processes that occur on the surface of ice partly because chemical reactions occur more easily on the surface, where the molecular diffusivity is higher than that in the interior of ice. Additionally, various surface spectroscopic techniques are available for the analysis of the chemical states of ice surfaces in ultrahigh-vacuum (UHV) environments.

When the ice temperature increases close to the melting point, a quasi-liquid layer (QLL) may form on the ice surface, as well as a liquid-phase compartment at the interface between the ice grain boundaries.^{4,5,16} Such distinctly different microscopic environments of ice can act as a host for diverse types of reactions and have many interesting effects, such as accelerated reaction rates and new pathways due to the freeze-concentration effect in the liquid compartment,^{17–20} as well as the synthesis of new materials on the QLL-covered ice surface.²¹ These high-temperature chemical processes are important issues in environmental research related to terrestrial, oceanic, and atmospheric ices.^{17,22,23} Such subjects are beyond the scope of the present review, and interested readers are referred to excellent reviews annotated above. The present review is restricted to ice processes occurring at low temperatures (typically below 160 K), at which an ice surface has a solid-like property without a QLL. Additionally, an ice sample can be prepared and maintained under UHV conditions at these low temperatures, which is an important advantage for conducting experiments on ice samples in the absence of impurities owing to the adsorption of environmental gases.

Recent progress in the studies on proton behaviors and chemical reactions of ice would not have been possible without parallel development in the studies on other related phenomena of ice, e.g., the morphology of vapor-deposited ice films,^{24–26} the phase transition of ASW to crystalline ice,^{24,25,27–32} the diffusion of molecules in ice,^{33,34} the mixing and segregating behaviors of foreign additives,^{35–48} the structure of the ice film/metal interface,^{49–52} and the roughening transition of thin ice films on metal substrates.^{24,53–56} A majority of credible information about these phenomena has been accumulated during the past two decades through extensive experimental studies that employ a thin-film growing technique and spectroscopic analysis of ice samples under UHV conditions. During the investigation of chemical processes of ice, unwanted side processes related to these phenomena may concomitantly occur for ice samples and interfere with the observation, depending on the temperature and preparation conditions of the samples. Therefore, knowledge of these processes is essential for discriminating their effects from experimental observations or avoiding them via careful design of the experiment.

2. PROTON TRANSPORT IN ICE

The transport phenomena of excess protons in ice have been a subject of interest in the physics and chemistry of ice for a long time. In the late 1950s, Eigen and De Maeyer^{57,58} studied the proton transport phenomena in ice and liquid water and concluded that the proton mobility in ice is higher than that in liquid water, probably by 1–2 orders of magnitude, based on the measurements of the electrical conductivity of ice available at that time. They attributed the high proton mobility in ice to

efficient proton jumps along the hydrogen-bonded network of an ice crystal, in contrast to the structural diffusion of protons in an aqueous solution, which involves the rearrangement of the protonated water complex as the rate-determining step. The electrical conductivity measurements for ice were subjected to a large uncertainty because of the contribution of complicating factors of unknown magnitudes related to the ice–electrode interfacial phenomena.⁵⁷ This led to the reports of very different conclusions regarding the proton mobility in ice in other investigations.^{4,5,59,60} Around the same time, Jaccard^{61–63} and Onsager⁶⁴ developed the theory of charge conduction in ice based on the properties of ionic and Bjerrum (orientational) defects in ice.⁶⁵ According to this molecular-level theory, charge conduction occurs through a combination of ionic defect transfer, which involves successive proton jumps along the hydrogen-bond network of ice, and Bjerrum defect transfer, which involves the reorientation of water molecules. Figure 1 illustrates this proton-transport mechanism. A proton-

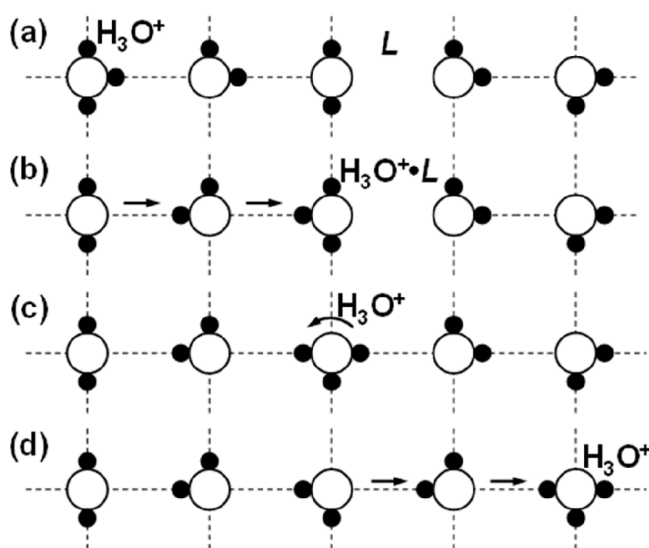


Figure 1. Pictorial illustration of the proton-transport mechanism in ice. The ice lattice is represented by a straightened-out chain of water molecules (“square ice” model) for convenience. The hydrogen bond is indicated by the dotted lines. (a) H_3O^+ indicates a hydronium structure with extra proton attached to water molecule, and L indicates a Bjerrum orientational defect. (b) Hydronium moves via successive jumps of excess protons (straight arrows) along the water chain until a proton is trapped by forming a stable $H_3O^+ \cdot L$ defect complex. (c) Reorientation of water in the complex (circle arrow) releases a proton and (d) resumes a proton-hopping relay. The actual mechanism for the trapping and release of a proton at a Bjerrum L defect is more complex than that drawn in this figure. A proton is trapped as a result of electrostatic stabilization of the $H_3O^+ \cdot L$ structure in the ice lattice,^{5,66} but this process is difficult to illustrate in the one-dimensional chain model. Additionally, a Bjerrum defect is moved by the reorientation of water, but this process is inaccurately represented by hydronium reorientation in the figure.

hopping relay occurs along the water chain with proper hydrogen-bond polarization (Figure 1a), but the proton transfer path is interrupted by the trapping of a proton at the Bjerrum L defect (Figure 1b). The reorientation of water releases a proton from the trap (Figure 1c), and proton transfer in the ice resumes (Figure 1d). For the next proton to pass through the same path, the hydrogen-bond polarization direction of the water chain must be returned to its original

state via Bjerrum defect transfer (not shown). This elegant theory has provided a basis for interpreting the conductivity and dielectric relaxation measurements for ice and yielded information about the mobility and relative charge of ionic and Bjerrum defects.⁵

In the 1980s, Devlin and co-workers^{67–69} used IR spectroscopy to study proton-transport phenomena in ice. They investigated the H/D isotopic exchange process of D₂O-doped H₂O-ice films and observed that intact D₂O molecules undergo stepwise conversion to coupled (HOD)₂ units and ultimately to individual isolated HOD molecules. The results provided clear molecular-level evidence that proton conduction in ice occurs through proton hopping and water reorientation steps (“hop-and-turn” mechanism). In addition, they concluded that excess protons are trapped by Bjerrum defects in the ice lattice at a low temperature, and the protons become mobile upon thermal activation of Bjerrum defect motion at a temperature above ~120 K.⁶⁹ There have been opposing experimental observations regarding proton mobility in ice also;^{59,70} however, as will be discussed in section 3, these results most likely resulted from the ice surface phenomena rather than reflecting the properties of protons in the bulk phase, according to further investigations.^{59,71} Two decades later, Lee et al.^{71–73} confirmed the proton mobility and transport mechanism by conducting surface spectroscopic measurements for thin ice films, which revealed that excess protons migrate through an ice film via the hop-and-turn mechanism at temperatures above 125 K. The study also indicated that a small portion of protons may be transmitted through the ice film via a hopping relay process without water reorientation at temperatures below 100 K.⁷³

Huppert and co-workers^{74–76} studied proton transport in ice by conducting time-resolved fluorescence experiments for ice samples containing excess protons and proton-sensitive fluorescent molecules. They found that the diffusion rate of protons in ice at temperatures of 235–270 K is 10 times faster than that in liquid water at 295 K. The diffusion coefficient exhibits a weak temperature dependence in this range, with an activation energy of $E_a < 1$ kJ/mol. The proton-hopping time was estimated to be approximately 0.2 ps. Surprisingly, this value is in accordance with the conclusion drawn by Eigen and De Maeyer in the 1950s from the electrical conductivity of ice despite the large uncertainty in the measurements.⁵⁷ In the range of 175–235 K, the diffusion coefficient varied significantly with changes in the temperature with $E_a \approx 30$ kJ/mol, indicating that water reorientation is the rate-determining step of proton diffusion.⁷⁶ Quasi-elastic neutron scattering (QENS) experiments performed by the same group revealed a good correspondence between the proton-hopping times estimated from the time-resolved fluorescence experiments and the neutron scattering experiments.⁷⁷ Timmer et al.⁷⁸ studied proton transport from photoacids to bases embedded in ice using femtosecond pump–probe spectroscopy. They observed that proton transfer occurs in two distinct time scales: a fast (~1 ps) transfer across a short distance independent of temperature at 240–270 K and a slow (~300 ps at 270 K) transfer across a longer distance with strong temperature dependence. The fast proton-transfer processes observed in the foregoing time-resolved spectroscopic experiments may correspond to proton-hopping events along the water wire between the proton donor and acceptor. The length of the proton-conducting wire in these experiments may be short and dependent on the sample preparation conditions.

The slow transfer processes with strong temperature dependence may result from the rate-determining behavior of other steps of the proton-transport mechanism, such as Bjerrum defect migration and rearrangement of the hydration structures of proton donors and acceptors.

Theoretical studies using quantum mechanical (QM) calculations and molecular dynamics (MD) simulations have provided valuable insights into the structure, energy, and dynamics of excess protons in ice. Ohmine and co-workers^{79,80} investigated the potential energy surfaces associated with proton transfer in ice using *ab initio* calculations combined with an empirical method (called the QM/MM method). In ice (in contrast to liquid water), a stable hydrated proton structure is not formed, because of the structural constraints of the ice lattice. Thus, excess protons are not trapped in a deep energy minimum in an ice crystal but transferred along the ice network on small energy barriers.⁷⁹ The stretching and shrinking motions of intermolecular O–O distances of the ice structure around the excess proton are mutually coupled to facilitate sequential proton transfers in a concerted fashion. Recent MD simulations^{66,81,82} indicated that proton transfer occurs on a time scale of ~1 ps with an Arrhenius energy barrier of 1.5 kJ/mol. The rate of proton diffusion decreases with a decrease in the temperature, for example, by a factor of 20 when the temperature decreases from 270 to 50 K.⁸¹ These trends are in accordance with the results of real-time spectroscopic measurements.^{74–76,78}

The proton transport in ASW was also studied by theoretical calculations.^{83,84} The local trapping structure of excess protons in ASW somewhat resembles the hydronium structures in liquid water but has evolved to a network with enhanced directionality.⁸³ Excess protons undergo sporadic jumps between these structures through a water bridge. QM/effective fragment potential (EFP) calculations at the B3LYP level revealed that the average proton-hopping time is approximately 0.3 ps in ASW at 160 K and increases to 0.05 ps at 300 K.⁸⁴ The energy barrier for the proton hopping is approximately 2.7 kJ/mol.⁸⁴

Although the major features of the proton transport phenomena in ice have been well established through extensive experimental and theoretical studies, there are uncertain features that need further clarification. In the following, two specific issues are discussed. (1) Does proton hopping occur in ice even at very low temperatures? (2) How different or similar are the transport mechanisms of hydronium and hydroxide? The first question arises from the consideration that proton hopping along the ice network is assisted by geometrical relaxation in the ice structure.⁷⁹ In this case, the effective mass of the proton transfer is expected to be large, and the proton may be less mobile at very low temperatures. MD simulations indicate that the proton-hopping rate in ice I_h is significantly reduced as the temperature decreases from 270 to 50 K, and it becomes almost zero in ice I_c at 50 K.⁸¹ Lee et al.⁸⁵ investigated this issue by performing experiments to measure the proton-transfer efficiency from a donor (H₃O⁺) to an acceptor (NH₃) embedded in ASW at temperatures of 10–80 K. The proton-transport distance was controlled by changing the separation distance between the donor and the acceptor in the samples. They observed that protons migrated across a distance of approximately 10 water molecules on average. Importantly, the proton-transfer efficiency did not change significantly from 80 to 10 K. The results indicate that proton hopping occurs at temperatures as low as 10 K and that its

efficiency is not significantly affected by the lattice temperature.

In the experiment performed by Lee et al.,⁸⁵ the transient mobility of excess protons in ASW was observed; a mobile proton is released from a stable hydronium structure by the external stimulus of ammonia adsorption on the ASW film surface.⁸⁵ One might question the idling mobility of excess protons in a perfectly crystalline ice, but this would only be a hypothetical question because excess protons are almost always trapped at defects in real ice at low temperatures.^{68,69,86,87} There was a report about the observation of idling mobility of protons in a neutral ice I_h lattice at 5 K in QENS experiments,⁸⁸ but this claim was refuted by further investigations.⁸⁹

The second issue addresses the assumption of the “mirror image” transport mechanisms of hydronium and hydroxide in ice; i.e., hydroxide moves through sequential “proton hole” transfers in analogy to hydronium transport through proton-hopping events.^{4,5} Recent studies indicate that fundamentally different molecular mechanisms may operate for the transport of hydronium and hydroxide in ice.^{84,90–93} Moon et al.⁹⁰ examined the migratory behaviors of H_3O^+ and OH^- in ASW at ~ 80 K and observed that the migration distance of H_3O^+ is much longer (< 23 ML) than that of OH^- (< 5 ML). Lee et al.⁹³ measured the migration speeds of H_3O^+ and OH^- from the interior of an ASW film sample to its surface. The H/D exchange reactions that these ions underwent along the passage through a D_2O –ASW film were also monitored. The study revealed that hydronium migrates through ASW faster than hydroxide to appear on the sample surface at temperatures of > 140 K during a gradual increase in the sample temperature, in contrast to the slower appearance of hydroxide on the surface at > 155 K. Furthermore, hydronium undergoes extensive H/D exchange with D_2O , whereas hydroxide does not. Figure 2 shows the extent of the H/D exchange reactions for hydronium and hydroxide observed in these experiments.⁹³ Hydroniums and water molecules detected on the surface had virtually identical H/(H + D) ratios (HDRs) at all the investigated temperatures (Figure 2a), indicating efficient H/D exchange between hydronium and water molecules during the hydronium migration via proton transfer. In contrast, the HDR of surface hydroxide was far higher than that of surface water at 154–168 K (Figure 2b). Using this HDR value, the probability that hydroxide undergoes proton-hole transfer during passage through one monolayer of D_2O is estimated to be $< 4\%$ at 160 K.⁹³ This shows that hydroxide moves exclusively via molecular hydroxide diffusion rather than proton-hole transfer.

Different proposals were also reported for the transport mechanism of negative charge carriers in ice. Recently, Watanabe and co-workers^{94–96} studied the behavior of OH radicals produced by ultraviolet (UV) photolysis of ASW. When the ASW films grown on a metal substrate were exposed to both UV photons and low energy electrons at 10–50 K, negative current was measured at the metal substrate along with a decrease in OH radical population at the ASW surface. They proposed that the negative current results from electron attachment to OH radicals and the transport of resultant OH^- ions through ASW via a proton-hole transfer mechanism. The negative current, however, may originate from multiple sources in these experiments, including electron transmission through ASW,^{97,98} electron attachment to OH radicals and defect structures in ASW, as well as the proposed OH^- transport. These various possibilities weaken the proposal of OH^-

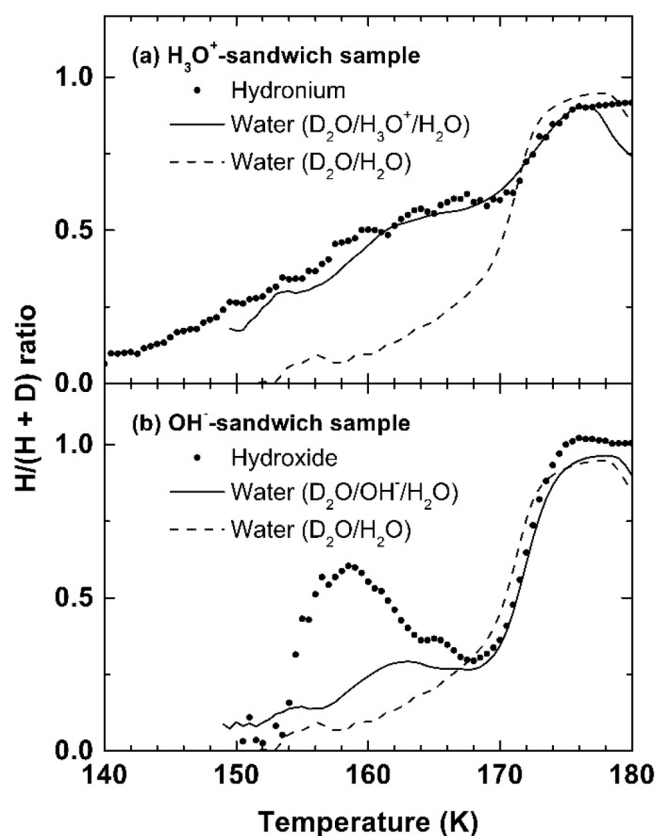


Figure 2. (a) HDRs of hydronium (black circles) and water (solid line) measured on the surface of a “hydronium-sandwich” ASW film, in which H_3O^+ and Cl^- (produced by ionization of HCl) are initially trapped between the bottom H_2O layer and the top D_2O layer [D_2O (~ 30 ML)/ $H^+ + Cl^-/H_2O$ (≥ 110 ML)/Pt(111)]. The virtually identical HDRs for hydronium and water above ~ 150 K indicate efficient H/D exchange due to proton transfer. The broken line indicates the HDR of water molecules measured on the surface of a pure ASW film [D_2O (~ 30 ML)/ H_2O (≥ 110 ML)/Pt(111)], where the H/D exchange reaction is not catalyzed by hydronium. (b) HDRs for hydroxide (black circle) and water (solid line) on the surface of a hydroxide-sandwich ASW film [D_2O (~ 30 ML)/ $OH^- + Na^+/H_2O$ (≥ 110 ML)/Pt(111)]. The HDR of hydroxide is significantly higher than that of water at 154–168 K owing to molecular hydroxide diffusion. The sample temperature was increased at a rate of 0.5 K s^{-1} . The surface populations and isotopomeric compositions of hydroniums and hydroxides were measured by means of low-energy sputtering (LES). In this technique, ions present at the ice surface are desorbed by the collisions of Cs^+ projectiles with the surface at low energy and the desorbed ions are detected by a mass spectrometer.⁹ The collision energy is controlled to be only slightly above the desorption threshold of the ions to minimize molecular fragmentation and suppress secondary ion emission. The isotopomeric composition of water molecules was measured by means of temperature-programmed desorption (TPD). Reproduced with permission from ref 93. Copyright 2014 American Chemical Society.

transport via a proton-hole transfer mechanism. Compelling evidence of this mechanism would be the direct observation of hydroxide diffusion and the H/D exchange of hydroxides and water molecules in the ice, but to our best knowledge, these processes have not yet been reported for ASW or crystalline ice at low temperatures (e.g., below 90 K).

Uddin et al.⁸⁴ investigated the origin of the different transport mechanisms of hydronium and hydroxide by performing QM/EFP-MD calculations for the transport of

these ions in a condensed-phase water model. The calculated free-energy barrier of proton transfer for hydronium is significantly lower (by ~ 5.4 kJ/mol) in height and narrower (by 0.02 nm) in width than that of proton transfer to hydroxide (i.e., proton-hole transfer). These differences in the potential energy surface strongly affect the transport dynamics of the two species and significantly reduce the efficiency of proton transfer for hydroxide at low temperatures. For example, hydroxide hardly undergoes proton transfer with water at 160 K within 100 ps, whereas 80% of hydronium does so within 1 ps. At 300 K, the proton transfer to hydroxide is still relatively suppressed, and the average time for proton transfer to hydroxide is 2 orders of magnitude longer than that of hydronium (~ 5 ps vs ~ 0.04 ps). These theoretical results agree with the experimental results observed for ASW at 154–168 K (Figure 2).⁹³ Furthermore, the studies suggest that molecular hydroxide transport may play a significant role for hydroxide diffusion in aqueous solutions also.⁸⁴

3. PROTONS AT THE SURFACE

Protons residing at the surface of ice can influence a variety of ice surface phenomena, including the electrical conductivity, charge imbalance, and acid–base properties of the ice surface. Recent studies have shown that excess protons tend to accumulate at the ice surface rather than disperse uniformly in the bulk phase.^{71–73,99–105} Additionally, the surface-residing protons exhibit significantly different properties from those in the interior. Historically, insufficient information about these properties has been a major problem that hampers accurate measurement of proton conductivity for ice samples.^{5,59,70} Evidence that excess protons have a propensity for ice surfaces has been obtained from several different experimental observations over the past two decades. Cowin et al.⁷⁰ deposited very low-energy (1 eV) beams of H_3O^+ ions onto an ice film surface and observed that hydronium ions did not migrate from the ice surface to the interior over a wide range of temperatures (30–190 K). This observation was initially interpreted as a lack of proton mobility through the ice. Later, on the basis of LES experiments for ice film samples, Lee et al.^{71,72} reinterpreted the observation as an indication of the thermodynamic affinity of protons for ice surfaces, rather than the immobility of protons through the ice. Further evidence came from the observation of asymmetric proton-transport behavior between the ice surface and interior; i.e., protons spontaneously migrate from the ice interior to the surface, but the reverse migration does not occur.^{73,99} Figure 3 shows the surface-segregating behavior of excess protons observed in TPD, LES, and reactive ion scattering (RIS) experiments for “hydronium-sandwich” ice films.⁹⁹ Upon gradual heating of the sample, protons migrate from the ice film interior to its surface to be detected as surface hydroniums at temperature above ~ 154 K (Figure 3b). Efficient H/D exchange between the hydronium and water molecules is indicated by the correlation between the isotopomeric compositions of hydroniums (Figure 3b) and water molecules (Figures 3a and 3c). Lilach et al.¹⁰⁰ observed a similar surface-segregative behavior for hydroniums that were generated by the dissociation of water at the interface of an ice film and a Pt(111) substrate.

Devlin and co-workers^{101,102} measured the H/D exchange rate at the surface of ice nanocrystals by monitoring changes in the populations of dangling H and D bonds using IR spectroscopy. The results indicate that the proton activity for inducing H/D exchange between H_2O and D_2O at the ice

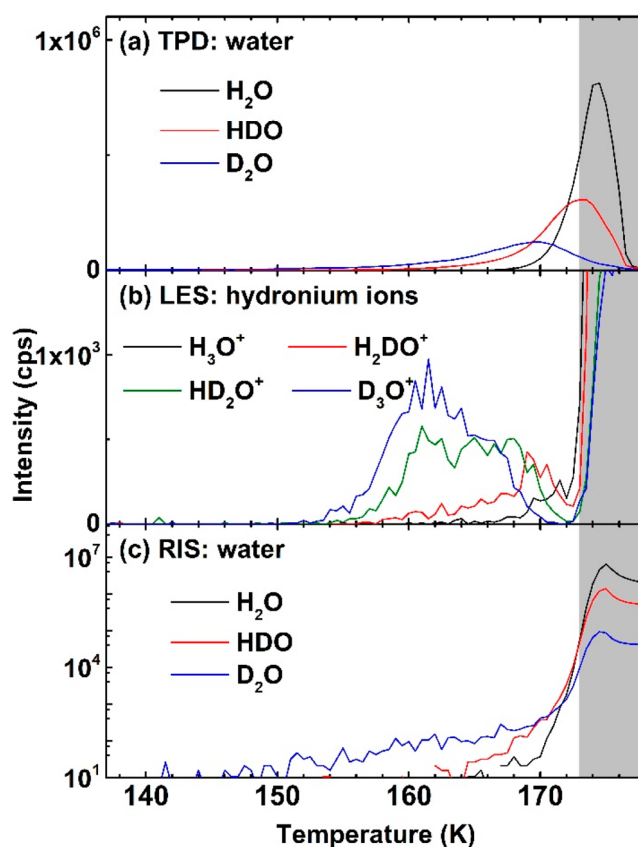


Figure 3. Results of TPD, LES, and RIS measurements for a “hydronium-sandwich” ice film [D_2O (~ 70 ML)/ $\text{H}^+ + \text{Cl}^-$ (0.3 ML)/ H_2O (~ 120 ML)/Pt(111)] during an increase in the temperature from 138 to 178 K. The ordinate scale indicates the mass spectrometric signal intensity (count per second) for each experiment. (a) TPD curves of water isotopomers. (b) LES signals of various hydronium isotopomers appearing on the surface. (c) RIS measurement of water isotopomers on the surface. In RIS, Cs^+ projectiles pick up molecules on the surface during the scattering process, and the resultant Cs^+ –molecule complex is identified by a mass spectrometer.^{9,106} The RIS signal is presented on a logarithmic scale. A roughing transition of the ice film occurred above ~ 173 K (shaded region), which destroyed the film structure.^{24,53–55} The TPD (a) and RIS (c) curves show changes in the isotopomeric composition of surface water molecules caused by diffusional mixing and H/D exchange reactions. The LES curves (b) indicate that hydroniums migrated from the film interior to the surface at a temperature above ~ 154 K. The temperature ramping rate was 0.5 degree s^{-1} for all the spectra. The Cs^+ beam energy for the LES and RIS measurements was 35 eV. Reproduced with permission from ref 99. Copyright 2012 American Chemical Society.

surface is enhanced by a factor of approximately 20 compared with that in the ice interior.¹⁰² More recently, Kato et al.¹⁰³ simultaneously measured the H/D exchange rates at the surface and in the interior of a pure ice film using isothermal desorption and reflection absorption IR spectroscopy (RAIRS), respectively. The proton activity at the topmost surface was increased by more than 3 orders of magnitude compared with that in the bulk. Because the proton activity is proportional to both the proton concentration and the mobility and because (as will be discussed shortly) the proton mobility is substantially lower on the ice surface than in the interior,¹⁰⁷ the enhanced proton activity at the surface is consistent with proton segregation at the surface.^{102,103} The

ratio of the proton concentration at the surface to that in the interior may be substantially higher than the corresponding ratio of the observed proton activity.¹⁰³

The surface propensity of excess protons is well supported by theoretical calculations.^{66,102,104,105,108–110} Density functional theory (DFT) calculations indicate that the hydronium structure is energetically stabilized at the ice surface compared with that in the tetrahedral ice lattice.^{102,104,108–110} The calculated surface segregation energy of hydronium varies sensitively with respect to the local structure of the ice surface, particularly the spatial arrangement of dangling surface hydrogens, in a wide range of 20–80 kJ mol⁻¹.¹⁰⁴ Hydroxide is also stabilized at the ice surface with a comparable magnitude of surface segregation energy.¹⁰⁴ In contrast, water molecules are destabilized at the ice surface. It follows that the degree of autoionization of the ice surface is correspondingly higher than that of a bulk ice crystal. The autoionization constant of an ice surface cannot be accurately determined at present. Studies on the H/D exchange rates of ice nanoparticles with adsorbed H₂S suggest that the autoionization constant of the ice surface may be on the same order of magnitude as the ionization constant of H₂S.¹⁰²

In the foregoing studies, similar surface-segregative properties of protons were observed for different forms of ice samples (thin films,^{71–73,99,100,103} nanocrystals,^{101,102} ice models^{66,102,104,105,108–110}) and different sources of protons (soft-landed hydroniums,⁷⁰ dissociation of acids,^{71,72,99,101} dissociation of interfacial water,¹⁰⁰ and autoionization of ice^{101–103}). These observations strongly indicate that the affinity of protons for ice surfaces is a thermodynamic property that is generally applicable to various ice conditions.

The depth distribution of surface-residing protons is an interesting subject, and it may be related to the depth of the ice surface region where the acidity is higher than that in the bulk ice.⁸² Lee et al.¹¹¹ studied the depth distribution of excess protons generated by the ionization of HCl into H⁺ and Cl⁻ at an ASW surface. Both H⁺ and Cl⁻ ions have a thermodynamic propensity to reside on the ice surface.⁹⁹ A negative voltage was observed for the space-charge layer (SCL) formed at the ASW surface, which indicates that H⁺ penetrates deeper toward the interior than Cl⁻, thereby generating a net negative charge at the outermost surface.¹¹¹ Assuming that Cl⁻ remained at the surface,⁴⁷ the average depth of H⁺ in the ASW surface was estimated to be $d(\text{H}^+) = 2.9 \pm 1$ ML.¹¹¹ Similar measurements for the SCL produced by adding CsOH on an ASW surface indicated that the average depth of OH⁻ was $d(\text{OH}^-) = 1.0 \pm 0.3$ ML. Therefore, protons are distributed over a wider depth than hydroxide, although both species prefer to reside at the surface. This difference was explained by the higher mobility of H⁺ compared with OH⁻ and the entropy of H⁺ diffusion in the ice.^{111,112}

The thermodynamic affinity of protons for ice surfaces influences the dynamics of proton transport on the surface. Because of the energetic stability of a surface hydronium structure, a proton cannot diffuse freely on the surface but experiences a substantial barrier in moving between the hydronium structures. This situation is illustrated in Figure 4 by a sketch of the potential-energy profile of proton diffusion along the ice surface. The barrier height for surface proton diffusion is expected to be on the order of 10 kJ mol⁻¹ and vary substantially depending on the local surface structure, according to MD simulation results indicating that the surface segregation energy of hydronium is in the range of 20–80 kJ

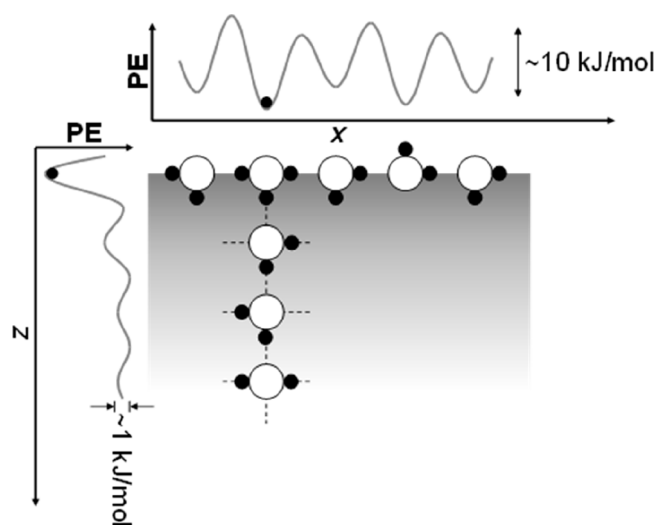


Figure 4. Illustration of the potential energy (PE) profiles for the migration of excess proton along the ice surface (x direction) and toward the ice interior (z direction). The ice lattice is represented by a square ice model for simplicity. A dot in the potential well indicates the location of an excess proton. The energetic stabilization of a surface hydronium structure makes excess protons reside preferentially at the surface and experience a large barrier for diffusion along the surface.

mol⁻¹.¹⁰⁴ The experimental activation energy for proton diffusion on a polycrystalline ice surface was 10 ± 3 kJ mol⁻¹, as estimated from the Arrhenius behavior of the rate coefficients for the H/D exchange reaction of the ice surface at temperatures of 90–110 K.¹⁰⁷ In this experiment, the H/D exchange rate was measured for an ice surface with preformed hydroniums, to eliminate the effect of the heat of acid ionization on proton diffusion and measure only the temperature effect.¹⁰⁷ These theoretical and experimental studies indicate that proton diffusion on the ice surface has very different characteristics from that inside the ice crystal, where it occurs over barriers with low and uniform heights (~ 1 kJ/mol).^{66,74–76,81,82} Consequently, the proton mobility on the ice surface is significantly lower than that inside the ice crystal and decreases rapidly as the temperature decreases.^{66,104,107}

We close this section by briefly mentioning the contributions of the increased surface population of protons and their reduced mobility to the proton activity on the ice surface. Studies on the H/D exchange process of ice in the temperature range of 110–160 K indicate that the proton activity on ice surfaces is higher than that in the ice interior,^{101–103} indicating that proton accumulation at the ice surface overwhelms the reduced mobility of surface protons at these temperatures. Whether this trend extends to higher temperatures is an interesting question related to the relative efficiencies of the surface and bulk reactions of ice particles in the atmosphere.^{17,22,23} The degree of proton accumulation at the ice surface is expected to decrease with the increasing temperature, according to the Boltzmann factor. However, high temperatures activate surface proton diffusion. The opposite temperature dependences of the two effects make it difficult to predict the proton activity of the ice surface at high temperatures, which requires experimental verification.

4. SPONTANEOUS CHEMICAL REACTIONS

Although molecular diffusion is suppressed in ice at low temperatures, certain types of reactions can occur spontaneously in the ice or on its surface. Reported examples include the dissociation of strong (HCl, HBr, HNO₃, and H₂SO₄)^{7,8,10,113,114} and weak protic acids (HF, halogen-substituted acetic acids)^{112,115–118} and the hydrolysis of acidic oxides (SO₂ and NO₂).^{108,109,119–122} These reactions occur at ice temperatures of 8–150 K when reactant molecules are adsorbed on the ice surface or codeposited with water molecules to form an ice mixture. A feature in common for these reactions is that they involve proton transfer with ice. For example, the dissociation of acids releases excess protons into the ice lattice. QM/EFP calculations¹⁰⁹ indicate that the hydrolysis of SO₂ on ice surfaces proceeds through transition states that involve proton transfer between the SO₂ adsorbate and ice. Experimental studies^{109,120–122} show that the reactions of SO₂ and NO₂ on ice surfaces produce various protonated species as a result of facile proton transfer, and these species are kinetically isolated on the ice surface as metastable products at low temperatures. The facile proton transfer in these reactions indicates that proton mobility plays a crucial role in removing the kinetic constraint of the reactions imposed by molecular immobility in the ice lattice.

Remarkably, for certain reactions, the reaction yield is higher in ice at a low temperature than in an aqueous solution at room temperature,^{112,115–118} indicating that the reaction becomes thermodynamically more favorable, not to mention kinetically feasible, in the ice. This effect is clearly manifested by the enhanced dissociation of weak acids in ice, as opposed to their nondissociation in aqueous solutions. Ayotte et al.^{115,116,118} observed that the adsorption of HF on the surface of an ASW film or dissolution within an ASW film at 40–80 K yielded strong continuous absorbance (“Zundel continuum”) across the 1000–3275 cm⁻¹ region in the RAIR spectrum, which is the hallmark spectroscopic signature of hydrated protons.¹²³ Additionally, extensive H/D-isotope scrambling occurred in the ASW sample. These features indicate extensive ionic dissociation of HF in ASW and on its surface, although HF is a weak acid in an aqueous solution. Park et al.^{112,117} reported that a series of fluoroacetic acids (CH_xF_{3-x}COOH; *x* = 0–2), which are weak acids, dissociated almost completely in ASW at 8–140 K, according to RAIRS detection of molecular and dissociated forms of the acids. Figure 5 shows the RAIR spectra of the acids dissolved in D₂O–ASW at 70–80 K, along with the spectra of pure acids. As indicated by the spectra of monofluoroacetic acid (MFA), difluoroacetic acid (DFA), and trifluoroacetic acid (TFA), the $\nu(\text{O-H})$ band of the molecular carboxylic acid appeared for a pure acid sample (black traces) but disappeared when the acid was dissolved in ASW (red traces). In addition, the shape of the $\nu(\text{C=O})$ band of the molecular carboxylic acid changed to that of the carboxylate anion in ASW. These changes indicate the complete dissociation of MFA, DFA, and TFA in ASW. That is, they behave as strong acids in ASW.

In contrast, the $\nu(\text{O-H})$ and $\nu(\text{C=O})$ bands of formic acid (FA) and acetic acid (AA) did not change significantly between the pure acid and acid–D₂O mixture samples (Figures 5d and 5e), indicating that these acids do not dissociate in ASW. Interestingly, FA underwent efficient H/D exchange between molecular FA and D₂O–ASW, similar to the proton exchange equilibrium of weak acids in an aqueous

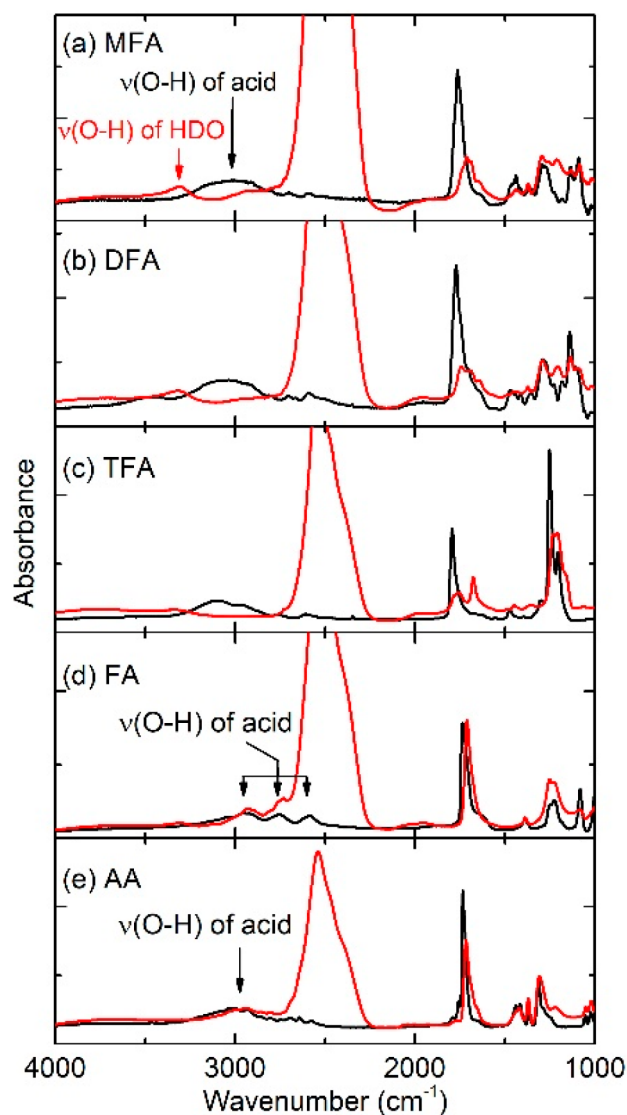


Figure 5. RAIR spectra of pure acid films (black traces) and acid–D₂O mixture films (red traces), which are shown overlapped for each acid for better visualization of the dissociation or nondissociation behavior of the acids. In each set of spectra, the spectral intensities are rescaled to equalize the molar amounts of acid in the pure and mixture films. The intense bulk $\nu(\text{O-D})$ band (~ 2540 cm⁻¹) of D₂O is truncated. (a) Spectra of a pure MFA and MFA–D₂O mixture (4% MFA in molar ratio) at 80 K. (b) Spectra of a pure DFA and DFA–D₂O (6% DFA) mixture at 70 K. (c) Spectra of a pure TFA and TFA–D₂O (4% TFA) mixture at 70 K. (d) Spectra of a pure FA and FA–D₂O (6% FA) mixture at 80 K. (e) Spectra of a pure AA and AA–D₂O (4% AA) mixture at 80 K. Differences between the spectra in (a–c) and those in (d, e) are clearly visible. For MFA (a), DFA (b), and TFA (c), the $\nu(\text{O-H})$ band of molecular carboxylic acid almost disappears for the mixture film, indicating acid dissociation. This differs from the case of FA (d) and AA (e), where the $\nu(\text{O-H})$ band of molecular acid remains after dissolution in D₂O at 70–80 K. Additionally, for MFA, DFA, and TFA, the $\nu(\text{C=O})$ band of a pure acid film and that of a mixture film differ significantly, in both intensity and shape. The sharp $\nu(\text{C=O})$ band shape of the molecular carboxylic group at ~ 1770 cm⁻¹ changes to the $\nu(\text{C=O})$ band shape of the carboxylate anion in the range of 1600–1800 cm⁻¹ for the mixture film. For nondissociating FA and AA, the shape of the $\nu(\text{C=O})$ band does not change significantly. Reproduced with permission from Supporting Information of ref 112. Copyright 2018 American Chemical Society.

solution.¹¹² These observations indicate that the boundary for acid dissociation and nondissociation in ASW is located between MFA ($pK_a = 2.82$) and FA ($pK_a = 3.75$), where the number in the parentheses is the acid dissociation constant for the aqueous solution. This suggests that the acid dissociation constant increases by a factor of $\sim 10^3$ in ASW compared with that in an aqueous solution at room temperature.¹¹²

The enhanced dissociation of weak acids in ASW indicates the thermodynamic effect of proton mobility for increasing the reaction yield. Park et al.¹¹² explained this observation in terms of an interesting proposition that the acid equilibrium is forward-shifted by the entropy of mobile protons injected from the acid into the ice. The excess proton diffuses into a large volume of the ice because of its high mobility.^{85,117} The diffusion of proton increases the configurational entropy of the system according to the relationship $\Delta S_{\text{conf}} = k_B \ln W$, where k_B is the Boltzmann constant and W represents the number of positions accessible by a proton in the volume of proton diffusion in the ice. The entropy increase lowers the free energy of acid dissociation and shifts the equilibrium in the forward direction. It is noted that ΔS_{conf} is an extra quantity added to the residual entropy of ice, and the Grotthuss proton diffusion does not change the residual entropy of the lattice. The authors estimated ΔS_{conf} to be approximately $63 \text{ J mol}^{-1} \text{ K}^{-1}$ for acid dissociation in an ASW sample prepared in corresponding experiments.¹¹⁷ From the thermodynamic relationship between the entropy and the equilibrium constant, they showed that ΔS_{conf} can increase the acid dissociation constant in ASW by a factor of $\sim 10^3$, which agrees well with the experimental results for fluoroacetic acids.

ΔS_{conf} is unusually large compared with other entropies of molecular solids (e.g., residual entropy of ice $I_h = 3.4 \text{ J mol}^{-1} \text{ K}^{-1}$) and is comparable in magnitude to the entropy of gas (e.g., entropy of water vaporization = $109 \text{ J mol}^{-1} \text{ K}^{-1}$). Therefore, ΔS_{conf} can significantly affect the thermodynamics of the reactions in ASW or crystalline ice. ΔS_{conf} is expected to be larger in crystalline ice than in ASW because of the longer proton-diffusion path in the former. This entropic effect can be pronounced when the enthalpy of the reaction is nearly thermoneutral, as in the case of dissociation of fluoroacetic acids in an aqueous environment.¹²⁴ If we consider that proton mobility is an intrinsic property of ice, we can imagine that this entropic effect operates for a wide range of physical and chemical phenomena of ice that involve proton transfer. Lee et al.¹²⁵ suggested that a similar entropic effect may promote the crystallization of ASW doped with acid impurities.

5. SUMMARY AND CONCLUDING REMARKS

Fundamental research on the chemical processes of ice is a relatively new area of study, and the discovery of additional interesting features is anticipated as further studies are performed in this area. Experimental and theoretical studies clearly indicate uniquely high mobility of excess protons in ice, which is attributed to a transport mechanism that involves a proton-hopping relay along the ice network and Bjerrum defect transfer. IR spectroscopic studies on the H/D exchange process of ice, ultrafast time-resolved spectroscopic studies on proton transport dynamics, and surface science studies on ice films containing excess protons have provided further detailed information about the proton-transport phenomena and the properties of excess protons in ice and on ice surfaces. A few reaction types investigated to date indicate that proton

mobility plays a crucial role in the occurrence of chemical reactions in ice at low temperatures.

The proton-hopping relay along the ice network occurs with a low barrier ($\sim 1 \text{ kJ/mol}$) on a subpicosecond time scale. Therefore, an excess proton can move in ice even at very low temperatures across a limited length of water chain of the ice network that fulfills the structural requirement for proton tunneling. However, the excess protons are typically trapped in the defects of the ice lattice, rendering them immobile. The reorientation of water molecules at high temperatures releases the protons from the traps and resumes the proton-transfer relay. These combined processes make protons migrate over a long distance, and the proton transport exhibits strong temperature dependence and a substantial activation barrier.

The protons at the ice surface exhibit significantly different properties from those in the interior of ice. Excess protons tend to accumulate at the surface rather than spread uniformly in the bulk crystal. The thermodynamic affinity of protons for ice surfaces results from the energetic stabilization of the hydronium structure at the surface. The stabilization also generates a substantial energy barrier for proton movement along the surface and significantly reduces the proton mobility. The activation energy for proton surface diffusion was estimated to be on the order of 10 kJ mol^{-1} . Because of the surface-accumulated protons, the electrical and chemical properties of the ice surface are expected to differ significantly from those of bulk ice.

In contrast to efficient proton transport in ice, hydroxide transport is relatively inefficient. Hydroxides can only move through the diffusion of molecular hydroxides without proton transfer. Therefore, at very low temperatures, excess protons are the only mobile charge carriers in ice, and the main role of hydroxides for electrical conductivity and chemical reactivity is to inhibit the activity of protons. Both protons and hydroxides have a propensity for the ice surface, but protons are distributed deeper into the ice interior than hydroxides.

Proton mobility is a key factor in the occurrence of chemical reactions in ice at low temperatures. The proton assists the reaction both kinetically and thermodynamically. Proton transfer between the reactant molecule and the ice lattice is kinetically feasible, even when the diffusion of molecules is suppressed. Furthermore, proton diffusion in ice generates a large amount of configurational entropy, which lowers the free energy of the proton-transfer reaction and shifts the equilibrium in the forward direction. This thermodynamic effect is clearly manifested by the dissociation of weak acids in ASW at low temperatures, in contrast to the nondissociation of these acids in aqueous solutions. In addition to efficient proton transfer, an important characteristic of reactions for ice is the strong kinetic constraint imposed on the reaction by the extremely low molecular diffusivity of ice.⁹ Thus, reactions in ice or on ice surfaces do not proceed to the final thermodynamic products but are halted at intermediate stages. This often leads to the formation of protonated species as metastable products, which are produced by efficient proton transfer accompanied by kinetic trapping in cold ice environments.^{9,109,120–122}

The facile occurrence of proton-transfer reactions implies that the acid–base reaction may be an important chemical process in cryogenic ice environments. For example, in the study of chemical reactions of ice particles in interstellar space, it has been assumed that the reactions are driven by external energy input, such as UV absorption, cosmic particle

bombardment, and thermal processing.^{2,3} However, one can also imagine that spontaneous acid–base reactions may occur under interstellar ice conditions, even without external energy input. Excess protons may be generated by the photolysis of ice particles under ionizing radiation or by the injection of cosmic protons into the ice. The excess protons can be stored as hydronium ion in the ice and utilized for subsequent chemical reactions.^{86,87} Moon et al.¹²⁶ proposed that such hydronium ion may act as an “invisible” acid for the reactions of interstellar ice particles. The acid–base reaction between hydronium ions and ammonia molecules trapped in the ice may explain the origin of the mysteriously large abundance of ammonium ions detected in interstellar molecular clouds.

Moving forward, it will be interesting to investigate whether the knowledge of the ice processes at low temperatures (<160 K) will be applicable to elucidate the corresponding processes occurring in terrestrial and atmospheric ice at higher temperatures. The transport mechanism, high mobility, and surface-segregative property of excess protons discussed herein are considered the intrinsic properties of the ice lattice and thus are not expected to drastically change at high temperatures. Therefore, this review will advance the research related to the chemistry of ice at various temperatures, although the microscopic environment of ice may differ at different temperatures.

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Notes

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Heon Kang received a B.Sc. in Chemistry from SNU in 1977 and a Ph.D. under the mentorship of Prof. Jack Beauchamp at the California Institute of Technology and conducted postdoctoral research with Prof. Wayne Rabalais at the University of Houston. He was a faculty member of the Department of Chemistry at Pohang University of Science and Technology in 1987–2000 and of SNU in 2001–2020. He is now a professor emeritus at SNU.

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