



Hydration of the HCl and NH₃ molecules adsorbed on amorphous water–ice surface

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Abstract

The interactions between HCl and NH₃ molecules adsorbed on amorphous solid water (ASW) have been investigated by temperature-programmed time-of-flight secondary ion mass spectrometry (TP-TOF-SIMS). The NH₄⁺ ion is sputtered predominantly from codeposited HCl and NH₃ molecules on ASW due to collision-induced proton transfer reactions. The NH₄⁺ yield is enhanced above 60 K as a consequence of the formation of the NH₄Cl molecule. The NH₄⁺ yield steeply decays above 100 K due to the hydration of the NH₄Cl molecules, and the almost complete hydration occurs above 140 K. The H/D exchange is induced rapidly between D₂O and NH₄Cl molecules above 120 K. These behaviors strongly suggest that mobile water molecules exist on the surface above 100–120 K.

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1. Introduction

The nature of water–ice is very important in astrophysical environment, because it is believed to be a major component of comets, planetary rings, and interstellar clouds. Recently, Antarctic ozone depletion is very serious problem. It is likely that Antarctic stratospheric clouds (PSCs) play the key role in inducing this phenomenon [1,2]. It is believed that PSCs mainly consist of water–ice [1], and Cl[−] ion has a lot to do with Antarctic ozone depletion. HCl is the simplest molecule that include Cl atom and plays

an important role in chemistry of PSCs. Hynes and co-workers insist that the HCl is ionized thermodynamically at the water–ice surface and that the formation of quasi-liquid surface layer is not necessary to induce ionization [1]. So far, Fourier transform infrared spectroscopy (FT-IR) [3–7], thermal desorption spectroscopy (TDS) [8,9], and ultraviolet photoelectron spectroscopy (UPS) [10,11] have been utilized to understand molecular reactions on the water–ice surface. SIMS may have a potentiality for characterization of molecules on the surface due to its extremely high surface sensitivity. The yield of sputtered ion depends much on chemical environment, which is called ‘matrix effect’. The hydrogen-bond matters are of interest in this respect. Rabalais and coworkers [12] revealed that the most abundant ions sputtered

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from pure water–ice films are protonated water cluster ions. Kang and collaborators [2,13] discussed interactions of NH_3 and HCl molecules adsorbed on water–ice films. They claimed that NH_4^+ and H_3O^+ ions, created as a consequence of acid–base reactions, can be sputtered. More recently, Souda et al. [14,15] discussed the mechanisms of collision-induced proton transfer reactions and thermally-activated H/D exchange and demonstrated that TOF-SIMS is a quite powerful technique for investigating the solvation and hydrogen-bond reactions on the water–ice surface.

In the present paper, we report on the reaction of HCl and NH_3 molecules by using TP-TOF-SIMS. Three adsorption systems are investigated in the temperature range from 15 to 180 K; (a) the HCl molecules adsorption on the NH_3 layer, (b) co-adsorption of the HCl and NH_3 molecules on the H_2O layer and (c) co-adsorption of the HCl and NH_3 molecules on the D_2O layer. So far, the NH_4Cl formation from the NH_3 and HCl molecules have been discussed extensively for the gas phase [16–18] as well as the condensed phase [19,20]. The sputtering of cations and anions from the NH_4Cl molecules is interesting, in comparison with the unreacted NH_3 and HCl molecules, in terms of its ionic nature in bonding. It is well known that amorphous solid water transforms into crystalline phase at 140 K. Therefore, it is of interest to know the temperature evolutions of the reaction and solvation of the HCl and NH_3 molecules on the water–ice surface. In addition, the system (c) would give us information on the contribution of the water–ice surface to the hydrogen-bond reaction by investigating the rate of the thermally-induced H/D exchange.

2. Experiment

Experiments were conducted in a stainless steel ultrahigh-vacuum chamber of base pressure below 1×10^{-8} Pa. The vacuum system was equipped with an electron-impact-type ion source, a linear-TOF tube, a quadrupole mass spectrometer for gas analysis, a hemispherical electrostatic analyzer, an X-ray source, a UV source, and a low-energy electron gun. He^+ ions were chopped by an electrostatic deflector into pulses with width of 200 ns and frequency of 40 kHz. The TOF-SIMS measurements were made in such a man-

ner that the sample, floated with a bias voltage of +500 eV (in case of negative ions, the bias voltage was set –500 eV), was irradiated with a primary He^+ beam of 2 keV through a grounded stainless-steel mesh placed 4 mm above the sample surface (the ion impact energy was 1.5 keV for cations and 2.5 keV for anions), and the positive or negative ions extracted into the field-free region of the TOF tube were detected with a channel electron multiplier. To minimize charging and damage of a surface, a pulsed He^+ beam with a low incident flux (0.2 nA/cm^2) was used. The substrate was a polycrystalline Ni sheet mounted on a sample holder cooled to 15 K by means of a closed-cycle He refrigerator. The surface was cleaned by annealing around 1200 K. The NH_3 , HCl , and H_2O (D_2O) molecules were dosed from separate gas inlet systems to the substrate by backfilling the vacuum system. One-monolayer (1-ML) coverage of the adsorbed molecules was determined from the decay curve of the sputtered ion yields from the substrate as a function of exposure, and the film thickness was estimated on the basis of this value.

3. Experimental results and discussion

3.1. HCl (2-ML) on NH_3 (50-ML)

Fig. 1 shows evolutions of typical secondary-ion intensities sputtered from the HCl -adsorbed NH_3 -ice surface as a function of temperature; the NH_3 (50-ML) and HCl (2-ML) molecules were deposited successively at 15 K. Fig. 1(a) and (b) show positive and negative ions and electrons. In this system, H^+ and NH_4^+ are the dominant cation species. The NH_4^+ yield at 15–60 K is about five times as high as that from the pure NH_3 layer. The NH_4^+ ion is caused by the proton transfer reaction during collisions between HCl and NH_3 molecules ($\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4^+ + \text{Cl}^-$), where the probability for the proton transfer reaction depends on the proton affinities. The yields of H^+ and NH_4^+ ions decreases at 60 K. These ion yields in the 70–100 K range are almost the same as those of the thick NH_3 layer. This result indicates that the surface is covered by the pure NH_3 molecules. Furthermore, the e^- yield is enhanced markedly, implying that the NH_3 molecules tend to emit electrons efficiently. Above 110 K, the yields of NH_4^+ and

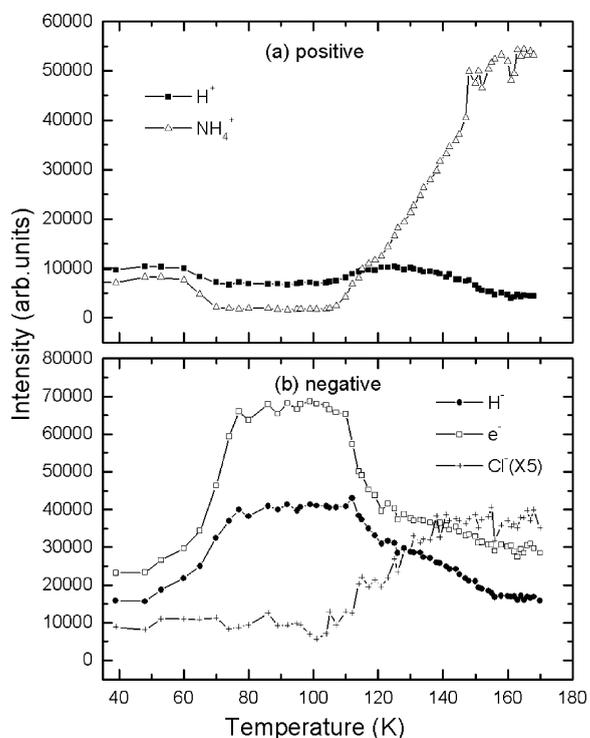


Fig. 1. Temperature evolutions of some secondary ion yields from the HCl-adsorbed NH₃ layer. The HCl molecules (2-ML) were deposited on the NH₃ layer (50-ML) at temperature of 15 K. The results for (a) positive ions and (b) negative ions and electrons are shown.

Cl⁻ ions are enhanced markedly, whereas the yields of e⁻ and H⁻ ion steeply decay. These changes show that the NH₄Cl molecules remain on the surface after desorption of the NH₃ molecules at 110 K. Judging from the fact that the Ni⁺ ion is not detected above 110 K, we conclude that the surface is completely covered by the NH₄Cl molecules. The yield of the NH₄⁺ ion sputtered from the NH₄Cl molecules is enhanced due to the polarization based on proton transfer reactions during energetic molecular collisions.

Regarding the electron emission, the amount of detectable electron depends on the electron affinity levels. Hence, the electron yield may have information about the state of the topmost surface layer. Note that the evolution curve of the yields of H⁻ and e⁻ is correlated; the H⁻ ion would be produced by accommodating such hot electrons into the affinity level

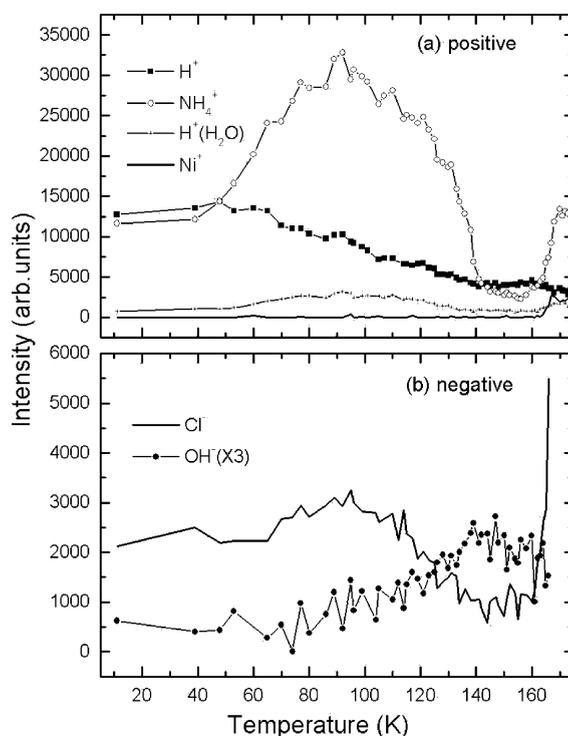


Fig. 2. Temperature evolutions of some secondary ion yields from the HCl and NH₃ molecules coadsorbed on the H₂O layer. The H₂O (50-ML) molecules were deposited at 100 K, and then the HCl (2-ML) and NH₃ (2-ML) molecules were coadsorbed after cooling down to 15 K. The results for (a) positive ions and (b) negative ions and electrons are shown.

(0.7 eV). On the other hand, the H⁺ ion is originated from the dissociative ionization of the dangling N–H bond at the topmost surface layer.

3.2. HCl (2-ML) and NH₃ (2-ML) on H₂O (50-ML)

Fig. 2 shows the yields of some secondary ions sputtered from the HCl and NH₃ molecules codeposited on the H₂O–ice surface as a function of temperature; the H₂O (50-ML) molecules were deposited at 100 K, and then the HCl (2-ML) and NH₃ (2-ML) molecules were coadsorbed on the surface after cooling down to 15 K. Thus, we prepared the nonporous amorphous solid water (ASW) to exclude the possibility that molecules are incorporated in the cavities of ASW [21]. Regarding the mechanism of the sputtered ion formation, the bare H⁺ and H⁻ ions come from the dangling O–H or N–H bond. On the other hand, the

hydrated H^+ ion is created in the course of the breakage of hydrogen bond ($\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^-$). The $\text{H}^+(\text{HCl})$ ion (not shown in Fig. 2) would be created as well ($\text{HCl} + \text{HCl} \rightarrow \text{H}^+(\text{HCl}) + \text{Cl}^-$), but it is hardly detectable because the HCl molecules have the highest ability to donate the proton in this system ($\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4^+ + \text{Cl}^-$ or $\text{H}_2\text{O} + \text{HCl} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$).

The yield of the NH_4^+ ion from this surface is higher than that from the pure NH_3 layer by more than an order of magnitude. Probably, the proton is not only donated from the HCl molecules but also from the H_2O molecules because of the higher proton affinity of the NH_3 . In contrast to the results shown in the preceding section, the yield of NH_4^+ ion is enhanced considerably above 50 K. This result suggests that the NH_4Cl molecules begin to be produced on the surface at 50 K. Moreover, the yield of the $\text{H}^+(\text{H}_2\text{O})$ ion increases above 50 K. This behavior should be ascribed to the proton transfer reactions enhanced by the HCl molecule ($\text{H}_2\text{O} + \text{HCl} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$) since the $\text{H}^+(\text{H}_2\text{O})$ yield in this system is higher than that of the pure water–ice layer. The NH_4^+ yield tends to decay above 100 K despite that the NH_4Cl molecules would not desorb. This is because the NH_4Cl molecules are gradually hydrated by the mobile H_2O molecules. Thus, the broad peak of the NH_4^+ yield at 100 K occurs as a result of the competition between the hydration and the formation of the NH_4Cl molecules. The phase transition occurs from ASW to crystalline ice at 140 K and, hence, the NH_4Cl molecules can be hydrated efficiently by the water molecules with higher mobility above 140 K. This presumption is supported by the fact that the yield of the OH^- ion (the Cl^- ion) is increased (decreased) above 120 K, providing the evidence that the water molecules cover the topmost layer. The yield of the $\text{H}^+(\text{H}_2\text{O})$ ion sputtered from this system at 140 K is almost the same as that from the pure H_2O layer. Moreover, the NH_4^+ ion does not disappear completely. This result may suggest that a small amount of the hydrated NH_4Cl molecules remain on the surface and do not diffuse completely into the thin-layer bulk of water–ice. It is thus concluded that the NH_4Cl molecules are basically hydrated on the surface at 140 K. Above 160 K, the NH_4^+ yield increases due to desorption of the water molecules. But desorption of the NH_4Cl molecules is not complete at this temperature,

as inferred from the fact that the yield of Ni^+ ion sputtered from the Ni substrate is negligibly small.

3.3. HCl (2-ML) and NH_3 (2-ML) on D_2O (50-ML)

Fig. 3 shows evolutions of typical secondary ions sputtered from the HCl and NH_3 molecules coadsorbed on the D_2O -ice surface as a function of temperature. This experiment is essentially the same as that in Fig. 2(a) except for utilizing the isotopic water molecules. At 15 K, the yields of the $\text{D}^+(\text{NH}_3)$ ion [$\text{NH}_3 + \text{D}_2\text{O} \rightarrow \text{D}^+(\text{NH}_3) + \text{OD}^-$] relative to the $\text{H}^+(\text{NH}_3)$ ion [$\text{NH}_3 + \text{NH}_3 \rightarrow \text{H}^+(\text{NH}_3) + \text{NH}_2^-$] would give us information about the relative amounts of the NH_3 molecules wetting the D_2O surface to those forming islands. The enhancement of the NH_4^+ and $\text{D}^+(\text{NH}_3)$ ions above 50 K may be ascribed to the formation of the polarized NH_4Cl and NH_3DCl molecules, respectively. Furthermore, the deuterated ammonium ions, such as $\text{D}^+(\text{NH}_3)$, $\text{D}^+(\text{NDH}_2)$,

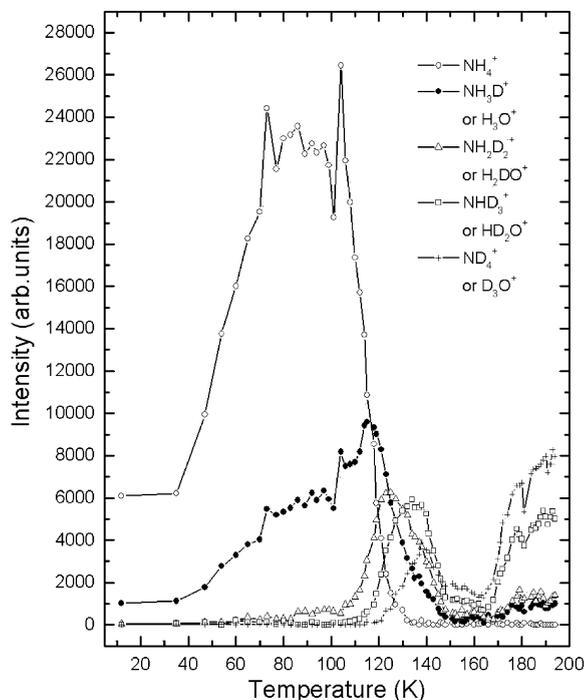


Fig. 3. Temperature evolutions of some secondary ion yields from the HCl and NH_3 molecules coadsorbed on the D_2O layer. The D_2O (50-ML) molecules were deposited at 100 K, and then the HCl (2-ML) and NH_3 (2-ML) molecules were coadsorbed after cooling down to 15 K.

$D^+(ND_2H)$ and $D^+(ND_3)$, become dominant above 120 K; $m/e = 19, 20, 21, 22$ can be assignable not only to the deuterated ammonium ion but also to the protonated heavy water ion, but the former should be dominant species by taking into account the proton affinities (see also Fig. 2(a) in which the yield of $H^+(H_2O)$ is much smaller than that of NH_4^+). With increasing temperatures, the relative yields of the deuterated ammonium ions increase but the absolute yields decay steeply in order of mass number as a result of the hydration. This result suggests that the hydration and the H/D exchange, respectively, occur drastically between the hydrophilic groups of the D_2O and NH_4Cl molecules above 100 and 120 K. These two processes are almost completed above 140 K. In order for the H/D exchange to occur in crystalline ice, proton transfer and molecular rotation are required [3,5,6,22]. However, this may not hold for the present case in which the mobile water molecules play a role. The deuteration rate of the detectable ammonium ion is determined by the amount of mobile D_2O molecules; i.e., the H/D exchange is correlated to how many NH_4Cl molecules are hydrated. The hydrated NH_4Cl molecules undergo almost complete H/D exchange as inferred from the dominance of the ND_4^+ ions sputtered from the ammonium chloride remaining on the surface above 170 K.

4. Conclusion

Temperature evolution curves of the sputtered secondary ions provide information about the hydrogen-bond reactions and hydration on the water–ice surface. The NH_4Cl molecules are produced from the HCl and NH_3 molecules above 50 K and remain above 180 K. The enhancement of the NH_4^+ ion occurs provided that the counter Cl^- ion is present in the nearest neighbors. Specifically, the yield of the NH_4^+ ion sputtered from the HCl and NH_3 molecules coadsorbed on the water–ice exhibits a broad peak at around 100 K. This result is interpreted by the competition between the reaction of the HCl and NH_3 molecules and the hydration of the resulting NH_4Cl molecules. The phase transition occurs from ASW to

crystalline ice at 140 K, where the water molecules become mobile remarkably and would hydrate the NH_4Cl molecules considerably. This presumption is supported by the fact that the H/D exchange is induced drastically above 120 K via the hydrogen-bond formation between the D_2O and NH_4Cl molecules. Furthermore, the fact that the NH_4^+ and Cl^- ions do not vanish completely suggests that the NH_4Cl molecules are hydrated on the surface, but not incorporated deep in the bulk.

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