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Reactive ion scattering from pure and mixed HCl, NH_3 and D_2O surfaces

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Abstract

We have sampled the various species present on the condensed molecular layers of HCl, NH_3, D_2O and their mixtures by Cs^+ reactive ion scattering (RIS) and low-energy sputtering. HCl and NH_3 exist in molecular states on pure molecular films, but the ammonium ion (NH_4^+) is readily formed when HCl and NH_3 are co-deposited, by proton transfer from HCl to NH_3. Water is unnecessary for the proton transfer, although enhances it. In the presence of water, HCl ionizes first to form the hydronium ion (H_3O^+), which subsequently transfers the proton to NH_3 to form NH_4^+. This work demonstrates the capability of RIS for probing chemical species on condensed molecular surfaces and monitoring their reactions. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

There is an increasing interest for studying reactions occurring on cold ice surfaces. Such interest arises from the recent discovery which suggests that the surfaces of cold ice particles may play important roles in the chemistry of the Earth's atmosphere [1] and formation of organic molecules in the interstellar space [2]. Current understanding of reactions on ice, 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 the 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 Cs^+ reactive ion scattering (RIS) technique, and their relative portions have been quantified [7]. RIS is a

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sensitive tool to monitor species at surfaces [8–10]; 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 this study, we use the RIS technique to examine the chemical states of HCl, NH_3, D_2O, and their mixtures frozen onto a cold substrate. Proton transfer of HCl to NH_3 in the frozen layers is examined in the presence and absence of water molecules.

The HCl–NH_3 system is a model case to study a proton transfer phenomenon and has long attracted attention. The reaction

$$NH_3 + HCl \rightarrow NH_4^+ + Cl^-$$

in aqueous solutions is instantaneous with an equilibrium constant (K_{eq}) of 1.7×10^9 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 NH_3 has been a question of great academic importance. Early calculations [11–13] lend support to the ionic character of the interaction in the gas phase. The Van der Waals complex, $NH_3 \cdots HCl$ has been detected in a microwave spectroscopy experiment [14,15], and several computational investigations supported the existence of such a molecular system [16–21]. 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 [22]. 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 NH_4Cl are formed when dry vapors of NH_3 and HCl 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 [23] showed that while proton transfer is not possible in a single NH_3–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 [24].

2. Experiment

In the 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/cm^2. The positive ions emitted from the sample surface were mass-analyzed by a quadrupole mass spectrometer (QMS) with its ionizer filament 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 an Ru single crystal with a (0 0 1) face, and its temperature could be varied in the range 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 D_2O vapor on an Ru(0 0 1) substrate kept at 120 K. At this temperature, the ice layer will have a non-porous, amorphous structure [25]. Frozen NH_3 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 [9,10]. The QMS for scattered ion analysis could also be operated in the residual gas analysis mode for thermal desorption spectrometry (TDS).

3. Results

In Fig. 1, we show the positive ion mass spectra of the scattering experiment performed on the frozen (a) NH_3 and (b) HCl layers deposited on a Ru(0 0 1) 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 $m/z = 150$ ($CsNH_3^+$) and 167 amu/charge

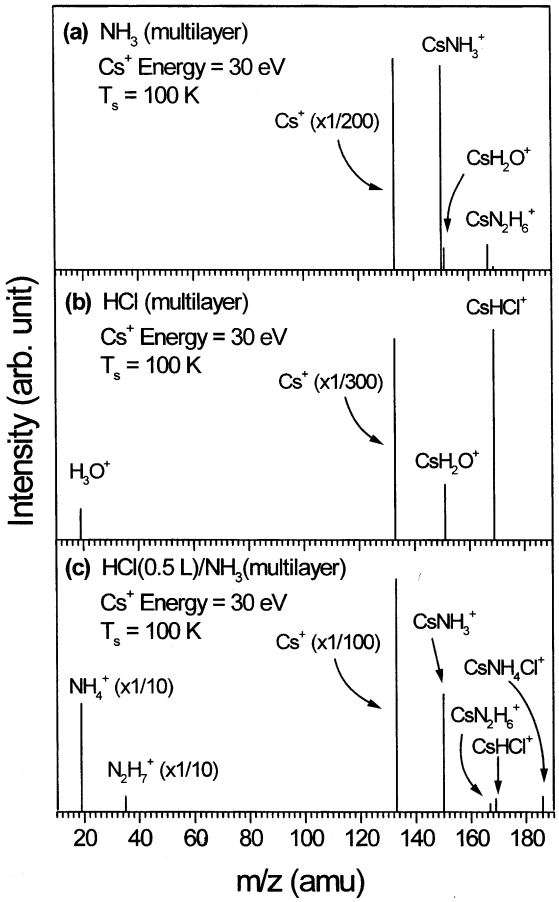

Fig. 1. Scattered ion mass spectra upon the collison of Cs^+ on pure NH_3 (a) and pure HCl multilayers (b), and NH_3-multilayer exposed to 0.5 L HCl gas (c). Each layer was prepared by condensing the corresponding gases on an Ru(0 0 1) surface at 100 K through separate tube dosers. The multilayer formation was checked by TDS and Auger spectroscopy. The species observed are labeled. Cs^+ impact energy was 30 eV.

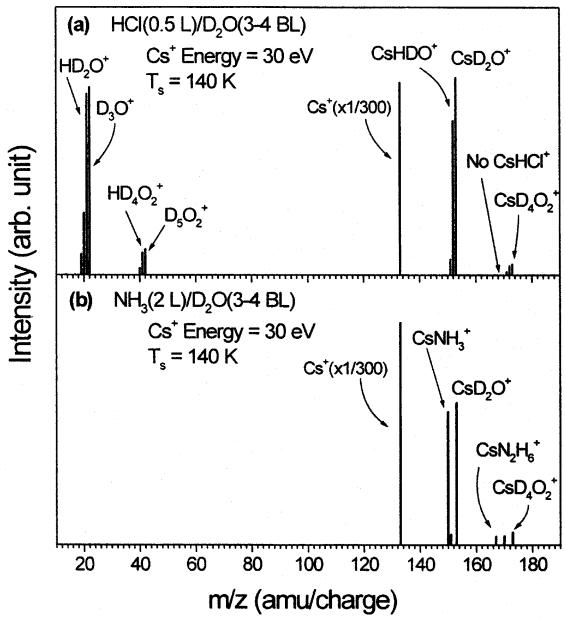

Fig. 2. RIS mass spectra obtained on D_2O–ice surface exposed to 0.5 L of HCl (a) and 2 L of NH_3 (b) at 140 K. The D_2O–ice layer was 3–4 bilayers (BL) thick, prepared on an Ru (0 0 1) surface at 120 K through D_2O backfilling. The exposures for HCl and NH_3 were controlled to give approximately the same concentrations of these species on the surfaces.

($CsN_2H_6^+$). The $CsNH_3^+$ peak is formed by pickup of an NH_3 molecule from the surface, and $CsN_2H_6^+$ by pickup of two NH_3 molecules. The RIS process leading to Cs^+-molecule clusters at condensed molecular surfaces has been described in detail in a previous paper on water–ice surfaces [26]. In spectrum (a) no secondary ions due to low-energy sputtering were seen in the region below 133 amu/charge. The appearance of the $CsNH_3^+$ peak and the absence of low-energy sputtered ions indicate that ammonia exists as a neutral molecule on the frozen surface. Fig. 2(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 $m/z = 161$ (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 [26], thus excluding the possibility that the H_3O^+ signal is produced by impact-induced ionization of water molecules.

In Fig. 1(c), we exposed 0.5 L of HCl 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. Fig. 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 due 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 $Cs(NH_3)_x(D_2O)_y^+$ $(x, y = 1, 2)$. The H/D exchange does not occur for these species. These results confirm that NH_3 remains unionized on ice.

Sticking probability of NH_3 and HCl gases at an ice surface is not well known at the temperatures employed in this study, and thus it is desirable to estimate the actual coverage of the species deposited on ice surfaces. We obtained NH_3-deposition curves by measuring $CsNH_3^+$ intensity as a function of NH_3 exposure on ice. Fig. 3 exemplifies the deposition curve, showing the variation of the intensity ratio of $CsNH_3^+$ to CsD_2O^+ against NH_3 exposure at 100 K. The plot is approximately

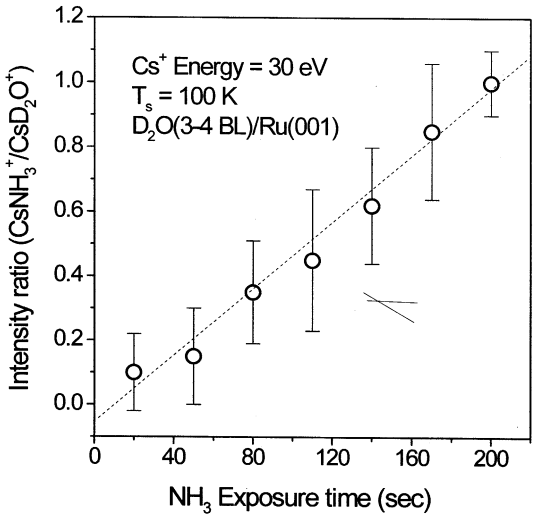

Fig. 3. Plot of the intensity ratio of $CsNH_3^+$ to CsD_2O^+ against NH_3 exposure. NH_3 gas had a partial pressure of 1×10^{-8} Torr during the exposure. Fresh surfaces were prepared for each data points to remove the Cs contamination effect from the beam.

linear for NH_3 exposure up to 200 s at a partial pressure of 1×10^{-8} Torr, indicating a constant sticking probability of NH_3 over this span. Since the sampling depth of RIS is 1–2 monolayers of ice at the present beam energy, the linearity of the curve also indicates that NH_3 has a fractional coverage on the surface.

We examined the reaction between NH_3 and HCl occurring on D_2O–ice. In Fig. 4(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 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 NH_3 to generate ammonium ions by proton transfer described in Reaction (1).

$$H_3O^+ + NH_3 \leftrightarrow H_2O + NH_4^+ \quad (1)$$

RIS peaks include CsD_2O^+ and $CsNH_3^+$, indicating the presence of D_2O and NH_3 molecules on the surface as well. Thus, all four species of Reaction

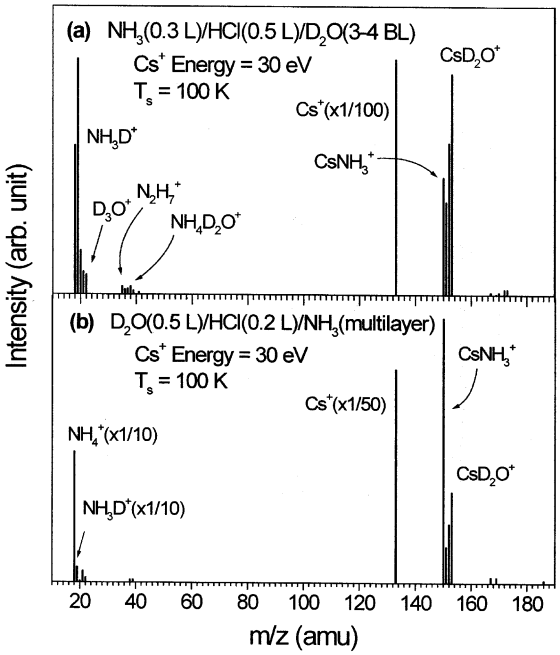

Fig. 4. Result of RIS measurement for the proton transfer reaction, $H_3O^+ + NH_3 \leftrightarrow H_2O + NH_4^+$. (a) Hydronium ions were generated on a D_2O–ice surface by 0.5 L exposure of HCl gas, which then were reacted with NH_3 gas for 0.3 L exposure. (b) Ammonium ions were first generated by 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.

(1) are present on the surface as identified by the spectrum. They all exhibit substantial intensities, indicating that Reaction (1) is incomplete.

The reverse process of Reaction (1) was also investigated, i.e., the proton transfer from NH_4^+ to D_2O. In Fig. 4(b), an NH_3 multilayer was prepared without water on Ru(0 0 1) and then exposed to HCl to produce NH_4^+ ions, as was done in Fig. 1(c). D_2O was then exposed to this surface. The spectrum shows an intense NH_4^+ peak, but an extremely small intensity for HD_2O^+. $CsNH_3^+$ and CsD_2O^+ peaks are also seen. The $CsNH_3^+$ peak must come from the underlying NH_3 layer, rather than from the reverse reaction. $CsHDO^+$ must be due to H/D exchange facilitated by HCl ionization in the presence of D_2O. The strong NH_4^+ signal and the almost absent HD_2O^+ signal indicate that the reverse proton transfer does not take place to any significant degree.

4. Discussion

The spectral features described in Section 3 reveal the chemical states of NH_3, HCl, and D_2O on the frozen layers. NH_3 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 NH_3 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 H_3O^+ signal in Fig. 1(b) is attributed to residual water vapor. HCl efficiently ionizes on D_2O–ice at temperature above 100 K, with the ionization degree varying with ice temperature [7]. When NH_3 and HCl are co-deposited to a frozen film, proton transfer reaction occurs from HCl to NH_3 to produce NH_4^+ (Fig. 1(c)). Since the NH_4^+ signal in Fig. 1(c) is far larger than the H_3O^+ signal in Fig. 1(b), it is clear the proton transfer readily occurs even in the absence of water molecules. Neighboring NH_3 molecules can assist the reaction by clustering and maximizing HCl–NH_3 electrostatic interactions. The enhanced proton transfer by solvating NH_3 molecules was predicted by theoretical calculation [23]. On a D_2O–ice surface (Fig. 4(a)), ammonium ions are also efficiently formed upon co-deposition of NH_3 and HCl. In this case, the ammonium species are created in a large part also by the proton transfer from hydronium ion to ammonia (Reaction (1)), the former generated by HCl ionization on D_2O–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.

An interesting species observed from the NH_3–HCl mixture (Fig. 1(c)) is the $CsNH_4Cl^+$ peak, which represents an association product of Cs^+ with NH_4Cl. NH_4Cl corresponds to either NH_4Cl salt or $NH_3 \cdots HCl$ Van der Waals complex. This ion is not seen or the intensity is very small as water is introduced at the surface (Fig. 4). In this respect, the $CsNH_4Cl^+$ signal in Fig. 1(c) may suggest the presence of $NH_3 \cdots HCl$ van der

Waals complex at the surface. The stability of the van der Waals complex will decrease in the presence of water, as expected from thermodynamics. It is also possible that NH_4Cl salt is formed on the frozen NH_3–HCl surface surrounded by ammonia molecules, as suggested by NH_4^+ peak, which then is pick up by Cs^+. Theoretical calculations [16–23], however, predict that a Van der Waals complex will be more stable when NH_4Cl unit exists as an isolated molecule.

Fig. 4 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 the following equation:

$$Q = [H_2O][NH_4^+]/[H_3O^+][NH_3] = I(CsH_2O^+)I(NH_4^+)/I(H_3O^+)I(CsNH_3^+) \quad (2)$$

Here $I(X^+)$ represents signal intensity of X^+. Note that the relationship of Eq. (2) 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. (2) because they appear both in the numerator and denominator. The Q value thus calculated is about 20 in the NH_3–HCl titration experimental of Fig. 4(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, $PA(H_2O) = 166$ kcal/mol and $PA(NH_3) = 207$ 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) at an ice surface does not reach a thermodynamic equilibrium but is in a metastable state.

5. Conclusion

We demonstrated here that RIS provides a suitable means for examining the chemical states of condensed molecular surfaces and for quantitatively monitoring their relative concentration. Neutral states of HCl and NH_3 were unambiguously identified from the RIS signals, and their ionized forms were detected by low-energy sputtering. Interesting feature of the experiment is that the acid–base reaction occurring right on the monolayer surface can be monitored. The simple evaluation of the quotient for the H_3O^+–NH_3 reaction on ice revealed that the reaction does not reach a thermodynamic equilibrium but is in a metastable state. Such a study may be extendible to the determination of the parameters appropriate for quantitative acid–base chemistry, such as proton affinity and acidity scale of ice surfaces. A complete study of the reaction aiming to deduce these quantities, including examination of the effect of ice temperature, morphology, reactant concentration, and solvation and subsurface diffusion of reactant species, is now underway.

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