

## Acidity of Hydrogen Chloride on Ice

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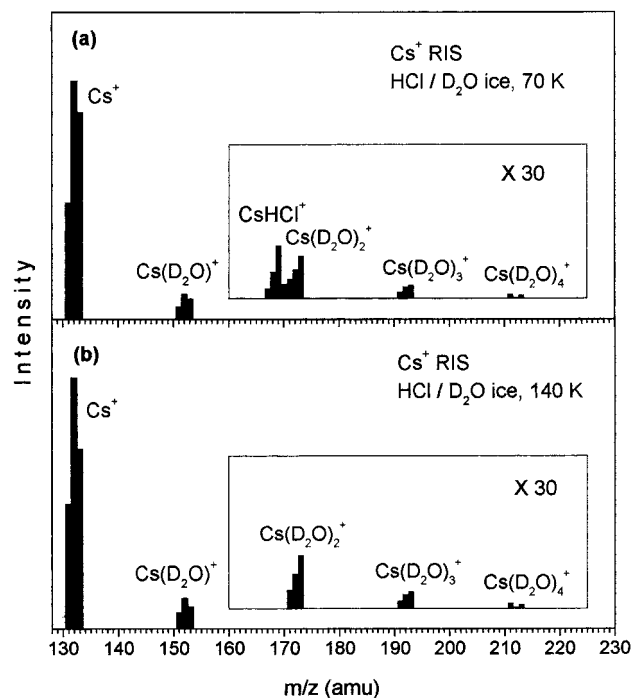
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Hydrogen chloride (HCl) dissociates completely in water to hydronium ( $\text{H}_3\text{O}^+$ ) and chloride ( $\text{Cl}^-$ ) ions. However, the extent of HCl ionization on cold ice remains unclear. We studied HCl ionization on the surface of ice by a  $\text{Cs}^+$  reactive ion scattering (RIS) method. Molecular and ionized states of HCl were unambiguously identified, and their relative portions were quantified at various ice temperatures.

There is increasing interest for studying reactions on ice. Such interest arises from the quest for knowledge about the catalytic role of polar stratospheric clouds (PSCs) in ozone depletion,<sup>1–3</sup> the formation of extraterrestrial organics on interstellar ice grains,<sup>4</sup> and the chemical and biological transformations taking place in the polar regions. Although our understanding of chemistry in aqueous solution has reached to molecular details, that of reaction on ice is still very limited. For instance, a simple process like ionization of HCl on a cold ice surface is not clearly understood. This reaction has recently emerged as a case-study subject,<sup>5–13</sup> owing to its fundamental nature and implications for the stratospheric ozone depletion. Though HCl is unreactive with most atmospheric gas-phase chemical species, PSC surfaces are known<sup>1–3</sup> to create a heterogeneous pathway that enhances ozone depletion rate. In understanding the PSC reaction mechanism, one critical unknown is the extent of HCl ionization. Extensive efforts have been made to probe the chemical nature of HCl on ice, including IR spectroscopy,<sup>5–8</sup> thermal desorption spectrometry (TDS),<sup>9</sup> secondary ion mass spectrometry (SIMS),<sup>10</sup> and theoretical calculations.<sup>11–13</sup> These studies indicate that HCl ionizes on ice,<sup>5–10</sup> but some evidence was also found for the presence of molecular HCl.<sup>5,8,9</sup> Discussion on these results has led to a consensus that at PSC temperatures (about 190 K) an ionized form of HCl will prevail.<sup>6</sup> Yet, quantitative evidence is lacking for the molecular and ionic states of HCl present under specific ice conditions. Herein, we applied an RIS method to this subject, and showed a clear picture for HCl ionization at the surface of ice.

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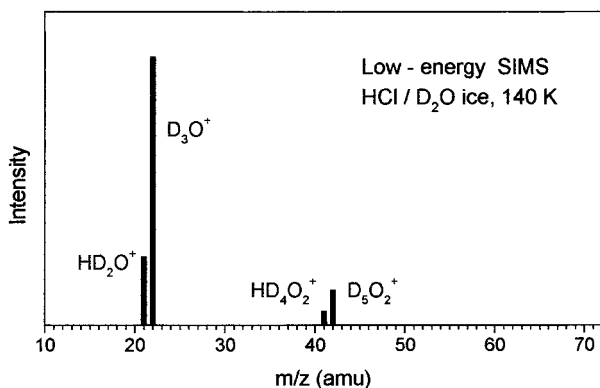
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**Figure 1.** Mass spectra of  $\text{Cs}^+$  RIS product ions obtained after exposing HCl on  $\text{D}_2\text{O}$  ice films for 0.3 L ( $1 \text{ L} = 1 \times 10^{-8} \text{ Torr} \times 30 \text{ s}$ ): (a) HCl exposure temperature of 70 K and (b) 140 K.  $\text{Cs}^+$  impact energy was 20 eV. The spectra are displayed in low mass resolution ( $m/\Delta m = 40$ ). Peak assignments were done through high-resolution experiment.

We prepared ice films by exposing  $\text{D}_2\text{O}$  water vapor of 10–20 L ( $1 \text{ L} = 1 \times 10^{-6} \text{ Torr s}$ ) on a Si(111) substrate in an ultrahigh vacuum chamber.<sup>14</sup> The substrate temperature was kept at 120 K during  $\text{D}_2\text{O}$  deposition to form a nonporous, amorphous ice phase.<sup>15–17</sup> After preparation of an ice film, the film temperature was fixed between 50 and 140 K, and HCl vapor was introduced. The HCl partial pressure was  $1 \times 10^{-8} \text{ Torr}$ , similar to a stratospheric condition. We identified neutral molecules present on ice by RIS and cationic species by low-energy SIMS. The analysis was done at the temperature of HCl deposition. In the RIS method, low-energy (10–30 eV)  $\text{Cs}^+$  ions are impinging onto a surface.  $\text{Cs}^+$  impact induces desorption of surface molecules, and the same  $\text{Cs}^+$  picks up desorbed molecules to form  $\text{Cs}^+$ -molecule ion clusters (reactive scattering process). Mass analysis of the ion clusters allows identification of the desorbed molecules. Experimental details for  $\text{Cs}^+$  RIS can be found elsewhere,<sup>14</sup> along with examples of identifying molecules chemisorbed on the surface.<sup>14,18,19</sup> Low-energy SIMS experiment was carried out with the same  $\text{Cs}^+$  beam, simultaneously with RIS measurement. The ion beam dose was low ( $< 10^{-11} \text{ ions cm}^{-2}$ ) enough to avoid unwanted side effects.<sup>20</sup>

Results of the RIS experiment on HCl-deposited ice films are shown by the mass spectra of Figure 1. In Figure 1a, a  $\text{D}_2\text{O}$ -ice film was exposed to HCl vapor at 70 K. A family of  $\text{Cs}(\text{D}_2\text{O})_n^+$

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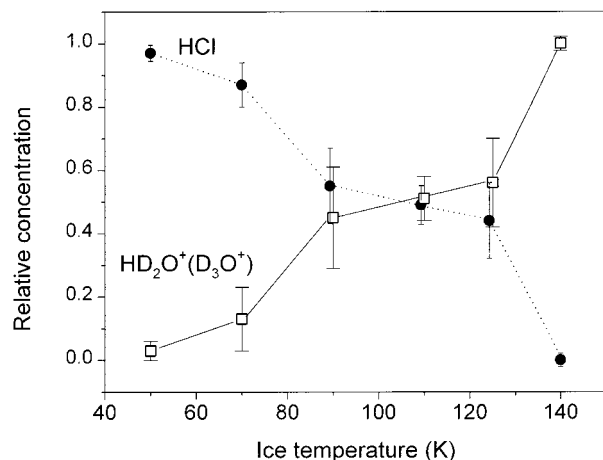


**Figure 2.** Low-energy SIMS spectrum from an HCl/D<sub>2</sub>O ice film prepared by HCl exposure of 0.3 L at 140 K. Cs<sup>+</sup> impact energy was 20 eV. The spectral mass resolution ( $m/\Delta m$ ) was 150.

( $n = 1-4$ ) peaks appears from Cs<sup>+</sup> RIS; Cs<sup>+</sup> picks up water molecules from the ice surface to form these clusters. These peaks appear from pure ice films as well, and the formation mechanism was previously described.<sup>21</sup> The other key product observed is CsHCl<sup>+</sup>, formed by pickup of molecular HCl present on ice. Because HCl molecules are picked off the surface instantaneously ( $<10^{-12}$  s) by scattered Cs<sup>+</sup> ions,<sup>14</sup> the CsHCl<sup>+</sup> signal is not affected by beam-induced local melting of ice. In Figure 1b, a D<sub>2</sub>O-ice film was exposed to HCl vapor at 140 K. Cs(D<sub>2</sub>O)<sub>*n*</sub><sup>+</sup> clusters also appear, but the CsHCl<sup>+</sup> peak is absent. This result indicates a transition from a molecular HCl state at 70 K to an ionic form at 140 K.

Figure 2 presents a low-energy SIMS spectrum taken from the same surface as in Figure 1b (140 K). The energy of the Cs<sup>+</sup> beam was 20 eV. Hydronium ions (HD<sub>2</sub>O<sup>+</sup> and D<sub>3</sub>O<sup>+</sup>) and their hydrated clusters (HD<sub>4</sub>O<sub>2</sub><sup>+</sup> and D<sub>5</sub>O<sub>2</sub><sup>+</sup>) were emitted from the surface. Pure ice films do not produce any of these ions in low-energy SIMS experiment.<sup>21</sup> Although ionization of water molecules can take place by keV ion impact,<sup>10,22</sup> the beam energy of 20 eV is too low to cause water ionization. Therefore, the hydronium ions clearly originate from the preexisting ions on the film, created by spontaneous HCl ionization on 140 K ice.<sup>23</sup> The intensity ratio of HD<sub>2</sub>O<sup>+</sup>/D<sub>3</sub>O<sup>+</sup> is about 0.25, revealing that H-D exchange has occurred significantly at this temperature. The intensity of HD<sub>2</sub>O<sup>+</sup> (D<sub>3</sub>O<sup>+</sup>) decreases as ice temperature decreases. At 50 K the HD<sub>2</sub>O<sup>+</sup> (D<sub>3</sub>O<sup>+</sup>) intensity falls to a background level, indicating a negligible concentration of hydronium ion and the almost absent ionization of HCl.

We examined the nature of the ionized and molecular states of HCl by varying Cs<sup>+</sup> impact energy. HD<sub>2</sub>O<sup>+</sup> (D<sub>3</sub>O<sup>+</sup>) ejection occurs at an apparent threshold energy of 10–12 eV and increases rapidly with energy. Note that this threshold energy is even higher than that of chemisorbed species, for example, H<sub>2</sub>O (7 eV), OH (8 eV), and SiO (5 eV) on Si surfaces.<sup>14,19</sup> On the other hand, the CsHCl<sup>+</sup> signal intensity is already strong at 10 eV and almost invariant with energy, indicating facile desorption of HCl. Such opposite trends indicate different adsorption structures for ionized



**Figure 3.** Relative concentrations of molecular HCl and hydronium ion present on HCl/ice film at various temperatures. HCl exposure was 0.3 L on D<sub>2</sub>O-ice film.

and molecular HCl. Molecular HCl must be weakly bonded to an ice surface, existing most likely on the top layer. On the other hand, the relatively high threshold for desorption of hydronium ions suggests that they are substantially hydrated, and their ejection requires the breakage of several hydrogen bonds of surrounding water molecules.<sup>24</sup>

We measured the CsHCl<sup>+</sup> and HD<sub>2</sub>O<sup>+</sup>(D<sub>3</sub>O<sup>+</sup>) signal intensities as a function of ice temperature over 50–140 K. Figure 3 summarizes these results, showing relative concentrations of molecular HCl and hydronium ion at various temperatures. The portion of ionized HCl increases from zero at 50 K to 1.0 at 140 K. The crossing point of the curves for molecular and ionized HCl occurs at about 110 K.

The results clarify several important issues for the nature of HCl on ice. Although HCl was considered to be ionizable on ice under present conditions,<sup>5-13</sup> the presence of molecular HCl was also indicated from IR spectra<sup>5,8</sup> and the H-D exchange rate measurement in HCl thermal desorption.<sup>9</sup> Our study reveals that both molecular and ionized HCl do exist, their relative portions varying with temperature as shown in Figure 3. Molecular HCl may exist on top of the ice surface, and it becomes ionized by migration and hydration of water molecules, consistent with theoretical predictions.<sup>11-13</sup> Figure 3 also confirms complete ionization of HCl under PSC conditions. In this context, the ionized HCl on PSCs will be able to make further reactions with HNO<sub>3</sub> and ClONO<sub>2</sub> go through ionic channels, acting as a promoter of ionic PSC reactions. In addition, this work demonstrates that the RIS and SIMS techniques can clearly resolve the chemical states of molecules present on ice. Such ability will have significant contribution to the study of ice chemistry.

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(23) The Si substrate did not catalyze HCl ionization according to the result obtained on a Si surface covered with submonolayer ice.

(24) To examine the subsurface diffusion effect of ionic species, we did control experiments on very thin (1–3 ice bilayers), crystalline ice films formed on Ru(100). In this case the Cs<sup>+</sup> beam probed the whole depth of the ice films, and we obtained the same ratio for HCl/H<sub>3</sub>O<sup>+</sup> as the one in Figure 3. This indicates that the diffusion of ionic species did not affect the signal intensities.