

Unique Chemistry at Ice Surfaces: Incomplete Proton Transfer in the $\text{H}_3\text{O}^+ - \text{NH}_3$ System**

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Proton transfer is one of the central issues of chemistry and biology and is related to diverse phenomena, from acid–base neutralization to enzymatic reactions.^[1] A simple and prototypical system for studying this phenomenon is proton transfer between the hydronium ion and the ammonia molecule [Eq. (1)], which has long attracted attention.^[2–6]



The reaction proceeds instantaneously in the aqueous phase with an equilibrium constant K_{eq} of 1.7×10^9 at 298 K, and it is even more facile in the gas phase ($K_{\text{eq}} = 1 \times 10^{30}$).^[7] Molecular details of the reaction have been examined by theoretical calculations on model cluster systems.^[4–6] However, it is still not well understood how the reaction proceeds on the surface of ice, which is an important subject with relevance to the chemistry of atmospheric and interstellar ice particles, as well as proton transfer across ordered water structures in biological systems and at electrochemical interfaces. Studies of reactions on ice to date,^[8–15] focused on the ionization of HCl, indicate that chemical reactivity on ice is governed by the ability of surface water molecules to migrate and stabilize the ionized species by hydration. Recently, Pursell et al.,^[16] using transmission infrared spectroscopy, observed that the reaction of HCl and NH_3 on ice produces NH_4^+ at temperatures down to 80 K.

Here we report on proton transfer in the $\text{H}_3\text{O}^+ - \text{NH}_3$ pair prepared on ice, which we examined with the Cs^+ reactive ion scattering (RIS) method. The greatest advantage of the RIS technique is the quantitative monitoring of reactions occurring right on the monolayer surface.^[17, 18] Using this technique, we identified all the species involved in the reaction and measured their concentration variation along the reaction coordinate, which allowed us to quantify the proton transfer reaction and to understand how it is controlled by the ice surface. In this technique,^[17] a low-energy (10–100 eV) Cs^+ ion beam is scattered from a surface, and the scattered positive ions are analyzed by mass. The scattered ions are composed of reflected primaries, RIS products that are association products of Cs^+ with neutral species at the surface, and preexisting

ions ejected from the surface. It was shown^[18–20] that RIS produces ions with narrow internal energy distributions, so that even fragile molecular species can be detected.

The experiments were conducted in a reactive ion scattering chamber previously described in detail elsewhere.^[17] In the UHV chamber with a base vacuum of 3×10^{-10} Torr, Cs^+ ions produced from a surface ionization source are scattered from a sample surface at the desired collision energy. The Cs^+ current density at the sample was $2 - 3 \text{ nA cm}^{-2}$. The scattered ions were measured with a quadrupole mass spectrometer (QMS) with its ionizer switched off. Each spectrum consisted of at least ten scans, which took about 15 s to acquire. The beam incidence and the detector angles were both 67.5° with respect to the surface normal. The sample was a Ru(001) single crystal and was mounted on a variable-temperature (85–1500 K) stage. Ice films were grown on this surface by introducing D_2O vapor into the chamber at a pressure of 3×10^{-8} Torr and at a substrate temperature of 120 K, unless otherwise specified. At this temperature, the condensed layer is nonporous, amorphous ice.^[21] The vacuum gauge was calibrated for D_2O vapor from the absolute coverage of ice bilayer (BL) on Ru(001), checked by thermal desorption spectroscopy (TDS).^[22] To avoid substrate effects, ice films were prepared to the thickness of several bilayers. HCl and NH_3 gases were exposed through separate dosing facilities to the ice film maintained at the desired reaction temperature. Quadrupole MS was used to check the purity of the gases and to perform TDS measurements. An Auger spectrometer was used to determine the surface composition and cleanliness of the substrate.

Figure 1 compares the RIS mass spectra of D_2O -ice surfaces exposed to HCl and NH_3 . The spectrum in the presence of HCl (Figure 1a) is characterized by two kinds of peaks apart from the elastic peak of Cs^+ . 1) The peaks above m/z 133 due to reactive ion scattering, that is, pickup of surface molecules

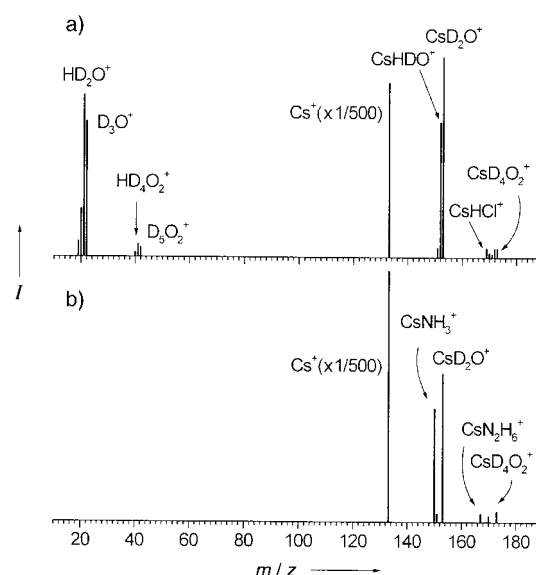


Figure 1. RIS mass spectra obtained on D_2O -ice surfaces exposed to HCl (a) and NH_3 (b) for 0.5 L ($1 \text{ L} = 1 \times 10^{-6}$ Torr) at 100 K. The D_2O layer was 3–4 BL (BL = bilayer) thick, prepared on a Ru(001) surface. The species observed are labeled. Cs^+ peak intensity was reduced by 1/500. Cs^+ impact energy was 35 eV.

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by incoming Cs^+ . The peak at m/z 153 (CsD_2O^+) is due to pickup of a water molecule, and that at m/z 169 (CsHCl^+) is due to pickup of an HCl molecule. The peak corresponding to the water dimer is also seen at m/z 173. 2) Peaks due to low-energy sputtering, corresponding to the ejection of preexisting ions at the surface. The ions detected were HD_2O^+ and its hydration cluster (HD_4O_2^+). The presence of HD_2O^+ confirms ionic dissociation of HCl.^[8–15] The RIS products and the sputtered ions exhibit characteristic isotope exchange. For convenience, however, we will denote hereafter the chemical species only by their representative isotopes. In Figure 1 b, the RIS mass spectrum from an NH_3 -exposed ice surface is shown, in which the only signals related to ammonia are CsNH_3^+ and CsN_2H_6^+ . NH_4^+ is not ejected by low-energy sputtering, and isotope exchange between NH_3 and D_2O is insignificant. These observations indicate that NH_3 exists as a neutral molecule at the surface and not as NH_4^+ .^[11, 23]

We prepared ice surfaces containing hydronium ions by HCl exposure and then added NH_3 to examine the proton transfer between H_3O^+ and NH_3 . The ratio of the proton donor to the acceptor was changed by varying the NH_3 concentration. Separate ice surfaces were prepared for each RIS measurement to avoid contamination by Cs^+ . Figure 2 shows the result of these H_3O^+ – NH_3 titration measurements at 100 K. Upon addition of a small amount of NH_3 (Figure 2 a), the spectrum immediately showed a peak due to NH_3D^+ , which indicates proton transfer from D_3O^+ to NH_3 to form an ammonium ion. The absence of a CsNH_3^+ peak at this stage indicates that all of the added NH_3 molecules have reacted. Hydronium ions still are present in large excess, as can be seen from the strong D_3O^+ peak. The hydration clusters of D_3O^+ and NH_3D^+ ions are also seen, along with their isotope-exchange species. Further NH_3 exposure (Figure 2 b) resulted in an increase in the NH_3D^+ peak relative to Figure 2 a and in a concomitant decrease in intensity of the D_3O^+ peak. Importantly, a CsNH_3^+ peak appears, which indicates that a substantial portion of NH_3 remains unconsumed on ice despite the coexistence of D_3O^+ . When NH_3 was added in large excess (Figure 2 c), ammonium ions were the dominant ionic species on the surface, and the concentration of hydronium ions was very low. A certain portion of HCl remains unionized on ice at 100 K, as indicated by the CsHCl^+ peak (see Figure 2 a), and so proton transfer is also possible from molecular HCl to NH_3 to produce NH_4^+ . However, the isotopic ratio $\text{NH}_3\text{D}^+/\text{NH}_4^+$ was greater than unity, and this indicates that hydronium ions (D_3O^+ , HD_2O^+ , etc.) are the major proton donors in the present case. Moreover, key features of Figure 2 were unchanged even when we increased the ice temperature to 140 K, at which temperature HCl is almost completely ionized.^[15]

We claimed before that the ions sputtered by low-energy Cs^+ in Figures 1 and 2 are preexisting ions on ice, but it might be argued that they are generated from neutral constituents of ice by impact-induced ionization, as is often the case in secondary ion mass spectrometry with beam energies in the keV region. To clarify this issue, we measured D_3O^+ and NH_4^+ signals as a function of Cs^+ impact energy (Figure 3). NH_4^+ (\blacksquare) and D_3O^+ (\circ) ions start to be emitted at energies of 17 and 19 eV (see also inset), respectively, when the surface was

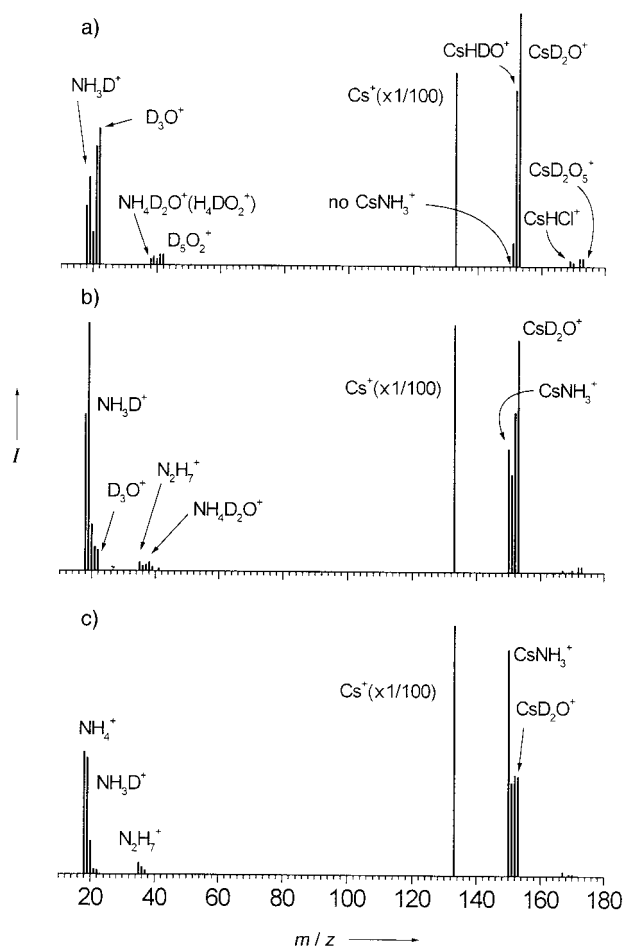


Figure 2. RIS mass spectra measured along the coordinate of the H_3O^+ – NH_3 reaction on ice. A D_2O (3–4 BL) surface was exposed first to 0.5 L of HCl to generate hydronium ions, and then to NH_3 at varying exposures: a) 0.02 L, b) 0.3 L, and c) 0.7 L. Sample temperature was 100 K. Cs^+ impact energy was 30 eV.

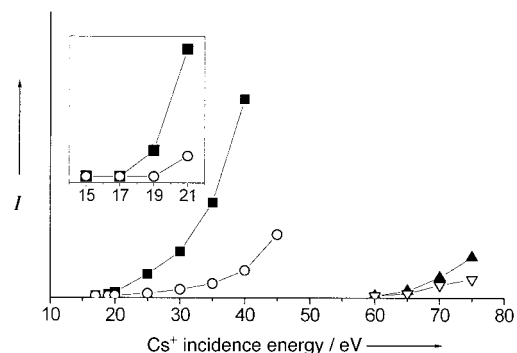


Figure 3. The intensity of hydronium and ammonium ion peaks as a function of collision energy for two types of surface. For details, see text. The beam incidence and the detector angles were both 67.5° with respect to the surface normal.

prepared by co-exposure to 0.3 L HCl and 0.15 L NH_3 on a D_2O -ice layer at 100 K. On frozen pure D_2O and NH_3 surfaces, respectively, D_3O^+ (\blacktriangle) and NH_4^+ (∇) appear only above 60 eV. Evidently, a large energy gap exists for ejecting the same ion from two different surfaces, one containing preformed, chemically generated ions, and the other having only neutral species. This threshold measurement verifies that

the D_3O^+ and NH_4^+ ions in Figures 1 and 2, ejected at energies of 35 eV or less, preexist on the surfaces. Solvated cluster ions ($D_3O_2^+$ and $N_2H_7^+$) are emitted several electron volts above the thresholds of the corresponding monomers, but still well below 60 eV. Therefore, the cluster ions must also be generated from preexisting species on ice.

Figure 4a presents the intensity variations for hydronium and ammonium ion signals obtained from the titration

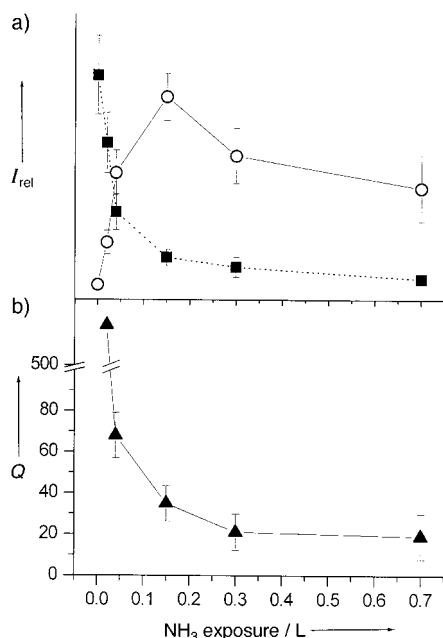


Figure 4. a) Variation of hydronium (■) and ammonium ion intensity (○) with NH_3 exposure. b) Variation of reaction quotient Q [Eq. (2)]. The experimental conditions were the same as in Figure 2.

experiment at 100 K. All isotopic intensities were added to these curves. The two curves cross at an NH_3 exposure of 0.05 L, which is considered to be the titration equivalent point. Note that the HCl and NH_3 exposures give only a relative measure for the amounts deposited on ice because the sticking probabilities of these species are uncertain. NH_4^+ peak intensity initially increases with NH_3 exposure due to proton transfer from H_3O^+ , but decreases again for NH_3 exposure greater than 0.15 L, possibly due to clustering or overlayer formation of excess NH_3 molecules around NH_4^+ , as indicated by the $N_2H_7^+$ peak in Figures 2b and 2c. Figure 4b presents the quotient Q of Equation (1), as defined by Equation (2). Here $I(X^+)$ represents the signal intensity of

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

X^+ . Again, the chemical formulas do not refer to specific isotopes. Note that the relationship of Equation (2) is quantitative, although the detection sensitivities differ between protonated ions (low-energy sputtering) and unprotonated neutral species (Cs^+ RIS). This is because the various sensitivity factors appear in both the numerator and denominator of Equation (2) and hence cancel out. The Q value decreases from near infinity at an initial NH_3 exposure to

reach a limiting value of ca. 20. Clearly, except at the very beginning of NH_3 titration, reaction (1) does not go to completion on ice. All the species involved in the reaction (H_3O^+ , NH_3 , H_2O , and NH_4^+) coexist on the surface in substantial populations. We examined the Q value as a function of ice temperature and found it to increase from 15 at 85 K to 50 at 140 K for an NH_3 exposure of 0.3 L.

The Q value measured in this study is much smaller than the equilibrium constant of reaction (1) in water (1.7×10^9) or in the gas phase (1×10^{30}). Since reaction on ice is characterized by partial solvation of reactants and products by water molecules according to theory,^[13, 14] we may well expect K_{eq} of the ice reaction to lie between the gas-phase and aqueous-phase values. However, this is not the case. The result indicates that reaction (1) does not reach a thermodynamic equilibrium on ice, but is instead controlled by kinetic factors.

The variation in Q in Figure 4b can be explained by kinetic constraints of the ice surface, imposed by the restricted motions of reactant and water molecules compared to the aqueous phase. First, Q approaches K_{eq} at a very small NH_3 exposure. This implies that NH_3 molecules have high enough mobility on the surface to undergo efficient reaction with H_3O^+ . The high mobility of NH_3 molecules is reasonable, because the similar H_2O molecules are mobile under these conditions.^[24] Second, Q drops rapidly as the NH_3 concentration on ice builds up. With a substantial population of NH_4^+ at this stage, surface NH_3 molecules can encounter not only H_3O^+ but also NH_4^+ to form ammoniated cluster ions like $N_2H_7^+$ (Figure 2). The ammoniated cluster ions are immobile on ice and act as kinetic traps for otherwise mobile NH_3 , that is, NH_3 molecules bound to NH_4^+ can not diffuse out and react with H_3O^+ . The immobility of NH_4^+ is supported by the recent finding of Cowin et al.^[25] that H_3O^+ is immobile on crystalline ice over a substantial temperature range (30–190 K). Therefore, the kinetic barrier to proton transfer on ice must result from the extremely low mobility of solvated ions, although unbound NH_3 and H_2O molecules may diffuse well under these conditions. Since Q increases only from 15 to 50 in the temperature range of 85–140 K, the NH_4^+ mobility appears not to increase drastically over this span, and this is also consistent with the result of H_3O^+ mobility measurements.^[25] The present ice films are considered to be amorphous films, on which the mobilities may be lower than on crystalline ice due to structural inhomogeneity.^[26] The difference between amorphous and crystalline surfaces, however, is not expected to affect the major conclusions of this study that the reaction quotient is lower than the equilibrium constant and that the kinetic barrier imposed by immobile solvated ions is responsible for these phenomena. It appears that the energy released by the neutralization reaction and inelastic collisions is efficiently removed by the sublayers, so that the observed processes are largely unaffected by extraneous factors.

This quantitative study showed that the proton transfer reaction between H_3O^+ and NH_3 on ice does not reach a true equilibrium. All species of the reaction (NH_3 , NH_4^+ , H_2O , and H_3O^+) coexist even at the titration equivalent point and represent metastable states trapped between kinetic barriers. The kinetic barriers result from the immobility of solvated ions, although neutral molecules may have high mobility. In

this respect, an ice surface allows diverse chemical species to be formed and kinetically stabilized, and this may play an important role in photochemical processes on interstellar or stratospheric ice particles.

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First Example of the $\mu_3\text{-}\eta^1,\eta^2,\eta^1\text{-C}_{60}$ Bonding Mode: Ligand-Induced Conversion of π to σ C_{60} -Metal Complexes**

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A consistent theme in the chemistry of exohedral metallofullerenes has been the pursuit of new bonding modes of C₆₀ with metal centers and their novel chemical reactivities. Continuous development in C₆₀-metal chemistry led to the synthesis of various π complexes with η^2 ,^[1] η^5 ,^[2] $\mu\text{-}\eta^2,\eta^2$,^[3] and $\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-C}_{60}$ ^[4] bonding modes. However, the chemistry of C₆₀ σ complexes has remained relatively unexplored, although such complexes are very important in selective functionalization of C₆₀. Examples of C₆₀-metal σ complexes have scarcely been reported, and none has been structurally characterized.^[5] We are interested in the conversion of existing C₆₀ bonding modes to new ones by modifying the coordination sphere of metal center(s) to which C₆₀ is coordinated. Our efforts resulted in the first example of reversible interconversion between $\mu\text{-}\eta^2,\eta^2$ - and $\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-C}_{60}$ on an Os₅C cluster framework by addition of 2e⁻ donor ligands such as carbon monoxide or benzyl isocyanide.^[3d] In contrast, a $\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-C}_{60}$ ligand on a triosmium cluster framework exhibits a drastically different behavior upon addition of benzyl isocyanide. It transforms into a new σ -type $\mu_3\text{-}\eta^1,\eta^2,\eta^1\text{-C}_{60}$ ligand with concomitant Os-Os bond cleavage, providing a new synthetic route to C₆₀-metal σ complexes. Here we report the first example of a novel ligand-induced conversion of π to σ C₆₀-metal complexes, as well as the first structural characterization of C₆₀-metal σ bonding.

A mixture of [Os₃(CO)₈(CNR)($\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-C}_{60}$)] (**1**) and an excess (30 equiv) of benzyl isocyanide in C₆H₅Cl was heated at 80 °C for 40 h. Removal of the volatile materials in vacuo, subsequent purification by a preparative TLC (SiO₂, CS₂), and recrystallization (CH₂Cl₂/*n*-C₆H₁₄) afforded two brown compounds **2a** and **2b** (Scheme 1). The two compounds were formulated as [Os₃(CO)₈(CNR)₂(C₆₀)] on the basis of micro-analytical data and molecular ion isotope multiplets at *m/z* 1750 (highest peak) in the positive-ion FAB mass spectra.

An X-ray crystallographic study revealed the structure of **2a** (Figure 1 a). The Os1-Os3 bond of the Os₃ triangle in **1** was ruptured on addition of an RNC ligand, which is coordinated

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