

Study of Frozen Molecular Surfaces by Cs⁺ Reactive Ion Scattering and Low-Energy Secondary Ion Mass Spectrometry

S.-C. Park^{*}, H. Kang^{**†}

^{}Department of Chemistry, Pohang University of Science and Technology, Pohang 790-784, South Korea*

*^{**}School of Chemistry, Seoul National University, Kwanak-ku, Seoul 151-742, South Korea*

(Received)

Abstract

We show that a combined technique of Cs⁺ reactive ion scattering (Cs⁺ RIS) and low-energy secondary ion mass spectrometry (LESIMS) provides a powerful means for probing molecular films and their surface reactions. Simple molecules, including HCl, NH₃, D₂O, and their mixtures, were deposited into a thin film of several monolayer thickness on Ru(001) at low temperature in vacuum, and the surface was characterized by Cs⁺ RIS and LESIMS. On pure films, D₂O, HCl, and NH₃ existed in the corresponding molecular states. When HCl and NH₃ were co-deposited, ammonium ion(NH₄⁺) was readily formed by proton transfer from HCl to NH₃. In the presence of water molecules, HCl ionized first to hydronium ion(H₃O⁺), which subsequently transferred proton to NH₃ to form NH₄⁺. The proton transfer, however, did not occur to a completion on ice, in contrast to the complete reaction in aqueous solutions.

1. Introduction

Recently, there is great interest for studying reactions occurring on frozen molecular surfaces. Such interest arises from the recent discovery that the surfaces of cold ice particles may play important roles in chemistry of the Earth's atmosphere [1] and in organic molecule formation in the interstellar space [2]. Current understanding of reactions on frozen water, however, is very limited, compared to that in aqueous media which has been pursued since the beginning of chemistry. For instance, a simple process like ionization of HCl on cold ice surface is not clearly understood to molecular details, despite recent active investigations using various experimental and theoretical approaches [3-7]. The molecular and ionized states of HCl on ice have recently been identified by the techniques of Cs⁺ reactive-ion scattering(RIS) and low-energy secondary-ion mass spectroscopy(LESIMS),

and their relative portions have been quantified [7]. These methods are sensitive in monitoring molecular species at surfaces [8,9]; the surface layer investigated is extremely thin, corresponding to depths of only one to two atomic layers in the energies employed (5-100 eV). In the present study, we examine the chemical states of HCl, NH₃, D₂O, and their mixtures frozen onto a cold substrate surface. Proton transfer from HCl to NH₃ in the frozen layers is examined in the presence and absence of water molecules.

The HCl-NH₃ system is a model case to study a proton transfer phenomenon and has long attracted attention. The reaction, NH₃ + HCl → NH₄⁺ + Cl⁻ in aqueous solutions is instantaneous with an equilibrium constant(K_{eq}) of 1.7 × 10⁹ at 298 K, and is one of the textbook examples of acid-base chemistry. The role of solvent molecules in the proton transfer of HCl to NH₃ has been a question of great academic importance. Early calculations [10] lend support to the ionic

[†] E-mail : surfion@snu.ac.kr

character of the interaction in the gas phase. The van der Waals complex, NH₃...HCl has been detected in a microwave spectroscopy experiment [11] and several computational investigations supported the existence of such a molecular system [12]. The situation, however, becomes drastically different once water molecules are added to this complex. While it is still a van der Waals molecule with a flat potential energy pathway for proton transfer with one water molecule, two and three molecules make it an ion pair [13]. Addition of water molecules increases the stability of the ion pair relative to the hydrogen-bonded system. Nevertheless, it is well known that particles of NH₄Cl are formed when dry vapors of the two gases are mixed, which has been explained in terms of the heterogeneous chemistry on liquid or solid particles preexisting in the system. In a recent calculation, Tao [14] showed that while proton transfer is not possible in a single NH₃-HCl system, in clusters containing two and four hetero-dimer units, complete proton transfer occurs by maximizing electrostatic interactions. This homogeneous nucleation may have implications to the processes in aerosols and clouds [15].

2. Experimental

In Cs⁺ RIS experiment, a Cs⁺ ion beam produced from a surface ionization source (Kimball Physics) was scattered from a sample being examined at the desired kinetic energy (5-100 eV). The Cs⁺ current density at the target was 1-5 nA/cm². The positive ions emitted from the sample surface were mass-analyzed with a quadrupole mass spectrometer (QMS) whose ionizer filament was turned off. The emitted ions are composed of reflected primaries, RIS products which are association products of Cs⁺ with the neutrals at the surface, and pre-existing ions sputtered by the low-energy Cs⁺ impact. Each ion mass spectrum consisted of at least 10 scans which took about 15 s to acquire. The substrate was a Ru single crystal with a(001) face, and its temperature could be varied in the

range of 90-1300 K on a variable-temperature sample stage. The beam incidence and the detector angles were both 67.5° with respect to the surface normal. The chamber has separate dosing facilities for gases. Frozen water films were prepared by exposing D₂O vapor on a Ru(001) substrate kept at 120 K. At this temperature, the ice layer will have a nonporous, amorphous structure [16]. Frozen NH₃ and HCl layers were made by condensing the corresponding gases at 100 K, unless specified otherwise. The chamber has a base vacuum of 3 × 10⁻¹⁰ Torr and is equipped with an Auger spectrometer to monitor surface cleanliness and surface composition. Detailed description for the UHV chamber can be found elsewhere [9]. The QMS for scattered ion analysis could also be operated in the residual gas analysis mode for thermal desorption spectrometry (TDS).

3. Results and Discussion

In Fig. 1, we show the positive ion mass spectra of the scattering experiment performed on the frozen (a) NH₃ and (b) HCl layers deposited on a Ru(001) surface. The Cs⁺ collision energy was 30 eV. Spectrum (a) shows a strong, elastic peak of Cs⁺ at m/z = 133 amu/charge, together with RIS peaks at m/z = 150 (CsNH₃⁺) and 167 amu/charge (CsN₂H₆⁺). The CsNH₃⁺ peak is formed by pickup of an NH₃ molecule from the surface, and CsN₂H₆⁺ by pickup of two NH₃ molecules. The RIS process leading to Cs⁺-molecule clusters at frozen molecular surfaces has been described in detail in the previous paper studying water-ice surfaces [17]. In spectrum (a), no secondary ions due to low-energy sputtering were seen in the region below 133 amu/charge. The appearance of the CsNH₃⁺ peak and the absence of low-energy sputtered ions indicate that ammonia exists as a neutral molecule on the frozen surface. Figure 1(b) presents an RIS spectrum from a frozen HCl layer. The RIS peak at m/z = 169 (CsHCl⁺) represents pickup of molecular HCl on the surface. The peak at m/z = 151

(CsH_2O^+) is due to residual water molecules inside the chamber that were deposited on the surface. In the low-mass region, secondary ion signals were observed at $m/z = 19$ (H_3O^+), indicating the presence of protonated water species on the surface produced by HCl ionization aided by deposited residual water species [7]. It may be noted that H_3O^+ ions are not emitted from a pure H_2O -ice surface by low-energy sputtering [17], excluding the possibility that the H_3O^+ signal is produced by impact-induced ionization of water molecules.

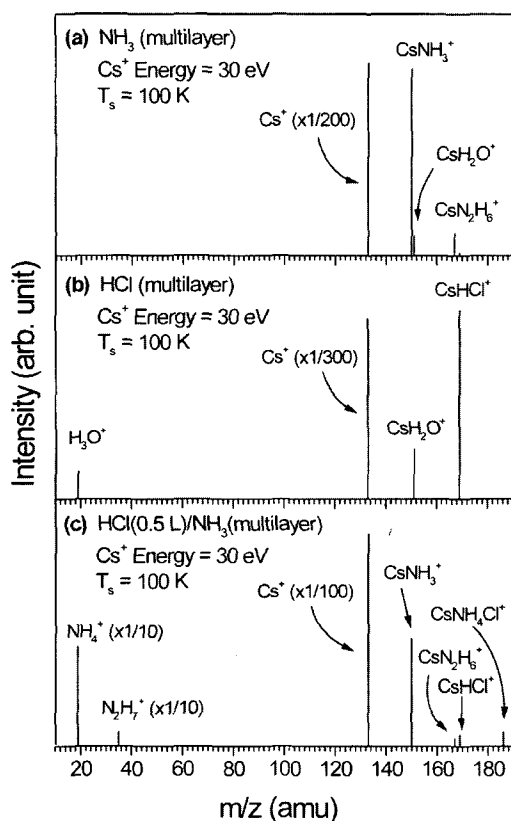


Fig. 1. Scattered ion mass spectra upon the collision of Cs^+ on pure NH_3 (a) and pure HCl multilayers (b), and NH_3 -multilayer exposed to 0.5 L HCl gas. Each layer was prepared by condensing the corresponding gases on a Ru(001) surface at 100 K through separate tube dosers. The multilayer formation was checked by TDS and Auger spectroscopy. The species observed are labeled. Cs^+ impact energy was 30 eV.

In Fig. 1(c), we exposed 0.5 L of HCl gas onto an NH_3 -predeposited surface. The NH_3 film was deliberately kept thick so that there is no effect caused by the interaction of HCl and the underlying Ru substrate. The first significant aspect to be noticed is the large NH_4^+ secondary ion intensity (note the reduced scale) which is quite unusual in such spectra. In addition, we also see the ammoniated ammonium ion, N_2H_7^+ . The RIS products observed are CsNH_3^+ , CsN_2H_6^+ , CsHCl^+ , and CsNH_4Cl^+ . The NH_4^+ species is solely due to the ejection of preformed ions as revealed by threshold measurements; while NH_4^+ had threshold energy of 17 eV on the HCl/ NH_3 surface, it was above 60 eV on a pure NH_3 surface. The strong NH_4^+ intensity, far greater than H_3O^+ in Fig. 1(b), reveals that NH_4^+ is formed by proton transfer from HCl to NH_3 on the frozen NH_3 layer at 100 K. Apparently, water is unnecessary to assist the proton transfer.

We examined the chemical states of HCl and NH_3 deposited on water-ice films. Figure 2 compares the RIS spectra obtained when (a) HCl and (b) NH_3 gases were deposited in a submonolayer coverage on D_2O -ice films at 140 K. As mentioned before, in both spectra, multilayers of D_2O were deposited to avoid any possible substrate effect in the measurement. In Fig. 2(a), the peak at $m/z = 153$ represents CsD_2O^+ , and its nearby peaks are H/D exchange products. CsHCl^+ peak is absent owing to complete ionization of HCl on ice at 140 K [7]. The secondary ion peaks include HD_2O^+ , HD_4O_2^+ , and their H/D-exchanged families. These spectral features confirm ionic dissociation of HCl reported previously [7]. In Fig. 1(b), where NH_3 is deposited on ice, no protonated species appear in the low-mass region. The RIS products include CsNH_3^+ , CsD_2O^+ , and $\text{Cs}(\text{NH}_3)_x(\text{D}_2\text{O})_y^+$ ($x, y = 1, 2$). The H/D exchange does not occur for these species. These results confirm that NH_3 remains unionized on ice.

We examined the reaction between NH_3 and HCl occurring on D_2O -ice. In Fig. 3(a), the surface was prepared by exposing a multilayer film of D_2O -ice to 0.5 L of HCl gas at 100 K, and then to 0.3 L of NH_3

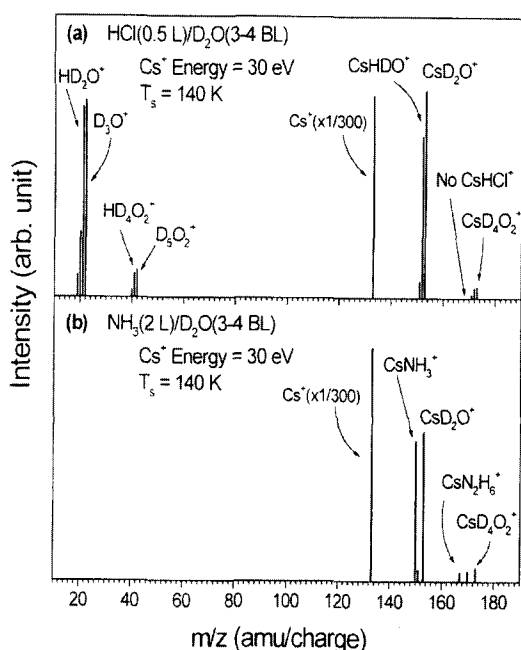
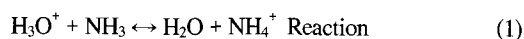


Fig. 2. Cs⁺ RIS and LESIMS result obtained on D₂O-ice surfaces exposed to 0.5 L of HCl (a) and 2 L of NH₃ (b) at 140 K. The D₂O-ice layer was 3-4 bilayers (BL) thick, prepared on a Ru (001) surface at 120 K through D₂O backfilling. The exposures for HCl and NH₃ were controlled to give approximately the same concentrations of these species on the surfaces.

gas. Secondary ion peaks include both ammonium and hydronium species. Apparently, hydronium ions are formed by ionic dissociation of HCl, as mentioned before, which then react with NH₃ to generate ammonium ions by proton transfer described in Reaction (1).



RIS peaks include CsD₂O⁺ and CsNH₃⁺, indicating the presence of D₂O and NH₃ molecules on the surface as well. Thus, all four species of Reaction (1) are present on the surface as identified by the spectrum. They all exhibit substantial intensities, indicating that Reaction (1) reaches only an intermediate

stage.

The reverse process of Reaction (1) was also investigated, i.e., the proton transfer from NH₄⁺ to D₂O. In Fig. 3(b), an NH₃ multilayer was prepared without water on Ru(001) and then exposed to HCl gas to produce NH₄⁺ ions, as was done in Fig. 1(c). D₂O gas was then exposed to this surface. The spectrum shows an intense NH₄⁺ peak, but an extremely small intensity for HD₂O⁺. CsNH₃⁺ and CsD₂O⁺ peaks are also seen. The CsNH₃⁺ peak must come from the underlying NH₃ layer, rather than from the reverse reaction. CsHDO⁺ must be due to H/D exchange facilitated by HCl ionization in the presence of D₂O. The strong NH₄⁺ signal and the almost absent HD₂O⁺ signal indicate that the reverse proton transfer does not take place to any significant degree.

The spectral features described above reveal the chemical states of NH₃, HCl, and D₂O on the frozen layers. NH₃ exists as a neutral molecule without protonation both in the presence and absence of water molecules [Figs. 1(a) and 2(b)]. This observation is well expected since NH₃ is a weak base in the aqueous phase as well. HCl is believed to be in a molecular form on a frozen HCl surface, and the small intensity of H₃O⁺ signal in Fig. 1(b) is attributed to residual water vapor. HCl efficiently ionizes on D₂O-ice at temperature above 100 K, with the ionization degree varying with ice temperature [7]. When NH₃ and HCl are co-deposited to a frozen film, proton transfer readily occurs from HCl to NH₃ to produce NH₄⁺ [Fig. 1(c)]. Water is unnecessary to assist the proton transfer. Neighboring NH₃ molecules can assist the reaction by clustering and maximizing HCl-NH₃ electrostatic interactions. The enhanced proton transfer by solvating NH₃ molecules was predicted by theoretical calculation [14]. Ammonium ions are also efficiently formed when NH₃ and HCl are co-deposited on a water-ice surface [Fig. 3(a)]. In this case, the ammonium species are formed in a large part also by the proton transfer from hydronium ion to ammonia (Reaction 1), the former created by HCl ionization on

water-ice. When NH_3 and HCl build up sufficiently high surface concentrations on the surface, the direct proton transfer between the two species may also become possible.

Figure 3 allows us not only to identify all the components of Reaction (1), but also to measure their relative concentrations at the surfaces. We can express the quotient (Q) of Reaction (1) by the peak intensities according to Eq. (1):

$$Q = \frac{[\text{H}_2\text{O}][\text{NH}_4^+]}{[\text{H}_3\text{O}^+][\text{NH}_3]} = \frac{I(\text{CsH}_2\text{O}^+) I(\text{NH}_4^+)}{I(\text{H}_3\text{O}^+) I(\text{CsNH}_3^+)} \quad (1)$$

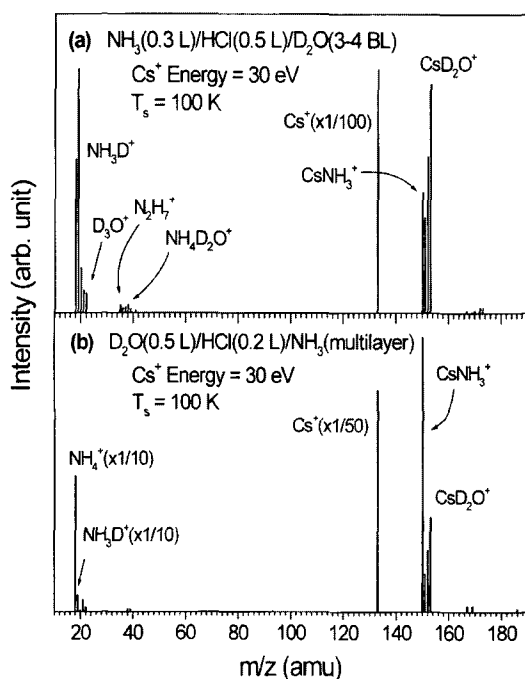


Fig. 3. Result of Cs^+ RIS and LESIMS measurements for the proton transfer reaction, $\text{H}_3\text{O}^+ + \text{NH}_3 \leftrightarrow \text{H}_2\text{O} + \text{NH}_4^+$. (a) Hydronium ions were generated on a D_2O -ice surface by 0.5 L exposure of HCl gas, which then were reacted with NH_3 gas for 0.3 L exposure. (b) Ammonium ions were first generated by exposing 0.2 L HCl to an NH_3 multilayer, and then 0.5 L of D_2O was added. The underlying multilayer films were grown at 120 K, and the acid-base titration experiments were carried out at 100 K.

Here $I(X^+)$ represents signal intensity of X^+ . Note that the relationship of Eq. (1) is quantitative. Although the detection sensitivities are different between the protonated HX^+ ions (detected as secondary ions) and the X neutrals (detected as Cs^+ RIS products), the different sensitivity factors will cancel out automatically in the expression of Eq. (1) because they appear both in the numerator and denominator. The Q value thus calculated is about 20 in the NH_3 - HCl titration experiment of Fig. 3(a).

The measured Q value is much smaller than the equilibrium constant of Reaction (1) in the aqueous phase (1.7×10^9). The gas-phase equilibrium constant for Reaction (1) is even larger (1×10^{30}), which is calculated from the gas-phase proton affinities, $\text{PA}(\text{H}_2\text{O}) = 166$ kcal/mol and $\text{PA}(\text{NH}_3) = 207$ kcal/mol. Since reaction on ice is characterized by partial solvation of reactants and products by water molecules, according to the theoretical works that investigated HCl ionization on ice [5], we may well expect that K_{eq} of the reaction on ice will be between the gas-phase and aqueous-phase values. The present observation, however, shows that this is not the case, indicating that Reaction (1) on ice does not reach a thermodynamic equilibrium but is in a metastable state.

4. Conclusions

We have demonstrated here that RIS provides a suitable means for examining the chemical states of frozen molecular surfaces and for quantitatively monitoring their relative concentrations. Neutral states of HCl and NH_3 were unambiguously identified from the RIS signals, and their ionized forms were detected by low-energy sputtering. An interesting feature of the experiment is that the acid-base reaction occurring right on the monolayer surface can be quantitatively monitored. The simple evaluation of the quotient for the H_3O^+ - NH_3 reaction on ice revealed that the reaction does not reach a true equilibrium but is in a metastable state. Such a study may be extendible to

the determination of the fundamental parameters appropriate for quantitative acid-base chemistry such as proton affinity and acidity scale of an ice surface, as well as for molecular formation processes in the interstellar space.

Acknowledgment

The work was supported by the BK 21 Program of the Ministry of Education, Republic of Korea.

References

- [1] M. J. Molina, T. L. Tso, L. T. Molina, and F. C. Y. Wang, *Science* **238**, 1253 (1987).
- [2] M. P. Bernstein, *et. al.*, *Science* **283**, 1135 (1999).
- [3] S. F. Banham, A. B. Horn, T. G. Koch, and J. R. Sodeau, *Faraday Discuss.* **100**, 321 (1995).
- [4] L. Delzeit, B. Rowland, and J. P. Devlin, *J. Phys. Chem.* **97**, 10312 (1993).
- [5] B. J. Gertner and J. T. Hynes, *Science* **271**, 1563 (1996).
- [6] C. J. Pursell, M. Zaidi, A. Thompson, C. Fraser-Gaston, and E. Vela, *J. Phys. Chem. A* **104**, 552 (2000).
- [7] H. Kang, T.-H. Shin, S.-C. Park, I. K. Kim, and S.-J. Han, *J. Am. Chem. Soc.* **122**, 9842 (2000).
- [8] R. G. Cooks, T. Ast, T. Pradeep, and V. H. Wsocki, *Acc. Chem. Res.* **27**, 316 (1994).
- [9] M. C. Yang, C. H. Hwang, and H. Kang, *J. Chem. Phys.* **107**, 2611 (1997); K. Y. Kim, T. H. Shin, S.-J. Han, and H. Kang, *Phys. Rev. Lett.* **82**, 1329 (1999).
- [10] R. S. Mulliken, *J. Phys. Chem.* **56**, 801 (1952); R. S. Mulliken, *Science* **157**, 13 (1967); E. Clementi, *J. Chem. Phys.* **46**, 3851 (1967).
- [11] E. J. Goodwin, N. W. Howard, and A. C. Legon, *Chem. Phys. Lett.* **131**, 319 (1986); N. W. Howard and A. C. Legon, *J. Chem. Phys.* **88**, 4694 (1988).
- [12] Z. Latajka, S. Sakai, K. Morokuma, and H. Ratajczak, *Chem. Phys. Lett.* **110**, 464 (1984); A. Brciz, A. Karpfen, H. Lischka, and P. Schuster, *Chem. Phys.* **89**, 337 (1984); P. G. Jasien and W. J. Stevens, *Chem. Phys. Lett.* **130**, 127 (1986); C. Chipot, D. Rinaldi, and J. -L. Rivail, *Chem. Phys. Lett.*, **191**, 287 (1992); G. B. Bacskay, *Mol. Phys.* **77**, 61 (1992); G. Corongiu, D. Estrin, G. Murgia, L. Paglieri, L. Pisani, G. Suzzi Valli, J. D. Watts, and E. Clementi, *Int. J. Quantum Chem.* **59**, 119 (1996).
- [13] M. Biczysko and Z. Latajka, *Chem. Phys. Lett.*, **313**, 366 (1999).
- [14] F.-M. Tao, *J. Chem. Phys.* **110**, 11121 (1999).
- [15] D. W. Oxtoby, *Acc. Chem. Res.* **31**, 91 (1998).
- [16] D. E. Brown, S. M. George, C. Huang, E. K. Wong, K. B. Rider, R. S. Smith, and B. D. Kay, *J. Phys. Chem.* **100**, 4988 (1996).
- [17] T. H. Shin, S.-J. Han, and H. Kang, *Nucl. Instrum. Methods in Phys. Res. B* **157**, 191 (1999).