

Segregation of hydroxide ions to an ice surface

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Hydroxide ions that are initially buried within an ice film segregate to the ice film surface at elevated temperatures. This process was observed by conducting experiments with an ice film constructed with a bottom H₂O layer and an upper D₂O layer, with an excess of hydroxide ions trapped at the H₂O/D₂O interface as they were generated by Na hydrolysis. The transport of hydroxide ions from the interfacial layer to the surface was examined as a function of time using a low energy sputtering method. The progress of the H/D exchange reaction in surface water molecules was also monitored with the Cs⁺ reactive ion scattering technique. At 90 K, only a small portion of buried hydroxide ions moved to the surface in the form of OD⁻ species. This was due to hydroxide transport via proton hopping through a D₂O layer, 3 BL thick, in the surface region. At 135 K, at which point water self-diffusion is active in the ice film, the majority of the buried hydroxide ions segregated to the surface after ~1 h. Both OH⁻ and OD⁻ species were produced at the surface, at an OH⁻/OD⁻ population ratio ≥ 1 . Based on kinetic measurements for the transport of OH⁻ and OD⁻ species and the H/D exchange of surface water molecules, we concluded that the major transport channel for hydroxide ions in this regime is the migration of molecular hydroxide species. H/D exchange reactions also occur between surface hydroxide ions and water molecules. No evidence was observed for the occurrence of the hop-and-turn process at 135 K, although it is known as an important mechanism of proton transport in ice. © 2011 American Institute of Physics. [doi:10.1063/1.3625435]

I. INTRODUCTION

An excess of protons or hydroxide ions present at an ice surface can have important consequences for the physical and chemical properties of the surface. For example, they may affect the interfacial charge distribution, electrical conduction,¹ and reactions on ice surfaces.^{2,3} Recent studies have shown that protons tend to reside at the surface of ice films rather than in the interior.⁴⁻⁹ Surface accumulation of protons can facilitate acid-base reactions with basic adsorbates on the surface.¹⁰⁻¹⁵ The transport mechanisms of protons within ice or on its surface have been investigated in detail using various spectroscopic tools, including FTIR,¹⁶⁻¹⁸ NMR,¹⁹ low energy sputtering (LES) and Cs⁺ reactive ion scattering (RIS),^{4,5,20} and time-resolved fluorescence emission measurements.^{21,22}

In the case of hydroxide ions, there have been relatively few investigations compared with the studies of protons on ice surfaces. Kempter and co-workers²³⁻²⁵ reported that surface hydroxyl species were formed by the adsorption of Na atoms onto ice films in their studies using metastable impact electron spectroscopy and ultraviolet photoelectron spectroscopy. Souda and co-workers^{25,26} investigated Na adsorption onto ice films with time-of-flight secondary ion mass spectrometry and showed that a NaOH layer was formed at the ice surface at a low temperature (13 K). Kim *et al.*²⁷ identified sodium and hydroxide ions as products of Na hydrolysis on ice films at temperatures of 95–135 K using LES and RIS techniques. The hydroxide ions thus produced remained on the ice film surface at all temperatures investigated, whereas sodium ions

migrated to the ice interior at temperatures above ~110 K. They also studied the effect of hydroxide ions on proton transfer and the H/D isotopic exchange of water molecules on the ice film surface.²⁸ The surface hydroxide ions promoted the H/D exchange reaction compared with that on a pure ice surface, but the promotion effect was only moderate, and the H/D exchange occurred with a substantial energy barrier.²⁸ Cwiklik *et al.*²⁹ reported that trace doping of ice surfaces with base adsorbates such as ammonia and methylamine eliminated proton activity for the H/D exchange reaction of water molecules, whereas this activity was restored when larger amounts of adsorbate were present. Based on quantum mechanical calculations,^{29,30} these observations were rationalized by the existence of traps that strongly bind hydroxide ions, both at the surface and in the ice interior.²⁹ Density functional theory (DFT) calculations^{29,31} showed that the energy of hydroxide ion species at an ice surface, on average, was significantly lower than that in the ice lattice, similar to the case of hydronium ions. The surface segregation energies of these species, however, were approximately equal to their trapping energies with Bjerrum defects in the ice lattice within the calculational accuracy.^{31,32}

The results of LES and RIS studies²⁷ show that hydroxide ions remain on the ice surface, whereas sodium ions migrate to the interior when these species are produced by Na hydrolysis, as mentioned above, indicating the existence of hydroxide traps at the ice surface. It remains unclear, however, whether this behavior is due to the thermodynamic affinity of hydroxide ions for the ice surface or to a lack of mobility for surface hydroxide ions to move to the ice interior. This question was the main purpose of the exploration in the present study. To

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this end, we prepared an ice film that contained hydroxide ions at the interface between H₂O and D₂O layers and examined if the buried hydroxide ions migrated to the film surface. In addition, we examined the transport mechanism of hydroxide ions in ice by monitoring the H/D exchange kinetics of hydroxide ions and water molecules on the ice films.

II. EXPERIMENTAL

The experiments were conducted in an ultrahigh vacuum surface analysis chamber equipped with instrumentation for RIS, LES, and temperature programmed desorption (TPD).^{2,33} Ice films were grown on a Pt(111) crystal mounted on the temperature control stage of a sample manipulator. The Pt surface was cleaned by standard sputtering and annealing procedures, and surface cleanliness was checked by TPD and RIS. It is known³⁴ that a crystalline ice film grows initially in an island structure on Pt(111), and a flat ice film with a bulk ice structure is formed when the film thickness is greater than 50 BL. We prepared a thick (>50 BL) crystalline ice film by introducing H₂O vapor through a capillary doser onto a Pt(111) substrate maintained at 140 K. The custom-fabricated doser consisted of a microcapillary plate (Hamamatsu) inside a stainless steel housing, and it was mounted on a linear motion manipulator. A growth rate of ~ 0.1 BL s⁻¹ (bilayer; 1 BL = 1.1×10^{15} water molecules cm⁻²) was used for the H₂O films, and the H₂O partial pressure inside the vacuum chamber was below 1×10^{-9} Torr during the growth, as read by an ionization gauge located away from the sample surface. A D₂O overlayer was deposited on top of the H₂O-ice films to a desired thickness of 1–5 BL at a temperature of 90 K by back-filling the chamber with D₂O vapor at a partial pressure of $\sim 1 \times 10^{-8}$ Torr. Diffusional mixing between the H₂O and D₂O layers was observed to be negligible at this temperature, and the overlaid D₂O film was of an amorphous structure. The thicknesses of the ice films were estimated by performing TPD measurements.^{35,36}

Na atoms were deposited onto ice films at 135 K using a commercial alkali metal dispenser (SAES Getters). The surface coverage of Na was determined by performing TPD experiments with Na atoms deposited on a bare metal surface.^{37,38} At a full monolayer coverage of Na on a Pt(111) surface, the Na layer has an incommensurate hexagonal structure on Pt(111) according to LEED measurements at 85 K.³⁷ This amount of Na coverage is referred to as one monolayer equivalent (MLE) (1 MLE = 0.59 ML of Pt surface atomic density). The Na deposition rate was estimated to be approximately 0.033 MLE min⁻¹, and the amount of Na exposure was controlled by manipulating a shutter installed between the evaporator and the sample.

Neutral and ionic species present at the ice film surface were analyzed by RIS and LES, respectively.^{2,33} In these experiments, a Cs⁺ beam from a low-energy ion gun (Kimball Physics) was scattered at a sample surface. The incident Cs⁺ energy was 35 eV, unless specified otherwise. Both positive and negative ions emitted from the surface were detected with a quadrupole mass spectrometer (QMS; ABB Extrel) with its ionizer filament switched off. The detected

ions are composed of reflected Cs⁺ primaries, RIS products which are association products of Cs⁺ with neutral molecules at the surface, and LES ions resulting from collisional desorption of preexisting ions on the surface. The mechanisms of RIS and LES processes on thin ice films have been explained previously.^{33,39} RIS gives a quantitative measure of the isotopomeric distribution of water molecules on the surface because the RIS process occurs rapidly (<1 ps).³³ The isotopomeric distribution of hydroxide ions measured by LES may not be as quantitative because collision-induced H/D exchange may interfere with the sputtering process. Hydroxide ion signals are not detected from a pure ice film in LES experiments at Cs⁺ incidence energies below 35 eV, as water molecules are not collisionally ionized at these energies.²⁷ The probing depth of LES and RIS methods is 1 BL of the ice surface at an energy below 35 eV.⁴⁰ The surface contamination by the Cs⁺ beam was adjusted so as to be negligible (<0.01 ML) during the kinetic measurement by employing the conditions of low Cs⁺ exposure, typically an incident Cs⁺ flux of 1×10^{11} ions cm⁻² s⁻¹, and an accumulated spectral acquisition time <80 s. Whenever necessary, fresh ice films were prepared for the kinetic measurements so as to reduce the accumulated Cs⁺ beam dosage.

III. RESULTS

A. Transport of buried hydroxide ions to the ice surface

To study the transport behavior of hydroxide ions in the ice interior, we prepared an ice film in which hydroxide ions were buried at the interface between the bottom H₂O layer and the upper D₂O layer (a “hydroxide-sandwich” ice film). The hydroxide-sandwich film was prepared in the following sequence. A crystalline H₂O ice film was grown on a Pt(111) substrate at 140 K to a thickness of 70 BL by introducing water vapor through a capillary doser. Na atoms were deposited onto the film to yield a coverage of 0.2 MLE at 90 K, and the sample temperature was raised to 135 K and maintained for 10 min to complete the hydrolysis of Na adsorbates to Na⁺ and OH⁻ ions. The sample was then cooled to 90 K, and a D₂O layer was overlaid on the sample at this temperature. Each of these sample preparation steps was checked by analyzing the surface with LES and RIS methods. The results of the surface analyses are shown in Fig. 1. Figure 1A shows the LES spectra of negative ions present on the sample surfaces, and Figure 1B shows the spectra of LES signals for positive ions (displayed for the region $m/z < 50$ amu/charge) and RIS signals ($m/z > 133$ amu/charge); these were simultaneously recorded in a single mass spectrum. Upon the adsorption of Na atoms onto the H₂O-ice film at 90 K, the negative-ion LES spectrum showed an OH⁻ peak with a low intensity at $m/z = 17$ [Fig. 1A(a)]. The positive-ion LES signals gave Na⁺ and Na(H₂O)⁺ peaks at $m/z = 23$ and 41, respectively, and the RIS signals showed Cs(H₂O)_{*n*}⁺ (*n* = 1, 2) peaks at $m/z = 151$ and 169 and a Cs(NaOH)⁺ peak at $m/z = 173$ [Fig. 1B(a)]. These peaks indicate that the hydrolysis of Na occurred to produce Na⁺, OH⁻, and molecular NaOH on the surface. Figure 1A(b) shows that the OH⁻ signal intensity increased

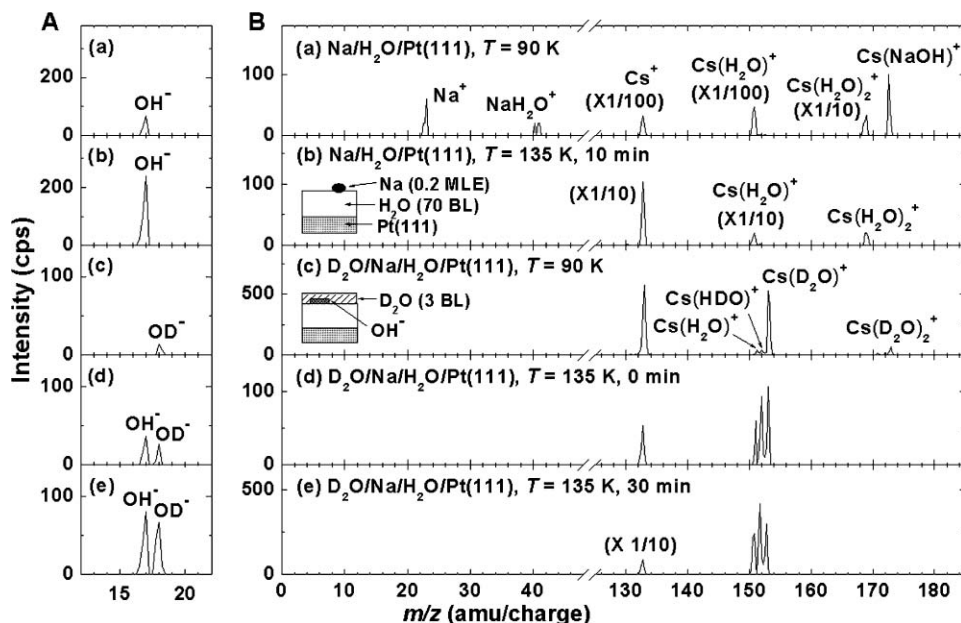


FIG. 1. (A) LES mass spectra of negative ions measured for each preparation step of a hydroxide-sandwich ice film. (B) The corresponding spectra of positive-ion LES signals and RIS signals. The ice sample was prepared in the following sequence: (a) A crystalline H₂O film (70 BL thick) was grown on Pt(111) at 140 K, and Na atoms were deposited onto the ice film at 90 K for a coverage of 0.2 MLE. (b) The ice film was warmed to 135 K and maintained at this temperature for 10 min. (c) A D₂O layer (3 BL thick) was overlaid on the film at 90 K to create a hydroxide-sandwich structure. (d) The sample temperature was raised to 135 K and (e) maintained at the same temperature for 30 min. Cs⁺ beam energy was 35 eV.

when the sample temperature was raised to 135 K. In addition, Na⁺, Na(H₂O)⁺, and Cs(NaOH)⁺ peaks disappeared from the surface, as shown in Fig. 1B(b). The OH⁻ signal did not further increase after 10 min at 135 K. These features indicate, in agreement with previous reports,²⁷ that Na atoms are completely hydrolyzed to Na⁺ and OH⁻ at 135 K, and the OH⁻ ions remain on the ice surface while Na⁺ ions move from the surface to the interior. The spectra show that only hydroxide ions and water molecules were present on the ice film surface.

A D₂O layer (3 BL thick) was overlaid on the H₂O-film with surface OH⁻ species at 90 K, thereby generating an ice film structure with hydroxide ions embedded between the bottom H₂O layer and the upper D₂O layer. The RIS spectrum obtained from this sample showed a strong Cs(D₂O)⁺ signal and a very weak Cs(H₂O)⁺ signal [Fig. 1B(c)], which confirmed that the D₂O overlayer effectively covered the H₂O-film surface and that diffusional mixing of H₂O and D₂O molecules was inefficient at 90 K. The OH⁻ signal disappeared from this surface at this temperature, as shown in the negative-ion LES spectrum [Fig. 1A(c)]. Instead, a new OD⁻ signal appeared with a low intensity. These changes suggested that the OD⁻ signal was produced via hydroxide transport through the D₂O layer that converted OH⁻ species to OD⁻. The low OD⁻ intensity indicated that such hydroxide transport occurred only partially, and the majority of the hydroxide ions remained trapped inside the hydroxide-sandwich ice film at 90 K.

When the temperature of the hydroxide-sandwich ice film was increased to 135 K, OH⁻ signals appeared on the surface and grew at a faster rate than the OD⁻ signals [Fig. 1A(d)]. Additionally, Cs(H₂O)⁺ and Cs(HDO)⁺ signals appeared in the RIS spectrum [Fig. 1B(d)]. These signals increased continuously with time when the sample was main-

tained at the same temperature for 30 min. After 30 min, as shown in Fig. 1A(e), the total OH⁻ and OD⁻ signal intensities almost reached the level of OH⁻ signal intensity obtained from an ice sample initially provided with surface hydroxide ions, which is shown in Fig. 1A(b). This behavior indicated that the majority of hydroxide ions were transported from the ice interior to the surface at this stage. The surface population of OH⁻ is slightly larger than that of OD⁻ in Fig. 1A(e). These observations are informative for understanding the transport mechanisms of hydroxide ions, which will be discussed in Sec. IV B. The RIS spectrum in Fig. 1B(e) showed that the Cs(H₂O)⁺, Cs(HDO)⁺, and Cs(D₂O)⁺ signals appeared with an intensity ratio of 0.26 : 0.46 : 0.28. The H₂O and HDO surface populations substantially increased at 135 K, which indicated the active occurrence of diffusional mixing of H₂O and D₂O molecules and H/D exchange between these molecules. This observation agrees with a prior report that self-diffusion and H/D exchange are active in water molecules in the ice surface region at 135 K.⁵

Figure 2 shows the variations in OH⁻ and OD⁻ signal intensities at 135 K measured for a hydroxide-sandwich ice film as a function of time. The ice sample was prepared with the same structure as the samples used for Figs. 1(c)–1(e). The data points before time zero represent the signals measured at 90 K, and the sample was warmed to 135 K over 3 min, as depicted by the temperature profile in the upper panel of the figure. It can be seen here that the hydroxide ion (OH⁻ and OD⁻) signals monotonically increased with time from $t = 0$ to 60 min, indicating a continued transport of hydroxide ions from the D₂O/H₂O interface to the surface. On comparing the relative intensities of the OH⁻ and OD⁻ signals, the OH⁻ signal was nearly absent from the surface at 90 K, but heating of the sample to 135 K quickly intensified the OH⁻

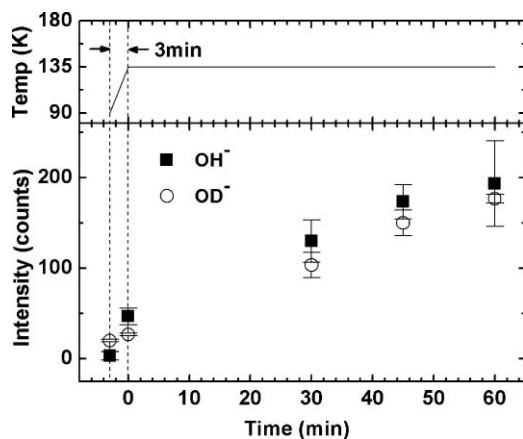


FIG. 2. OH^- and OD^- signal intensities measured by LES from a hydroxide-sandwich ice film at 135 K as a function of time. The ice sample was prepared to have the same structure as the samples used for Figs. 1(c)–1(e) [D_2O (3 BL)/Na (0.2 MLE)/ H_2O (70 BL)/Pt(111)]. The temperature profile of the experiment is displayed in the upper panel. Cs^+ beam energy was 35 eV.

signal. At 135 K, the OH^- and OD^- signals both increased with time, but the OH^- intensity remained relatively stronger, at least slightly, than the OD^- intensity.

The observations made for the hydroxide-sandwich ice films described above indicate that buried hydroxide ions transported through the film and became segregated at the surface at 135 K. For controls, we examined the possible interfering effects of incident Cs^+ beams on these observations, such as collisional ionization of water molecules, collision-induced mixing of D_2O and H_2O , and reaction of Cs atoms deposited on the surface after a prolonged beam exposure. The control experiments were performed with a pure ice film [D_2O (3 BL)/ H_2O (70 BL)] in the absence of embedded hydroxide ions and also with an ice film that contained hydroxide ions on the surface that were produced by Na hydrolysis. These experiments showed no indication that the Cs^+ beams affected the LES and RIS measurements of hydroxide ions and water isotopomers under the experimental conditions of Cs^+ beam energy and exposure.

Additional experiments were performed to determine the surface segregation of hydroxide ions, which involved multiple additions of D_2O overlayers. First, the experiment was conducted in the same way as that described in Fig. 1 with a hydroxide-sandwich ice film [D_2O (3 BL)/Na (0.2 MLE)/ H_2O (70 BL)], which resulted in the transport of hydroxide ions from the sandwich layer to the surface at an elevated temperature (135 K); the results are presented in Fig. 3(a). In the second stage, after the completion of the first experiment, the sample was cooled to 90 K and an additional D_2O layer (3 BL) was overlaid on the surface. LES measurements were then made on this sample while the temperature was raised from 90 K to 135 K over 3 min and then maintained at 135 K for 30 min. The results are shown in Fig. 3(b). The hydroxide ion signal was very small immediately after the deposition of the second D_2O overlayer at 90 K. However, the hydroxide ion signal increased again as the temperature was increased to 135 K, and after 30 min, the signal grew to an intensity similar to that attained in the first stage experiment.

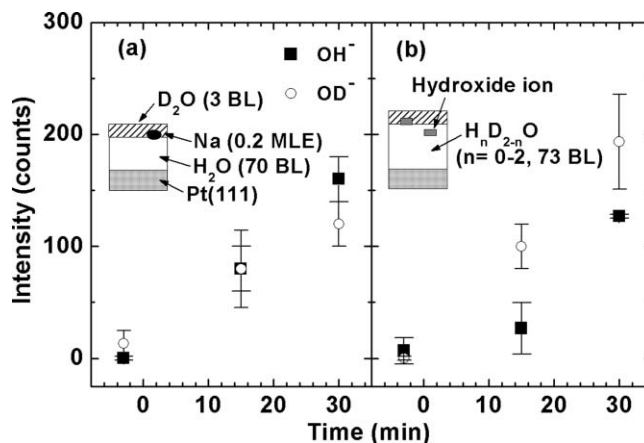


FIG. 3. (a) LES signal intensity of hydroxide ions measured as a function of time on a hydroxide-sandwich ice film [D_2O (3 BL)/Na (0.2 MLE)/ H_2O (70 BL)/Pt(111)]. The first kinetic data points ($t = -3$ min) were measured at 95 K immediately after sample preparation, and the second and third points were measured at 15 and 30 min, respectively, after the sample temperature reached 135 K at $t = 0$. (b) After the kinetic measurement shown in (a), the sample was again cooled to 90 K, a second D_2O overlayer (3 BL) was deposited onto the sample, and the kinetic measurement was resumed along the same temperature profile as for the first experiment. Cs^+ beam energy was 35 eV.

The continued emergence of hydroxide ions at the ice film surface through the multiple D_2O overlayers clearly demonstrates that the hydroxide ion transport to the surface is due to its thermodynamic tendency to reside at the ice surface rather than in the interior. Figure 3(b) shows that the OH^-/OD^- intensity ratio was smaller in the second stage experiment than in the first stage experiment, which can be attributed to the fact that the added D_2O overlayers decreased the hydrogen content near the surface, affecting both water and hydroxide species.

B. H/D-substituted water isotopomers

H/D-substituted water isotopomers can emerge at the ice film surface via several pathways, including the diffusional mixing of H_2O and D_2O molecules in the film, and proton transfer and H/D exchange between H_2O and D_2O . Measurements of these water isotopomers at the ice film surface and their temporal changes can also provide useful information about the transport mechanism of hydroxide ions within the ice. The RIS technique is ideally suited for such a study because it can be used to identify unambiguously the isotopomers and quantitatively measure their relative populations. Owing to their structural similarity, all water isotopomers have nearly the same detection efficiency by RIS, and therefore, their RIS signal intensities are directly proportional to their relative surface populations. Furthermore, these molecules do not undergo isotopic scrambling inside the mass spectrometer in the absence of the ionizer function. Figures 4(a) and 4(b) show the RIS spectra of water isotopomers measured on a pure ice film [D_2O (3 BL)/ H_2O (70 BL)/Pt(111)] at temperatures of 90 and 135 K, respectively, after waiting for 30 min from the time of sample preparation at the corresponding temperature. Figure 4(c) shows the RIS spectrum of a

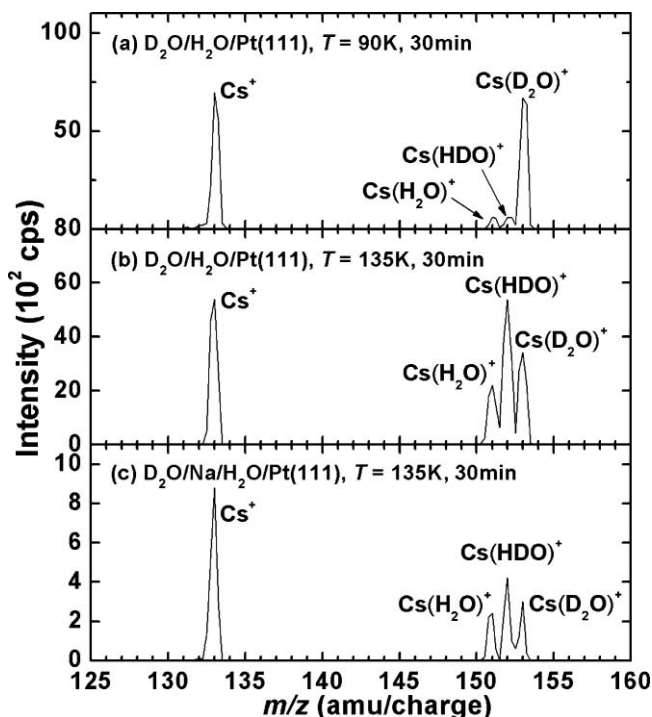


FIG. 4. RIS spectra obtained for three different water-ice films that were prepared under the following conditions: (a) An amorphous D_2O (3 BL) overlayer was added at 90 K onto the H_2O crystalline ice film (70 BL). The sample was held at 90 K for 30 min before the RIS measurements. (b) A sample was prepared as for (a) and held at 135 K for 30 min. (c) A hydroxide-sandwich ice film was prepared in the same way as for the sample shown in Fig. 1(e), and it was held at 135 K for 30 min. RIS measurements for samples (b) and (c) were made at $T = 135$ K. The ion scattering signal intensities substantially decreased on the hydroxide-sandwich ice film (c) relative to those on the pure ice films [(a) and (b)], but the RIS yield for water molecules, or the ratio of $Cs(\text{water})^+$ to Cs^+ signal intensities, was not much different on these surfaces.

hydroxide-sandwich ice film [D_2O (3 BL)/Na (0.2 MLE)/ H_2O (70 BL)/Pt(111)] measured after 30 min at 135 K.

Figure 4(a) shows that the surface population ratio of $H_2O : HDO : D_2O$ was approximately 0.08 : 0.07 : 0.85 for the pure ice film at $T = 90$ K and at $t = 30$ min. This ratio did not change significantly from that measured immediately after the sample preparation [$H_2O : HDO : D_2O = 0.04 : 0.07 : 0.89$]. Therefore, the diffusional mixing of H_2O and D_2O and their H/D isotopic exchange reactions were negligible at this temperature. The results also indicated that the adsorption of residual gases onto the ice sample was insignificant over 30 min; after backfilling the chamber with D_2O for the sample preparation, the most abundant residual gas in the chamber was HDO.

Upon increasing the sample temperature to 135 K (Fig. 4(b)), the surface population ratio of $H_2O : HDO : D_2O$ changed to 0.20 : 0.49 : 0.31. The large increases in the H_2O and HDO populations indicate the active occurrence of water self-diffusion and H/D exchange reactions, in agreement with a previous report.⁵ The measurement of the hydroxide-sandwich ice film at 135 K (Fig. 4(c)) shows that the surface population ratio of $H_2O : HDO : D_2O$ was 0.26 : 0.46 : 0.28. When only the ratio of H_2O and D_2O molecules is compared for Figs. 4(b) and 4(c), the H_2O/D_2O ratio increases slightly

from 0.65 (Fig. 4(b)) to 0.93 (Fig. 4(c)) in the presence of buried hydroxide ions.

Figure 5 shows variation in the surface population ratio of H_2O , HDO, and D_2O measured for the pure and hydroxide-sandwich ice samples at 135 K as a function of time. The increase in the H_2O population and the accompanying decrease in the D_2O population were attributed to the occurrence of self-diffusion, which caused H_2O in the bottom layer to mix with D_2O in the upper layer. The increase in the HDO population was attributed to H/D exchange reactions between H_2O and D_2O . For the pure ice film (Fig. 5(a)), the diffusional mixing continued to occur until the measurement ended at $t = 40$ min, at which time the $H_2O : HDO : D_2O$ ratio was approximately 0.25 : 0.49 : 0.26. In contrast, for the hydroxide-sandwich film, this ratio reached a steady-state value more quickly; the $H_2O : HDO : D_2O$ ratio was approximately 0.26 : 0.46 : 0.28 after 20 min. For both samples, the $H_2O : HDO : D_2O$ ratio was close to 1 : 2 : 1 at the end of the kinetic measurements. This indicated that approximately equal amounts of H_2O and D_2O molecules were supplied to the surface by self-diffusion, mixing water molecules in the upper ~ 6 BLs

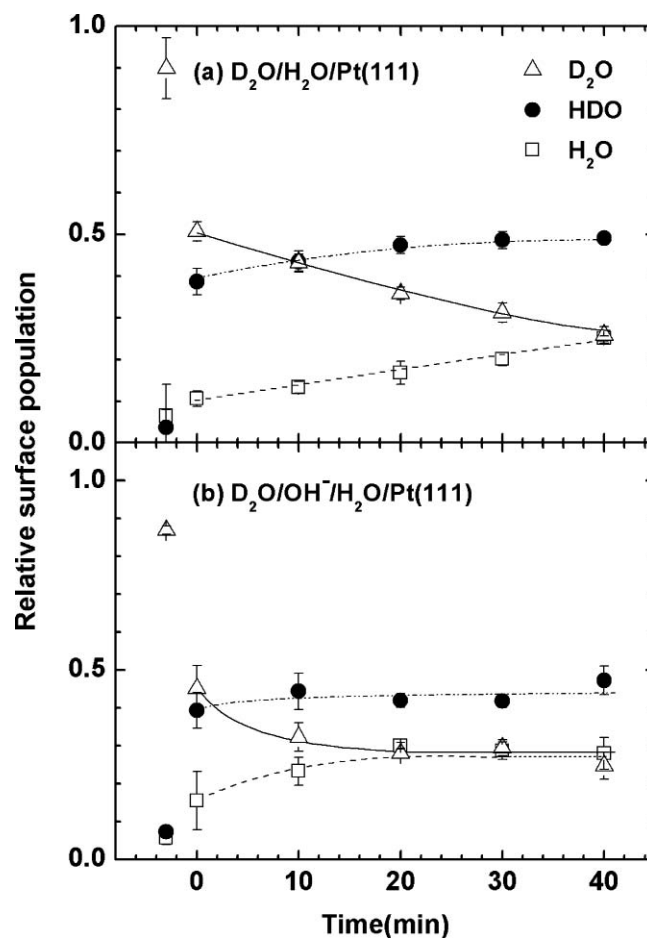


FIG. 5. Relative surface populations of H_2O , HDO, and D_2O measured as a function of time on a pure ice sample (a) and a hydroxide-sandwich ice sample (b), both at 135 K. These samples had the same structures as those in Fig. 4, i.e., D_2O (3 BL)/ H_2O (70 BL)/Pt(111) for the pure ice film (a) and D_2O (3 BL)/Na (0.2 MLE)/ H_2O (70 BL)/Pt(111) for the hydroxide-sandwich ice film (b). The data points at $t = -3$ min represent the measurements made at 90 K before the sample was warmed to 135 K. Cs^+ beam energy was 35 eV.

(~ 3 BLs of D_2O and H_2O each). As evidenced by the changing slopes of the H_2O , HDO , and D_2O curves in Fig. 5, self-diffusion occurred more efficiently in the hydroxide-sandwich ice sample than in the pure ice sample. The increased self-diffusion in the presence of buried hydroxide ions may be, in its fundamental origin, analogous to the lowering of ice melting temperature in the presence of foreign impurity species.

The relative surface populations of H_2O , HDO , and D_2O were close to their isotopic scrambling ratio (1 : 2 : 1) for both pure and hydroxide-sandwich ice films after 40 min (Fig. 5). This behavior was observed even when the H_2O : D_2O ratio was changing significantly due to the occurrence of self-diffusion during the kinetic measurement, except during the very early kinetic period. For instance, the H_2O : HDO : D_2O ratio at $t = 10$ min was approximately 0.12 : 0.44 : 0.44 for the pure ice film and approximately 0.23 : 0.45 : 0.32 for the hydroxide-sandwich film, which indicated that H/D exchange reactions occurred, with yields of $\sim 100\%$ and $\sim 80\%$, respectively. Therefore, the H/D exchange of surface water molecules must have been very active at 135 K for both samples, such that it occurred faster than the diffusional mixing of water molecules in the vertical direction. Further discussion of the water isotopomeric distributions will be presented in Sec. IV B in relation to the transport mechanism for hydroxide ions.

IV. DISCUSSION

A. Surface preference of hydroxide ions

The results presented in Sec. III A provide convincing evidence that the hydroxide ions embedded in a sandwich layer move to the ice film surface at high temperature. As shown in Figs. 1 and 2, the hydroxide ion (OD^-) signal is very weak on the surface of a hydroxide-sandwich ice film at 90 K, but as the temperature is increased to 135 K, an OH^- signal appears on the surface, and the intensities of both OD^- and OH^- signals substantially increase over a period of 60 min. The results presented in Fig. 3 further confirm the upward migration of buried hydroxide ions by showing that they continue to be transferred to the surface through multiple D_2O overlayers.

It may be questioned, however, whether hydroxide ions reach the ice film surface as a result of diffusion in all directions, which would uniformly spread the hydroxide ions over the entire volume of the sample, rather than migrating preferentially toward the surface. We observed that the hydroxide ion signal intensities are similar for the cases when the ice sample is prepared with preexisting hydroxide ions on the surface (Fig. 1(b)) and when the ice sample initially has buried hydroxide ions but is kept at 135 K for a long time (Fig. 1(e)). Similar results were observed in the multiple D_2O overlayer experiments (Fig. 3), where the final intensity of hydroxide ion signal was not significantly reduced by the addition of the second D_2O overlayer. These observations support the directional transport of hydroxide ions to the surface rather than isotropic hydroxide diffusion. It might be also questioned that the hydroxide transport is driven somehow by the Coulombic attraction forces of counter Na^+ ions. Na^+ ions, however, tend to migrate from the ice surface to the interior at an elevated

temperature,^{27,36,41} and thus they cannot assist the hydroxide transport toward the surface.

According to the previous study,²⁷ hydroxide ions produced by Na hydrolysis on ice films remain on the ice surface and hardly migrate to the interior at temperatures 95–135 K. On the other hand, the present experiments demonstrate that hydroxide ions are mobile within the ice film, especially when water self-diffusion is activated at 135 K. Moreover, the buried hydroxide ions become segregated at the ice surface at this elevated temperature. A conclusion accordingly derived from these observations is that the observed surface residence of hydroxide ion is due to its thermodynamic preference for the ice surface rather than its kinetic immobility. This, in turn, indicates that a hydroxide ion is energetically stabilized at the ice surface compared with its presence in the interior. This interpretation is consistent with the results of an earlier study on H/D exchange kinetics on ice films reporting that a substantial energy barrier (9.6 ± 2.0 kJ mol⁻¹) exists for proton transfer mediated by hydroxide ions on the surface.²⁸ Because a hydroxide ion is stabilized in a potential energy well at the ice surface, extra energy is needed for protons to move from water molecules through the stabilized hydroxide ions on the surface.

Previous studies⁴⁻⁹ have shown that hydronium ions, like hydroxide ions, have a thermodynamic affinity for the ice surface. The surface preference displayed by both hydronium and hydroxide ions, although they are oppositely charged, raises an interesting question of chemical origin. This preference may be attributable to the fact that in general, an ice crystal is a poor solvent for foreign materials. There are, however, distinct exceptions to this general expectation. For example, when NaF, NaCl, and NaBr salts are ionized on ice films at 135 K, the Na^+ and F^- ions migrate to the film interior, while the Cl^- and Br^- ions reside at the surface.^{36,41} Figure 1(b) also confirms Na^+ migration to the ice film interior. The segregation behavior of these ions on an ice surface is similar to that for a liquid water surface,⁴² suggesting that the chemical specificity of the dissolving species is important for the segregation behavior. DFT calculations²⁹ predict the surface preference of hydroxide species for an ice crystal but not for liquid water, and the difference between ice and liquid has been attributed to the poor solubility of hydroxide ions in an ice crystal. However, the ice films examined at 135 K in this study likely had an amorphous structure in the surface region rather than a crystalline structure, especially because substantial amounts of Na^+ and hydroxide ions were dissolved within them. This weakens the possibility that hydroxide ions were expelled to the surface by ice crystallization in the present work.

If chemical specificity is important for the surface segregative behavior of hydroxide ions in ice, we may anticipate a similar behavior for liquid water. The interfacial distribution of hydroxide ions in liquid water has been a subject of active investigations and disputes in recent studies.⁴³⁻⁵¹ For example, experiments with microbubbles and oil droplets in aqueous solutions^{46,48,49} indicated the presence of negative charges at the gas-water interface, which in turn suggests the accumulation of hydroxide ions at the interface. Conversely, molecular dynamics simulations⁴⁴ predicted that

hydroxide ion does not have a strong preference for the interface. Studies of aqueous solution surfaces with second harmonic generation⁴⁷ and sum frequency generation (SFG) spectroscopies^{43,45} suggested a depleted hydroxide concentration at the air/water interface of NaOH solution. However, re-examination of this system with the phase-sensitive SFG technique⁵¹ suggested the opposite behavior, i.e., hydroxide ions are in excess at the interface.

B. Transport mechanism of hydroxide ions in ice

At a low temperature (90 K), only the OD⁻ signal appeared on the surface of a hydroxide-sandwich ice film, with a low intensity (Fig. 1). This signal appeared instantaneously after the sample preparation, and its intensity did not increase much with time at 90 K. Owing to the presence of a D₂O overlayer above the hydroxide ions in the ice sample, the exclusive transfer of OD⁻ to the surface indicates the occurrence of sequential proton (D⁺) transfers from surface D₂O molecules to the underlying hydroxide ions (via the Grötthuss mechanism). Such proton transfers may occur in discrete steps during the sample preparation, i.e., via D⁺ hopping from an individual D₂O molecule arriving at the sample surface to a hydroxide ion on the surface. Alternatively, the proton transfers may occur in a concerted relay mechanism along the hydrogen bonds of water molecules in the ice after sample preparation. Such a hydroxide transfer mechanism is conceptually a mirror image of the proton transfer mechanism for hydronium ions in ice, which has been studied in depth.^{1,4,5,16,17,52} However, without the assistance of Bjerrum defect motion or self-diffusion at a low temperature, the proton hopping mechanism alone can transfer a proton only across a limited range of distance in ice.^{4,5,16} This may explain why only a limited portion of the buried hydroxide ions are transported to the ice film surface at 90 K.

At a high temperature (135 K), both OD⁻ and OH⁻ signals appeared on a hydroxide-sandwich sample surface, and their intensities increased with time. This behavior suggests the occurrence of additional transport mechanisms for the hydroxide ions. Several distinct features can be observed in the LES and RIS spectra of hydroxide-sandwich samples measured at 135 K: (i) An OH⁻ signal appears in addition to the OD⁻ signal [Fig. 1A(d)]. (ii) The OH⁻ signal grows more quickly than the OD⁻ signal during sample heating from 90 K to 135 K (Fig. 2). When the sample temperature is maintained at 135 K, the OH⁻ and OD⁻ signals grow together at similar rates (Fig. 2). (iii) Water self-diffusion mixes H₂O and D₂O molecules near the ice film surface. As a result, the H₂O/D₂O ratio for surface water molecules reaches a steady state after 20 min for the hydroxide-sandwich ice film, but it continuously changes up to 40 min for the pure ice film (Fig. 5). (iv) H/D exchange reactions actively occur at 135 K for surface water molecules on both pure and hydroxide-sandwich ice samples (Fig. 5). The H/D exchange of surface water molecules occurs faster than vertical self-diffusion at 135 K (Fig. 5).

Based on these observations, several plausible mechanisms may be considered for the transport of hydroxide ions

in ice at 135 K. First, for the appearance of OH⁻ at the surface (observation (i)), we consider that OH⁻ species migrate from the H₂O/D₂O interface to the surface retaining the hydroxide molecular unit. The migration of hydroxide molecular ion must be assisted by water self-diffusion, which is active near the ice surface at 135 K,⁵ and also by the disordered ice structure near the surface. The difference between the OH⁻ migration and water self-diffusion is that the former occurs, on average, preferentially toward the ice surface, whereas the latter occurs in random directions. Since OH⁻ migration is driven by the energy of hydroxide stabilization at the ice surface, it can occur even against the hydroxide concentration gradient near the ice surface, somewhat analogous to reverse diffusion, eventually leading to hydroxide accumulation at the surface. Because OH⁻ migration occurs with directionality, the effective speed of transporting OH⁻ to the surface can be faster than the rate of random diffusional mixing of H₂O and D₂O molecules. These expectations agree with observations (ii) and (iii) itemized above; OH⁻ intensity starts to grow as soon as the sample temperature is increased to 135 K and at a faster rate than the increase in surface H₂O population due to self-diffusion. Note that molecular OH⁻ migration is the only mechanism that can preferentially produce OH⁻ on the surface when the diffusional mixing of H₂O and D₂O is still insignificant in the early stage of sample heating. Any other hydroxide transport mechanisms that involved proton transfer would produce more OD⁻ species than OH⁻ on the surface due to the presence of the D₂O overlayer.

H/D exchange reactions may occur between hydroxide ions on the ice surface and water molecules at 135 K. Once OD⁻ is transported to the surface via the proton hopping mechanism, it can undergo H/D exchange reactions with H₂O molecules that reach the surface via self-diffusion at a later stage to form OH⁻. Likewise, OH⁻ species that are transported to the surface via the molecular transport mechanism can be converted into OD⁻ species by H/D exchange reactions. As a result, the OH⁻/OD⁻ population ratio at the surface reflects the isotopomeric distribution of surface water molecules. Figure 5(b) shows that the H₂O/D₂O ratio for surface water molecules, and therefore also the H/D content ratio, decreased to a steady-state value of approximately 1.0 after ~20 min due to self-diffusion. This H/D ratio is close to the OH⁻/OD⁻ ratio (≈1.0) measured at $t \geq 30$ min in Fig. 2, supporting the occurrence of facile H/D exchange processes between surface hydroxide ions and water molecules. Furthermore, although the OH⁻/OD⁻ ratio was close to 1.0 at $t \geq 30$ min, it never fell below 1.0 during the kinetic measurement (Fig. 2). In particular, in the early period (≤ 10 min) of the kinetic measurement, the observed OH⁻/OD⁻ ratio (>1.0 in Fig. 2) differed significantly from the H/D ratio of the surface water molecules (<1.0 in Fig. 5(b)). This degree of difference indicates the occurrence of molecular OH⁻ migration to the surface without undergoing H/D exchange with D₂O molecules in the upper layer. Again, it supports the idea that OH⁻ migration occurs faster than self-diffusion.

A transport mechanism involving proton hopping steps coupled with water reorientational motion (the “hop-and-

turn" process) may be considered for hydroxide ion. This mechanism is a conceptual mirror image of the hop-and-turn process for the transport of extra protons in ice,^{16,17} which is known to occur near ice surfaces at temperatures above 125 K.^{4,5} Similar to the case of protons,^{16,17} the repeated occurrence of the hop-and-turn process for hydroxide ions should produce H/D-exchanged water isotopomers. Therefore, in our system, it is expected that the hop-and-turn process first produces OD⁻ species at the surface and then OH⁻ species. In addition, this mechanism is expected to increase the H/D ratio in surface water molecules, albeit at a slower rate than the rate of hydroxide transport to the surface, because the H-enrichment of water molecules requires multiple occurrences of these processes. However, no such evidence was observed in the present study. Our results indicate that the H/D ratio in surface water molecules (Fig. 5(b)) increases faster than the rate of hydroxide transport to the surface (Fig. 2). Therefore, the hop-and-turn mechanism must be inactive for hydroxide ions in ice at 135 K, and if it occurs at all, its contribution is minor compared with the molecular hydroxide transport mechanism.

V. CONCLUSIONS

The results of the present study show that hydroxide ions initially buried within an ice film segregate to the ice surface at high temperature. Combined with the results of a previous study²⁷ that hydroxide ions remain on the surface of an ice film when they are produced by Na hydrolysis on the ice film, the present study provides convincing evidence that hydroxide ions have a thermodynamic preference for residing at the ice surface rather than in its interior. We consider that the surface segregation of hydroxide ions is due to the chemical specificity of the ions rather than ice crystallization, because this process occurs under the condition that water molecules are mobile near the ice surface but ice crystallization is unlikely in the presence of dissolved sodium and hydroxide species at 135 K. Accumulation of hydroxide ions on an ice surface may have an important influence on the acid-base chemistry of the surface and its other physical and chemical properties. It is interesting that the segregative behavior at ice surfaces appears for hydroxide ions as well as hydronium ions.⁴⁻⁹

Two types of transport mechanisms were identified for hydroxide ions in ice. At 90 K, a small portion of hydroxide ions are transported from the ice film interior to the surface by a proton hopping mechanism, which is conceptually a mirror image of the transport mechanism of hydronium species in ice. As water self-diffusion is activated near the ice surface at 135 K, the migration of hydroxide molecular ions to the surface becomes the major transport channel. The hop-and-turn mechanism, which plays an important role for hydronium transport in ice, is either inactive or less important than the above two mechanisms for the transport of hydroxide ions. The dominant molecular hydroxide migration and the inactive proton hopping relay process highlight the different features of hydroxide transport in ice near the surface compared with hydronium transport.

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