# Adsorption, Ionization, and Migration of Hydrogen Chloride on Ice Films at Temperatures between 100 and 140 K

## Seong-Chan Park[†,§] and Heon Kang*[,‡]

*Department of Chemistry, Pohang University of Science and Technology, Pohang 790-784, South Korea, and School of Chemistry, Seoul National University, Kwanak-ku, Seoul 151-742, South Korea*

Adsorption of hydrogen chloride (HCl) on water ice films is studied in the temperature range of 100–140 K by using $Cs^+$ reactive ion scattering ($Cs^+$ RIS), low energy sputtering (LES), and temperature-programmed-desorption mass spectrometry (TPDMS). At 100 K, HCl on ice partially dissociates to hydronium and chloride ions and the undissociated HCl exists in two distinct molecular states ($\alpha$- and $\beta$-states). Upon heating of the ice films, HCl molecules in the $\alpha$-state desorb at 135–150 K, whereas those in the $\beta$-state first become ionized and then desorb via recombinative reaction of ions at 170 K. An adsorption kinetics study reveals that HCl adsorption into the ionized state is slightly favored over adsorption into the molecular states at 100 K, leading to earlier saturation of the ionized state. Between the two molecular states, the $\beta$-state is formed first, and the $\alpha$-state appears only at high HCl coverage. At 140 K, ionic dissociation of HCl is completed. The resulting hydronium ion can migrate into the underlying sublayer to a depth <4 bilayers, suggesting that the migration is assisted by self-diffusion of water molecules near the surface. When HCl is covered by a water overlayer at 100 K, its ionization efficiency is enhanced, but a substantial portion of HCl remains undissociated as molecules or contact ion pairs. The observation suggests that three-dimensional surrounding by water molecules does not guarantee ionic dissociation of HCl. Complete ionization of HCl requires additional thermal energy to separate the hydronium and chloride ions.

## 1. Introduction

There has been growing scientific research interest in the interactions of HCl molecules with cold ice surfaces, motivated by a sequence of discoveries that HCl adsorption and ionization on the surface of ice particles in polar stratospheric clouds is an essential step in ozone loss chemistry in the Antarctic region.[1–3] Experimental studies of the reaction of HCl with ice surfaces range from laboratory model studies at stratospheric temperatures of 180–210 K to investigations of elementary processes such as HCl adsorption, diffusion, and ionization on well-defined ice films in ultrahigh vacuum (UHV) at lower temperatures (<160 K). Various surface spectroscopic methods have been employed for the UHV studies, including temperature-programmed-desorption mass spectrometry (TPDMS),[4–8] IR spectroscopy,[9–15] secondary ion mass spectrometry,[16] laser-induced thermal desorption,[17] reactive ion scattering (RIS),[18] near-edge X-ray absorption spectroscopy,[19] electron-stimulated desorption,[20] and molecular beam scattering techniques.[21–23] These studies have greatly enlarged the scope of understanding of the subject, in particular, the sticking coefficient, the uptake kinetic parameters, the stoichiometry of the product (the $H_2O$:HCl ratio), and the extent of HCl ionization.

Two aspects have been emphasized in the exploration of HCl interactions with ice: (i) kinetic properties such as adsorption, desorption, and migration of HCl, and (ii) the chemical nature of adsorbed HCl. These features are interesting not only for

fundamental reasons but also because they are intimately related to the factors controlling the overall reaction rates, such as availability of HCl molecules for heterogeneous reactions at ice surfaces and their reactivity toward counterpart molecules like $ClONO_2$. In efforts to investigate the kinetic properties, molecular beam scattering experiments[21–23] have shown that HCl trapping at ice surfaces occurs with high probability close to unity. Absorption of HCl into the bulk of ice, however, is not so feasible according to some uptake experiments,[3,17] where the uptake of HCl is observed to be restricted to about 1 monolayer (ML) even at the temperature of water desorption (170 K). Contrary to these results, TPDMS studies[4–6] and molecular beam studies combined with IR spectroscopy[23] report that HCl migrates into the ice bulk above 125 K, although there seem to be some minor disagreements among these works, such as the possibility of HCl migration at temperatures below 125 K and the influence of the ice morphology. Regarding the second issue of the chemical nature of HCl on ice, early studies[12,13,16] report exclusive ionization of HCl over a considerably wide range of ice temperature. However, recent studies[9–11,18] indicate that HCl is prevalently in the molecular forms at low temperature (<50 K) and transforms to the ionized states upon temperature increase to 140 K. Apparently, there exist discrepancies in the literature reports about some important features of the kinetic properties and the chemical states of HCl on ice. The discrepancies seem to indicate that our understanding of the ice surface properties at the molecular level is still very incomplete. Water molecules at an ice surface can be thermally activated in rotational and translational motions at the temperature of interest,[24–27] and such a dynamic nature may often complicate the exploration of the interactions between HCl and the ice surface.

* Corresponding author. Fax: + 82 2 889 1568. E-mail: surfion@ sn5u.ac.kr.
† Pohang University of Science and Technology.
‡ Seoul National University.
§ Current address: Department of Chemistry, University of Wisconsin–Madison, Madison, WI 53706-1322.

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In a previous study of HCl adsorbed on ice surfaces,[18] we quantified the relative portions for the molecular and ionized forms of HCl on the surfaces at temperatures of 50−140 K. In this work, we have taken a step further to investigate the chemical state, adsorption, desorption, and migration properties of HCl in various conditions of surface coverage, temperature, and surface morphology. $Cs^+$ RIS and low energy sputtering (LES) analyses of the surface gave information about the molecular and ionized states of adsorbed HCl with a depth resolution of 1 ML. Desorption characteristics of HCl were examined by TPDMS. Through these investigations, we could correlate the chemical identity and kinetic properties of adsorbed HCl and obtain a more comprehensive picture for the interactions of HCl with the ice surface.

## 2. Experimental Section

The substrate was a Ru single crystal with a (0001) face attached to a UHV sample manipulator, and its temperature could be varied in the range of 90−1500 K. Following the substrate cleaning by $Ar^+$ sputtering and annealing in UHV, ice films were deposited on the substrate maintained at a selected temperature between 100 and 140 K by backfilling the chamber with $D_2O$ vapor at partial pressures of $(1-5) \times 10^{-8}$ Torr. A film grown by this method at temperatures below 130 K is known to have an amorphous structure usually containing micropores, whereas deposition above 135 K produces a crystalline film, in either cubic or hexagonal phase.[28,29] We prepared ice films at different deposition temperatures between 135 and 155 K and also by annealing an amorphous ice film, deposited at 100 K, to 170 K. All these films exhibited identical adsorption features for HCl; thus we assumed that crystalline films were formed by deposition at ≥135 K. Ice films of 1−10 bilayers (BLs) were deposited, where the thickness was estimated from TPDMS measurements. $D_2O$ was degassed by several freeze−vacuum−thaw cycles before introduction into the chamber. HCl gas (Aldrich, 99+% purity) was introduced into the chamber through a separate leak valve and a tube doser. The HCl partial pressure was controlled to be $1 \times 10^{-8}$ Torr in the sample region. The pressure difference of the dosing gases in the sample and ionization gauge regions was calibrated with an accuracy of <50% and taken into account in calculating the amount of gas exposure.

Experimental procedures for $Cs^+$ RIS analysis of ice films have been described in detail previously.[26,30] In the UHV chamber with a base pressure of $1 \times 10^{-10}$ Torr, a $Cs^+$ ion beam was generated from a surface ionization source and was scattered at a sample surface to be analyzed.[31] The $Cs^+$ beam energy was chosen between 10 and 50 eV, and the current density at the sample was $1-3$ nA $cm^{-2}$. The scattered positive ions were measured with a quadrupole mass spectrometer (QMS) with its ionizer filament off. Each RIS mass spectrum consisted of at least 10 scans. The angles of the beam incidence and the detector both were 45° with respect to the surface normal, making a total scattering angle of 90°. The sampling depth of RIS analysis on ice films can be controlled to be 1 ML by lowering the incident beam energy.[26] A detailed explanation has been given for the RIS mechanism leading to the pickup of physisorbed molecules.[32] Surface contamination by incident $Cs^+$ beams was avoided by use of controlled beam doses and by preparing separate films for RIS measurements whenever necessary. Residual gas analysis and TPDMS experiments were done with a QMS detector that was used also for RIS.
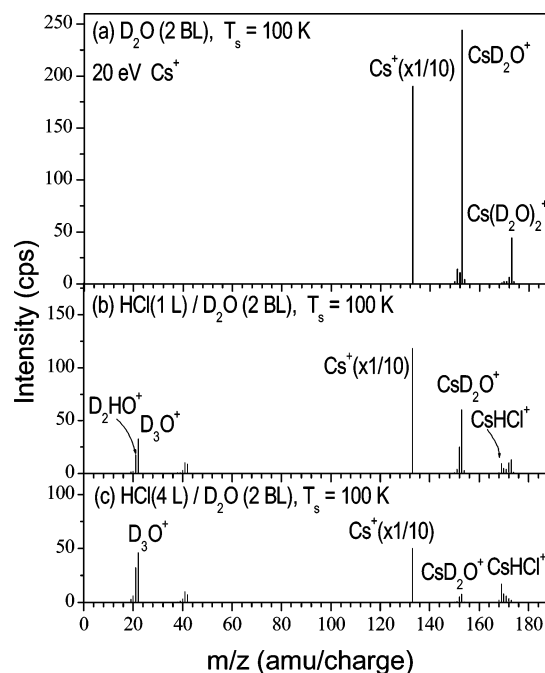


**Figure 1.** RIS mass spectra from crystalline $D_2O$ ice films covered with different amounts of HCl at 100 K. The HCl exposures were 0 L (1 L = $1 \times 10^{-6}$ Torr s) (a), 1 L (b), and 4 L (c). The $D_2O$ films were formed 2 BL thick on Ru(0001) at 135 K in a slow deposition rate of 0.005 BL $s^{-1}$. A new sample was prepared for each spectrum. RIS measurements were made with 20 eV $Cs^+$ beams at 100 K. The $Cs^+$ intensities are reduced by the factors indicated.

## 3. Results

**3.1. Adsorption of HCl on Ice Films at 100 K.** We prepared a crystalline ice film by depositing $D_2O$ vapor on a Ru(0001) substrate at 135 K. HCl was then added to the film surface after the film was cooled to 100 K, and RIS measurements were made at the same temperature. Figure 1 shows the spectra from $D_2O$ ice films exposed to different amounts of HCl. Figure 1a corresponds to a spectrum in the absence of HCl exposure to the film, showing a strong peak of reflected $Cs^+$ primaries at $m/z = 133$ amu/charge, together with RIS products at $m/z = 133 + 20n$ ($n = 1-2$). These RIS peaks are due to the pickup of $n$ water molecule(s) by the $Cs^+$ projectile.[18] In Figure 1b, a small amount of HCl was added to the film. New peaks appeared at $m/z = 20n + 1$ ($n = 1, 2$) and at $m/z = 169$. The $m/z = 169$ peak ($CsHCl^+$) is the RIS product from molecular HCl at the surface. The peaks at $m/z = 20n + 1$ ($n = 1, 2$) represent LES signals, corresponding to low-energy sputtering of hydronium ion ($HD_2O^+$) and its hydration complex $[HD_2O(D_2O)^+]$, preformed at the surface by ionic dissociation of HCl, which has been discussed in detail in a previous study.[33] The LES and RIS peaks are accompanied by neighboring peaks due to H/D exchange reactions of each species.[27] In the text hereafter, however, a group of the H/D-exchanged peaks will be symbolized only by their original isotopomer, unless specified otherwise. The hydronium ion and $CsHCl^+$ peaks indicate coexistence of ionized and molecular forms, respectively, of HCl on the surface at temperature of 100 K.[18]

In Figure 1c, a larger amount [4 langmuirs (L)] of HCl was added to the film. The spectrum shows several noticeable changes. The hydronium ion intensity has increased (note the relative decrease of $Cs^+$ intensity), the $CsD_2O^+$ intensity has decreased, and the $CsHCl^+$ intensity has increased. These results indicate the increase in surface coverages of both molecular and
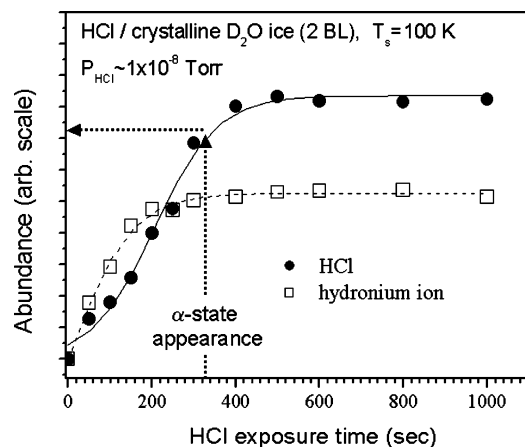
**Figure 2.** Variation of hydronium ion intensity (open squares) and RIS yield for molecular HCl (filled circles) measured on crystalline D₂O ice films at 100 K with increasing exposure of HCl. The partial pressure of HCl was about $1 \times 10^{-8}$ Torr. The hydronium ion intensity and the RIS yield represent the sum of all isotopomeric intensities. The D₂O film was 2 BL thick. Cs⁺ energy was 20 eV.



**Figure 3.** (a) Result of measurement similar to that in Figure 2 repeated on thicker (4 BL) films. The data in Figure 2 are shown in repeat, after rescaling them by the factors indicated to make the saturation values of the two curves be equal. Cs⁺ energy was increased to 35 eV on the thicker films to compensate the more efficient energy dissipation. (b) Variation of RIS yield for water molecules with increasing HCl exposure measured on ice films with thicknesses of 2 and 4 BL. The RIS yield is normalized to the value on pure ice films.

ionized HCl upon addition of HCl. Also, the absolute intensity of scattered Cs⁺ signal has decreased.

Upon further increase of the HCl exposure beyond 4 L, the RIS spectrum (not shown) did not noticeably change from Figure 1c. The intensity of neither hydronium ion nor CsHCl⁺ further increased, which indicates that their surface concentrations become saturated despite the additional HCl exposure.

The amounts of ionized and molecular HCl present at the surface are plotted in Figure 2 as a function of HCl exposure. The surface abundances in the figure correspond to the sum of all isotopomeric peak intensities, and this is also the case in other figures presented hereafter. The CsHCl⁺ intensity is normalized to the scattered Cs⁺ intensity to display the RIS yield, whereas the hydronium ion intensity is normalized to the incident Cs⁺ intensity. The ice films were prepared at 135 K to a thickness of 2 BL. The figure shows that both the ionized and molecular concentrations of HCl increase with HCl exposure and then saturate at higher exposures. Ionized HCl reaches saturation earlier than molecular HCl.

The saturation in the HCl content can be interpreted in two ways: (i) a static saturation in the surface concentration of HCl or (ii) a steady-state kinetic balance between HCl adsorption at the surface and HCl migration into the subsurface region. HCl cannot form a condensed multilayer at this temperature because the multilayer evaporates at 50 K in a vacuum.[4,5] The possibility of subsurface migration was checked by performing three control experiments. First, we probed the amount of HCl in the subsurface region of a sample that reached surface saturation, by increasing the Cs⁺ energy to a sufficiently high value. When the surface prepared in the same way as in Figure 1c was examined at Cs⁺ energy of 36 eV, the RIS intensities were unchanged from those measured at 20 eV, indicating that the subsurface HCl concentration did not increase after HCl saturation occurred at the surface.

In the second experiment, we examined the possibility of subsurface migration on thicker ice films. In Figure 3a, hydronium ion and CsHCl⁺ intensities were measured as a function of HCl exposure on D₂O films of 4 BL thickness. The result from the 4 BL film (filled symbols) is compared with that from the 2 BL film (open symbols), after rescaling their saturation intensities to be equal to each other. The curve shapes from the two films are almost identical, indicating that the saturation is developed at the same HCl exposure on both films
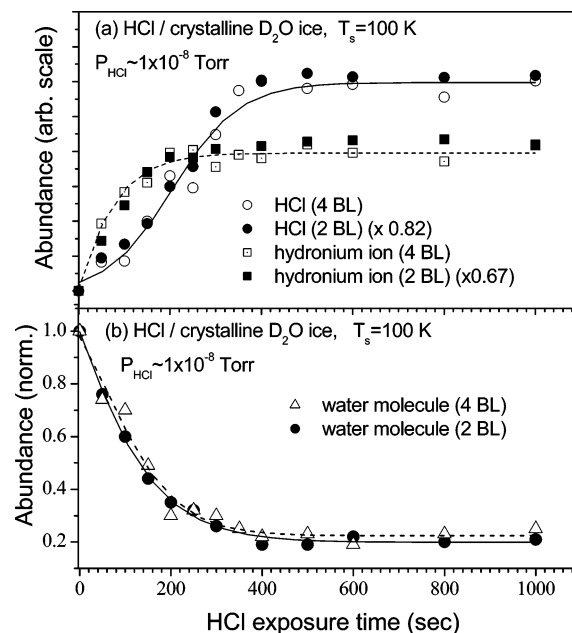
for molecular HCl as well as for hydronium ion. The result supports the absence of subsurface migration for these species. Figure 3b displays the RIS intensity for water molecules (D₂O and its isotopomers) as a function of HCl exposure on D₂O ice films of 2 and 4 BL thicknesses. The data are normalized to the intensities measured on pure ice films. On both films the water intensity decreases in almost identical ways in response to the increasing HCl exposure. The water intensity declines until commencement of saturation of molecular HCl and then remains at the level of 20% of the initial value. To estimate the absolute coverage of HCl at the saturation, a calibration experiment was conducted, in which the RIS intensity for D₂O was monitored on H₂O-adsorbed D₂O ice films as a function of coverage of the H₂O overlayer. The D₂O intensity decreased to 20% of the initial value when the H₂O coverage reached 0.92 ± 0.15 BL, i.e., when 8% of surface D₂O molecules were considered to remain uncovered by H₂O molecules. If we assume that the RIS pickup probability is the same for D₂O molecules on both the H₂O-covered and HCl-covered D₂O films, and that H₂O and HCl remain at the surfaces without inward migration at 100 K, then the calibration result indicates that the saturation coverage of HCl on the ice film is about 0.9 of the water bilayer concentration. This value agrees with the HCl saturation coverage of 1.0 ± 0.1 reported by Haq et al. for temperatures below 90 K.[23]

In the third experiment, we measured the saturation exposure for molecular HCl and hydronium ion on ice films of various thicknesses from 0.5 to 5 BL. The result on crystalline ice films (Figure 4a) indicates that the saturation exposure is almost independent of the film thickness. The observation confirms the surface residence of both molecular HCl and hydronium ion on crystalline ice films at 100 K, without their inward migration or consolidation with the ice lattice. Similar measurements were performed on amorphous ice films deposited at 100 K under D₂O partial pressure of $5 \times 10^{-8}$ Torr (Figure 4b).

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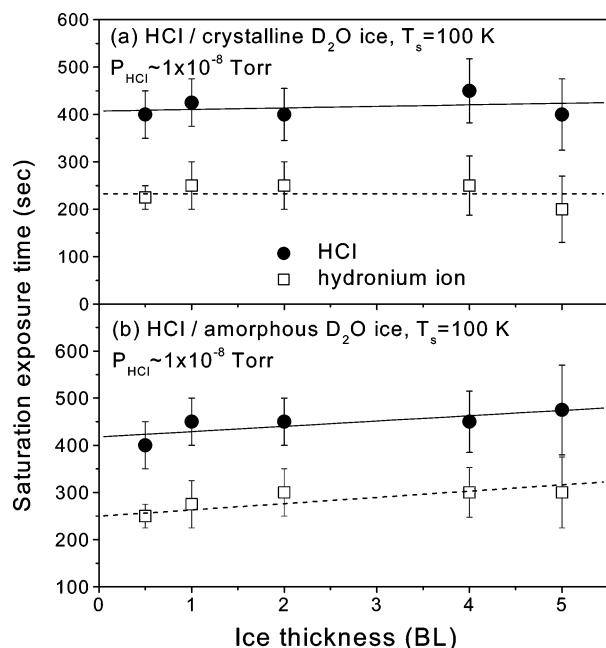*J. Phys. Chem. B, Vol. 109, No. 11, 2005* **5127**



**Figure 4.** HCl exposure time required for saturation of molecular HCl (filled circles) and hydronium ion (open squares) on ice films of various thicknesses from 0.5 to 5 BL. The partial pressure of HCl was about $1 \times 10^{-8}$ Torr. The ice film was deposited at 135 (a) and 100 K (b). HCl exposure was made at 100 K for both films.

Comparison of parts a and b of Figures 4 reveals that the HCl saturation exposure is about the same on both films within experimental uncertainty. The saturation exposure seems to increase slightly on the thicker amorphous films, but this effect is small. Such a small increase can be attributed to the increased surface area in the presence of defects and pores at the amorphous surfaces. These defect features, however, do not seem to signify the inward migration of HCl.

**3.2. Adsorption of HCl at 140 K.** At 140 K, the adsorbed HCl molecules dissociate to hydronium and chloride ions on ice surfaces.[4−16] In this section, we examine the ionization mechanism and the spatial distribution of the ionized species. For the experiment, we deposited $D_2O$ films at 135 K, raised the sample temperature to 140 K, and then added HCl. After maintaining the HCl-added samples at 140 K typically for 5 min, RIS measurements were made at 100 K. The reason that we made RIS analyses at the same temperature of 100 K in sections 3.1 and 3.2 was to minimize the possible difference in RIS sensitivity due to surface temperature. We occasionally expanded the time delay between the HCl addition and the RIS analysis up to 25 min, but the resulting RIS spectral features did not much change. Figure 5 displays RIS spectra obtained from 2 BL crystalline $D_2O$ ice films exposed to HCl for 0 (a), 1.5 (b), and 5 (c) at 140 K. Spectrum b shows the peaks of the hydronium ion and its hydrated complex, and in spectrum c these peak intensities are further increased. The $CsHCl^+$ peak is absent from all these spectra, even after saturation of the hydronium ion concentration at very high HCl exposures. Therefore, HCl must be completely ionized at all coverages. Notably, the $CsHCl^+$ signal was readily observable at 130 K, even when HCl exposure was small. This reveals that complete ionization of HCl is achieved only at temperatures close to 140 K.

The absolute intensity of scattered $Cs^+$ signal is much reduced in the spectra by exposing HCl to the ice surfaces at 140 K. When we compared the attenuated degree of $Cs^+$ intensity on the 100 and 140 K surfaces, the $Cs^+$ intensity dropped to 25%
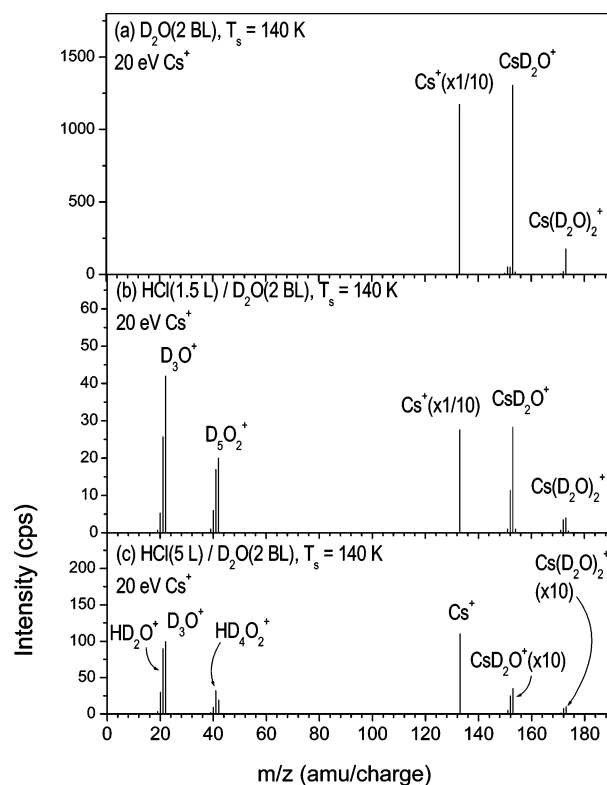


**Figure 5.** RIS mass spectra from crystalline $D_2O$ ice films covered with different amounts of HCl at 140 K. The HCl exposures were 0 (a), 1.5 (b), and 5 L (c). The HCl partial pressure was $1 \times 10^{-8}$ Torr. The ice films were deposited at 135 K, and RIS measurements were done at 100 K with a 20 eV $Cs^+$ beam. Some peak intensities are rescaled by the factors indicated.

of that from a pure ice surface when the surface was saturated with hydronium ions at 100 K, whereas it dropped to 1% on the saturated surface at 140 K. The $Cs^+$ intensity is attenuated primarily due to softness and roughness of the ice surface. Other factors such as film thickness and chemical composition of the film can also attenuate the scattered intensity, but these factors cannot account for the observed 25 times difference between the two surfaces. We interpret that HCl exposure at 140 K causes serious roughening of the surface. This aspect will be discussed again in section 4.2.

In Figure 6a, the intensity of the hydronium ion signal is measured as a function of HCl exposure at 140 K on two ice films of different thicknesses. The hydronium ion intensity increases with HCl exposure and then reaches saturation. To saturate the 4 BL film, a higher HCl exposure is required than for the 2 BL film. Figure 6b shows the variation of the RIS intensity for water molecules measured on the same films as those in Figure 6a. The water intensities are normalized against pure ice films. The water intensity decreases with increasing amounts of the adsorbent, and the thinner film exhibits an earlier decline than the thicker one. A calibration experiment showed that, at the point of adsorbent saturation, the $D_2O$ surface coverage was $0.26 \pm 0.07$ and $0.32 \pm 0.07$ BL for the thinner and thicker films, respectively. This shows that a thicker film has a slightly higher abundance of water molecules at the top layer than the thinner one.

When the HCl adsorption curves in Figure 6 are compared with those at 100 K (Figure 3), a few differences can be noted. First, a larger amount of HCl exposure is needed to saturate the films at 140 K than at 100 K. Second, at 140 K the saturation exposure is higher on a thicker film than on a thinner one, whereas at 100 K the saturation exposure is the same on two
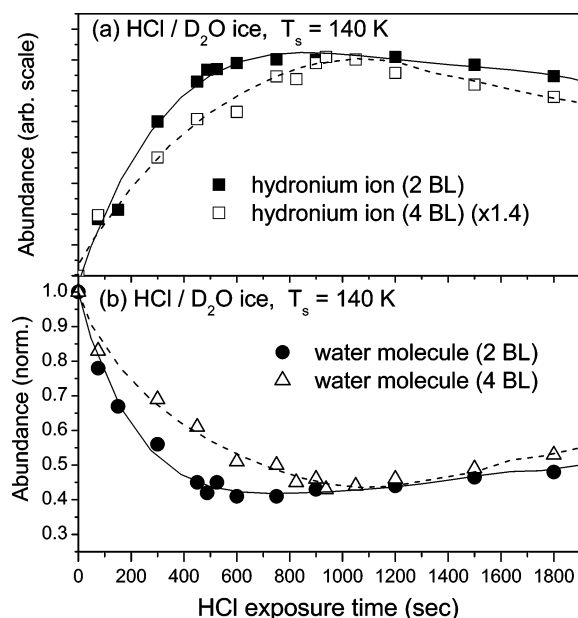
**Figure 6.** Variation of hydronium ion intensity (a) and RIS yield of water molecules (b) measured as a function of HCl exposure on ice films of two different thicknesses at 140 K. In (b), the data are normalized to the yield from pure ice films. $Cs^+$ energy was adjusted to 20 and 35 eV for 2 and 4 BL films, respectively, to compensate the different degrees of energy dissipation on the films.
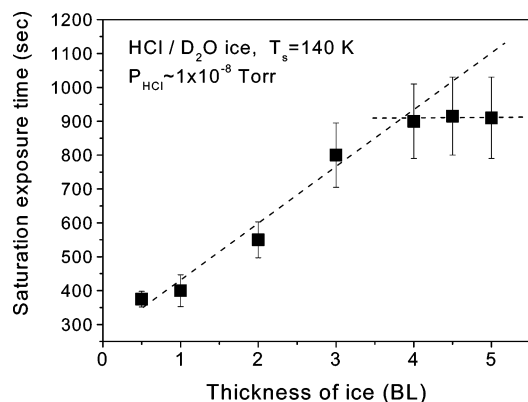


**Figure 7.** HCl exposure time required for saturation of hydronium ion intensity at 140 K versus thickness of $D_2O$ ice films. The HCl partial pressure was $1 \times 10^{-8}$ Torr. The ice films were deposited at 135 K.

films. Third, the amount of water molecules remaining at the surface after HCl saturation is higher at 140 K (0.26 ± 0.07 BL for the thicker film and 0.32 ± 0.07 BL for the thinner one) than at 100 K (~0.1 BL for both films). These differences indicate that hydronium ions migrate from the surface to the sublayer at 140 K. Fourth, the hydronium ion intensity slightly deceases after reaching a saturation at 140 K, with accompanying increase in surface water concentration. A similar behavior is not observed at 100 K. This difference, however, might be hindered by adsorption of residual water molecules during the experiment, because the HCl exposure time is longer in Figure 6 than in Figure 3. If the residual water adsorption is negligible, it might reflect an increased rate for subsurface migration of hydronium ions at 140 K due to structural changes of the HCl-incorporated surface.[23]

To examine the subsurface migration of hydronium ion more systematically, we measured the saturation exposure for hydronium ion on ice films of various thickness. The result is plotted in Figure 7, which shows that the saturation exposure increases quite linearly with increasing film thickness up to 4 BL, but
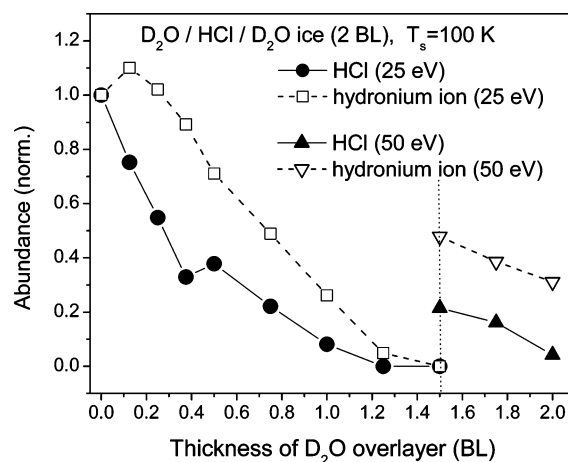


**Figure 8.** Hydronium ion and $CsHCl^+$ signal intensities measured on samples where HCl molecules are sandwiched between an underlying crystalline $D_2O$ film and a $D_2O$ overlayer at 100 K. The amount of HCl exposure was 0.5 L. The hydronium ion (open squares) and $CsHCl^+$ intensities (filled circles) were measured first with a 25 eV $Cs^+$ beam as a function of the $D_2O$ overlayer coverage. At $D_2O$ coverage of 1.5 BL, where neither HCl nor hydronium ion was detected at 25 eV, the beam energy was increased to 50 eV. $CsHCl^+$ (▲) and hydronium ion signals (▽) reappeared at this energy.

then it remains constant for the thicker films. This indicates that the subsurface migration of hydronium ion is spatially restricted to a depth of about 4 BL. When we increased the time delay for the RIS measurement up to 30 min, the hydronium ion intensity from the surface did not decay much and remained strong for the extended time periods. Therefore, the major portion of hydronium ions must have resided at the surface, and only a part of the ions migrated into the subsurface region for depth ≤4 BL.

**3.3. Effects of Water Overlayer and Temperature on HCl Ionization.** We examined ice films prepared to have HCl molecules sandwiched between an underlying $D_2O$ film and a $D_2O$ overlayer. For this, a crystalline $D_2O$ film was deposited at 135 K, HCl was added to the surface for 0.5 L at 100 K, and then $D_2O$ was added on top of this surface at the same temperature. Figure 8 shows the result of surface analysis on this film as a function of the $D_2O$ overlayer coverage. $Cs^+$ impact energy was 25 eV to detect only the surface residing species. The intensities for hydronium ions and $CsHCl^+$ are normalized to the initial value at zero $D_2O$ coverage. These intensities gradually attenuate as the $D_2O$ overlayer develops and eventually disappear when the overlayer is completed at an estimated coverage of 1.2 BL. At this point, both hydronium ions and HCl must be almost completely buried underneath the $D_2O$ overlayer. It is noteworthy that the hydronium ion intensity deceases more slowly than the $CsHCl^+$ intensity. Such a tendency can occur if the added water molecules cause extra ionization of HCl molecules or if hydronium ions move toward the surface.

After the $D_2O$ overlayer was completed at coverage of 1.5 BL, the $Cs^+$ beam energy was increased to 50 eV to detect the buried species as well. Figure 8 shows that $CsHCl^+$ and hydronium ion signals reappear at 50 eV. The ratio of the hydronium ion to $CsHCl^+$ intensity observed from the sandwiched layer is 2.3, which is greater than the initial value of 1.0 (in the normalized scale) in the absence of $D_2O$ overlayer. This indicates enhanced HCl ionization by overlaid water molecules. Interestingly, however, a substantial portion of HCl molecules remain undissociated even underneath the water layer
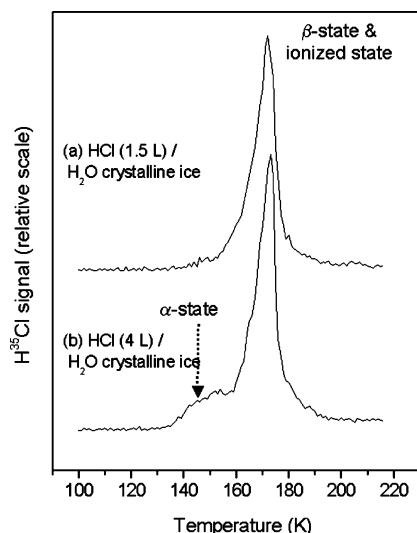
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**Figure 9.** TPDMS spectra of HCl ($m/z = 36$ amu/charge) from $H_2O$ ice films covered with HCl. HCl exposure was 1.5 L in (a) and 4 L in (b). The ice films were deposited at 135 K, and HCl was added at 100 K. The heating rate was 5 K s$^{-1}$.

at 100 K, indicating that three-dimensional surrounding by water molecules does not guarantee ionic dissociation of HCl.

The effect of temperature on HCl ionization was examined by preparing an HCl-adsorbed ice film at 100 K and then warming it to 140 K. The CsHCl$^+$ signal that existed at 100 K disappeared completely after sample heating to 140 K, regardless of the amount of HCl added to the surface. The RIS spectra became very similar to Figure 5 measured from ice films exposed to HCl at 140 K. The observation indicates that the increased temperature removes all HCl molecules from the surface. Two possible paths can account for for this observation: thermal desorption of HCl from the surface and ionization of the molecules. These possibilities are explored by TPDMS experiments in the following section.

**3.4. TPDMS Study.** A TPDMS experiment was conducted for HCl adsorbed on a crystalline $H_2O$ ice film at 100 K. Figure 9 shows the HCl desorption signal at $m/z = 36$ amu/charge (H$^{35}$-Cl$^+$) recorded at the sample heating rate of 5 K s$^{-1}$. Spectrum a was obtained from a sample exposed to 1.5 L HCl, and this exposure corresponds to about 60% of that required for hydronium ion saturation and 40% for the molecular HCl saturation (see Figure 2). The spectrum shows a single desorption peak at 170 K, and it appears simultaneously with the water desorption peak (not shown). No desorption peak is seen below 150 K. According to previous TPDMS studies,[4−8] the 170 K peak is assigned to recombinative desorption of ionized HCl. In contrast, Figure 2 shows that molecular HCl should exist on this film in a substantial amount (about 30% of the saturation concentration). In the absence of any other peak in the spectrum, we are forced to interpret that the HCl molecules present at 100 K also desorb in this peak. Therefore, this peak must be derived from two HCl components: (i) HCl preionized at 100 K and (ii) molecular HCl that ionizes during the temperature scan and then desorbs through recombinative reaction.

Spectrum b was obtained from an $H_2O$ ice film with its surface saturated with HCl at 100 K. Notably, a new desorption feature appears at 135−160 K as a shoulder next to the major peak at 170 K. This spectrum is similar to that reported by Graham and Roberts,[4,5] obtained after heavy exposure of HCl on ice films deposited on W(100). They assign the shoulder peak to a molecularly adsorbed state based on its inefficient H/D exchange between HCl and $D_2O$. We also consider that

this peak corresponds to molecularly adsorbed HCl because it does not appear upon HCl exposure at >140 K. We denote this molecular state as α-state, to be distinguished from the other molecular state (β-state) that produces the 170 K peak. RIS measurements reveal that the shoulder peak emerges only near the saturation of the molecular HCl intensity and after the saturation of the hydronium ion intensity (marked in Figure 2). Figure 2 shows that the α-state comprises 11% of the total molecular HCl content present on the HCl-saturated surface at 100 K. Upon further exposure of HCl, the shoulder peak grew slowly toward saturation. Change of the sample heating rate between 1 and 5 K s$^{-1}$ did not significantly affect the onset of HCl exposure for the shoulder peak. Thus, a substantial kinetic barrier exists from the α-state to the ionized state.

On the basis of the observations described above, we interpret that two distinct molecular states of HCl exist on the ice films at 100 K. The α-state desorbs as a low-temperature shoulder peak at 135−160 K in TPDMS experiment, whereas the β-state first ionizes during the temperature scan and then recombinatively desorbs at 170 K. The 170 K peak also contains the desorption flux from the preionized HCl on the surface. The absence of the α-state in the early HCl exposure suggests preferential occupation of the β-state during HCl adsorption and later formation of the α-state.

## 4. Discussion

**4.1. Chemical States of HCl on Ice.** The chemical states of HCl adsorbed on ice have been the subject of numerous investigations and debates.[4−23,34−39] Though controversies may still exist, some convincing evidence from recent studies[9−11,18] indicates that both molecular and ionic states coexist at 100 K. Here we discuss first the molecular states of adsorbed HCl. The presence of molecular HCl on the 100 K film is evidenced by the RIS signal of CsHCl$^+$. Quantitative monitoring of this species as a function of HCl exposure (Figures 2 and 3) and the result of TPDMS measurement (Figure 9) have led to the interpretation that the molecular HCl exists in two distinct states, the α- and β-states. Upon a temperature increase, the α-state desorbs simply as a molecule at 135−160 K, and the β-state first becomes ionized and then desorbs via recombinative reaction at 170 K. These TPDMS peaks have already been observed in previous studies,[4−7] where they assign the 135−160 K peak to molecular HCl (or HCl monohydrate) and the 170 K peak to the ionized state (or a hydrate phase with higher $H_2O$:HCl stoichiometry). In addition, Graham and Roberts[4,5] report that the H/D exchange between HCl and $D_2O$ molecules is incomplete in the low-temperature peak, whereas it is almost complete in the high-temperature peak. Also, the low-temperature peak does not appear until saturation of the high-temperature peak. These observations agree perfectly with our new interpretation that the high-temperature peak is comprised of both the ionized state and the molecular β-state, and that the shoulder peak is desorption from the molecular α-state. Because the β-state molecules become fully ionized before desorption, they can undergo extensive H/D exchange with $D_2O$ molecules, just like the preionized HCl species.

HCl molecules in the α-state desorb at 135−160 K, and thus they are more strongly bound to the ice surface than physisorbed HCl, which desorbs around 50 K.[4,5] The desorption temperature of 135−160 K corresponds to a desorption energy of 30−33 kJ/mol,[4,5,8,23] if the desorption is assumed to be first order. A similar desorption energy (28 kJ/mol) has been measured from a pulsed-molecular beam study.[21] These values are approximately half the HCl desorption energy (67 kJ/mol) from a bulk

film of HCl trihydrate.[8] The lower desorption energy from the α-state suggests that HCl is hydrogen bonded to probably one or at most two water molecules. The saturation coverage of HCl on a crystalline ice film is $0.92 \pm 0.15$ BL at 100 K, and the α-state starts to form at a coverage corresponding to 89% of the HCl saturation. At this coverage, an HCl molecule sticking at the ice surface can find most likely just one dangling bond left available for hydrogen bonding, because a majority of surface dangling bonds have been preoccupied by other HCl molecules. An HCl molecule may also bind to a chloride ion located at the surface of high HCl concentration.[10]

The molecules in the β-state are more strongly bound to the surface than those in the α-state, because they do not desorb until water molecules sublime. Obviously, the β-state molecules appear to have higher coordination numbers than the α-state ones. The mechanisms for adsorption and ionization of HCl on ice at 50−90 K explored by Devlin and co-workers[10,11] are informative for elucidating the nature of the β-state. According to these studies, hydrogen bonding between surface dangling bonds and HCl is a decisive factor that determines the fate of HCl at the surface. When coordinated by two hydrogen bonds, the HCl molecule is considerably stretched, but not yet ionized. Acquiring a third hydrogen bond, HCl is ionized in the form of a contact ion pair $[H^+ \cdot Cl^- (H_2O)_n]$, ultimately followed by proton transfer along the hydrogen bonding network on the surface to generate the dissociated ions $[H^+ (H_2O)_n Cl^-]$.

In the discussion up to now, the RIS signal of $CsHCl^+$ has been considered to represent HCl molecules at the ice surface, but we cannot exclude the possibility that contact ion pairs, if they existed, also contributed to this signal. Though the RIS pickup process by the scattered $Cs^+$ ions occurs instantaneously ($<10^{-12}$ s) such that only molecular units can be detected,[32] the $H^+ \cdot Cl^-$ moiety of the contact ion pair may also be able to be lifted up by $Cs^+$ as for an HCl molecule and give rise to $CsHCl^+$. On the other hand, the contact ion pair should also produce the hydronium ion signal in the LES experiment by an alternative process of breaking the $H^+{-}Cl^-$ bond. Therefore, the hydronium ion signal can be used to distinguish the contact ion pair from the HCl molecule. In this guideline, at the ice temperature below 70 K where the hydronium ion signal is almost absent,[18] we can interpret that HCl exists exclusively as molecules. In the intermediate temperature range (70−130 K) where both the $CsHCl^+$ and hydronium ion signals appear, the $CsHCl^+$ signal results from the HCl molecules and possibly from the contact ion pairs as well. Likewise, the hydronium ion signal can be produced both from the separated ions and the contact ion pairs in this temperature range. In this respect, one can imagine that the "molecular" β-state observed at 100 K may include both the HCl molecules with multiple hydrogen bonds and the contact ion pairs. One cannot, however, determine the ratio of the two species from the present results alone. At 140 K, the $CsHCl^+$ signal completely disappears. At this stage, HCl molecules and the contact ion pairs all are dissociated to hydronium and chloride ions.

Ionization of HCl molecules must require multiple hydrogen bonding by water molecules, according to theoretical results.[10,11,34−37] In the experiment where HCl molecules are fully covered by a $D_2O$ layer at 100 K (Figure 8), however, a significant portion of HCl still remains undissociated as indicated by the remnant $CsHCl^+$ signal. The $CsHCl^+$ signal may result from molecular HCl and/or the contact ion pair, as mentioned above. Formation of the contact ion pair requires at least three hydrogen bonds by water molecules.[10,11] Whether the $CsHCl^+$ signal is due to molecular HCl or the contact ion pair, the result

indicates that HCl is not always dissociated to the separated ions solely due to surrounding by water molecules. Warming the sample to 140 K is necessary for complete ionic dissociation of the molecules. At this temperature, surface water molecules are mobile and can undergo active rotation and diffusion.[26] Under this condition, the contact ion pairs will no longer be stable inside the kinetic traps at the ice surface and they will dissociate irreversibly to the separated ions.

The reason for coexistence of molecular and ionized HCl at 100 K is because the ice surface offers different types of adsorption sites for HCl molecules. Among these sites, kinetic preference is found in the result in Figure 2. HCl adsorption into the ionized state somewhat precedes the β-state molecular adsorption in the early stage of HCl exposure. Also, the ionized state becomes saturated faster. This implies that, despite the restricted molecular diffusion at 100 K,[26] HCl molecules can preferentially find and occupy these sites to become ionized. Theoretical study[37] suggests that nonactivated ionization can occur when HCl is adsorbed into favorable sites, which have one dangling −O atom for accepting the hydrogen of HCl and two dangling −OH groups to which the chlorine can bind. The next preferred adsorption site is one that gives the β-molecular state, which also offers multiple hydrogen bonding to adsorbed HCl. The α-molecular state, considered to be a monohydrated species, is formed last, only after the ionized states are fully saturated and the β-molecular states also are substantially occupied.

**4.2. Surface Residence versus Subsurface Migration of HCl.** The saturation exposure for HCl adsorption is independent of the thickness of ice films at the temperature of 100 K (Figure 4a). Such behavior is expected only when the HCl uptake is limited to the top layer of ice films without migration of HCl into the interior of the films. Therefore, both HCl molecules and hydronium ions must reside at the surface at 100 K.

At 140 K, some evidence indicates that HCl migrates to the underlying sublayer. First, thicker films uptake higher amounts of HCl than thinner ones (Figure 7). A similar behavior has been observed[23] for adsorption of HCl molecular beams on ice at temperatures >130 K. The inward migration of HCl, however, is spatially restricted to 4 BL at 140 K, as shown by the uptake experiment on ice films of various thicknesses (Figure 7). Second, at HCl saturation the portion of water molecules present at the top layer is considerably larger at 140 K than at 100 K. For the HCl-saturated films with a thickness of 5 BL, the surface coverage of water molecules is 0.31 ML at 140 K, compared to 0.08 ML at 100 K. This suggests that subsurface water molecules are released to the surface at 140 K, displaced by HCl that migrates inward.[39] The displacement process may be driven by exothermic hydration to form stable multihydrates or dissociated ions. When water molecules hydrate HCl or the dissociated ions, some of the water molecules will appear at the surface. Third, the intensity of scattered $Cs^+$ is extremely attenuated at 140 K. The observation suggests serious roughening of surface morphology due to disruption of the crystalline bonding network by HCl incorporation into the sublayer.

Since all the HCl molecules and the contact ion pairs are dissociated to ions at 140 K, it is evident that HCl migration occurs as dissociated ions at this temperature. The ionic migration mechanism may be applicable to other temperatures as well. HCl molecules and contact ion pairs trapped in the subsurface region of ice are thermodynamically unstable with respect to the dissociated ions. Slight thermal rearrangement of surrounding water molecules, which is necessary for the

migratory motion, will convert these "molecular units" to the separated ions.

According to theoretical energy calculations,[40] protons prefer to stay at the surface of ice instead of migrating into the interior, because repulsive forces are present between the protonated water molecule and the fourth-coordinating water molecules. The result indicates that there is really no driving force for transporting hydronium ions from the surface into the ice lattice. Of course, the energy released from exothermic hydration reaction can relocate the positions of HCl and water molecules near the surface to enrich the surface layer with water molecules, as mentioned above, but this effect can occur only very near the surface and cannot move the hydronium ions to deeper layers. We consider that the hydronium ion migration is assisted by self-diffusion of surface water molecules, for the reasons discussed below. First, the majority of hydronium ions reside at the surface even after an extended time of migration, which suggests diffusional migration. Second, the maximum migration depth of 4 BL observed at 140 K is close to the thickness of the diffusion-active layer on ice surfaces at the same temperature,[26] in which water molecules can diffuse about 80 times faster than in the bulk.[24] The self-diffusion of water molecules assists propagation of the H/D exchange reaction between water molecules to a similar depth from the surface.[27] Third, the mobility of hydronium ions is much lower than that of water molecules near the ice surface,[33,41] another reason to consider that the mobile species are water molecules rather than hydronium ions.

Finally, the results of the investigations presented above demonstrate that the fate of HCl molecules stuck on the ice surface depends very much on experimental conditions, such as ice film temperature and thickness, HCl coverage, and microscopic morphology of the ice surface. These factors can affect the chemical states of adsorbed HCl, relative portions of these states, and their migratory behavior. Numerous investigations have been made on the interactions of HCl with ice surfaces by using diverse experimental approaches, and some of the reports might seem contradictory to each other. Such controversial observations might need to be carefully interpreted by paying attention to those details of the experimental conditions.

## 5. Summary and Conclusion

The findings and conclusions drawn from this study can be serialized as follows:

(i) HCl partially dissociates on ice films at 100 K to hydronium and chloride ions, and the undissociated HCl exists in two distinct molecular states. The molecular α-state desorbs simply as a molecule around 150 K in TPDMS experiment, and the molecular β-state is ionized first and then desorbs via recombinative reaction. The α-state molecule is bound probably through one hydrogen bond to a water molecule or chloride ion at the surface, and the β-state is bound through multiple hydrogen bonds to water molecules.

(ii) HCl completely dissociates to hydronium and chloride ions at 140 K. The ionic dissociation, however, cannot be fully achieved solely by the surrounding water molecules at 100 K. It requires both multiple hydrogen bonds to water molecules and thermal energy to activate molecular motions.

(iii) Kinetic preference is observed for adsorption into various chemical states of HCl. In the early stage of HCl exposure at 100 K, adsorption into the ionized state is somewhat favored. The next preferred adsorption state is the molecular β-state, and

the molecular α-state is formed last, only after the ionized state is fully saturated and the β-molecular state is substantially occupied.

(iv) HCl molecules and hydronium ions stay at the surface at 100 K. At 140 K, the dissociated hydronium ions can migrate to the subsurface region, but the migration occurs only partially and to a depth of about 4 BL. The hydronium ion migration is probably due to self-diffusion of water molecules in the surface region.

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