

Ionic dissociation of NaCl on frozen water

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Low-energy reactive ion scattering (RIS) experiments show that NaCl dissociates almost completely on condensed ice surfaces prepared on Ru(001) even at 100 K forming solvated ions. NaCl by itself does not dissociate on a Ru(001) substrate; however, submonolayer coverages of water sets-in dissociation. Na⁺ ions thus created are immobile such that they do not migrate across one water bilayer (BL) over several minutes. Accumulation of positive charge at the ice surface makes Na⁺ diffuse into the sublayers. © 2000 American Institute of Physics. [S0021-9606(00)51645-6]

The chemistry of sea salt aerosols is predicted to be important in the generation of active chlorine species both in the marine boundary layer and in the lower stratosphere.¹ Various laboratory and field experiments have shown that most of the predicted chemistry occurs at the surface of aerosols.² Mechanistic pathways involving ionic dissociation in the presence of water is the most important first step in the heterogeneous chemistry of these solid electrolytes.^{2,3} The role of ionic species may have a more general role, according to a recent study.⁴ Nevertheless, no investigation has been performed thus far to see whether ultrathin layers of NaCl does dissociate on water (or ice) surfaces at lower temperatures. In this communication, we present a low-energy reactive ion scattering (RIS) study to show that NaCl is almost completely dissociated even on a monolayer of frozen water down to 100 K. Although hydrated ions are observed, molecular NaCl does not exist in the hydrated form. The study supports the mechanistic conjecture thus far assumed in the heterogeneous chemistry and suggests that molecular NaCl may be impossible over water under atmospheric conditions, although the present experiments have been performed at colder temperatures.

Low-energy RIS has been shown to be a sensitive tool to monitor species at surfaces.⁵ The surface layer investigated is extremely thin, corresponding to the first atomic layer in the energies used, which is especially important in the chemistry of aerosols and clouds. The scattering can be performed with a versatile ion source generating atomic or molecular ions, or with one specific ion as in the present case. In the Cs⁺ RIS experiment, a low energy (3–100 eV) Cs⁺ ion beam is scattered from a surface and the scattered positive ions are mass-analyzed. The scattered ions are composed of reflected primaries, reaction products which are association products of Cs⁺ with neutrals at the surface, and pre-existing ions ejected from the surface. It has been shown that the RIS technique produces ions with low internal energy distribution so that even fragile species can be detected.⁶

The experiments were conducted in a reactive ion scattering chamber previously described in detail elsewhere.⁷ In the UHV chamber with a base vacuum of 3×10^{-10} Torr, Cs⁺ ions of desired kinetic energy produced from a surface ionization source (Kimball Physics) are scattered from a Ru(001) surface mounted on a variable-temperature sample stage. The Cs⁺ current density at the sample was 2–10 nA/cm², unless mentioned otherwise. The scattered ions were measured with a residual gas analyzer with its filament turned off. Each spectrum consisted of at least 10 scans which took about 15 s to acquire. The sample temperature can be varied in the range of 100–1300 K. The beam incidence and the detector angles were both 67.5° with respect to the surface normal. The chamber has gas dosing facilities and a thermal evaporation source for NaCl dosing. The deposition was done when the Ru crystal was biased at +10 V so that Na⁺, possibly formed by thermal ionization at the evaporation source, is not deposited. The chamber is equipped with an Auger spectrometer to monitor the composition and cleanliness of the substrate. The mass spectrometer for scattered ion analysis could also be operated in the residual gas analysis mode for thermal desorption experiments.

In Fig. 1 we show the scattered ion mass spectra upon the collision of Cs⁺ at various surfaces. Spectrum (a) corresponds to one bilayer (BL) of condensed water (D₂O) (Ref. 8) formed on multilayer NaCl over the Ru(001) substrate and the collision energy was 35 eV. The spectrum is characterized by three kinds of peaks. (1) The elastic scattering peak of Cs⁺; (2) the peaks above m/z 133, due to reactive scattering, i.e., association products of Cs⁺ with surface constituents, D₂O and NaCl; and (3) peaks due to low-energy sputtering, corresponding to the ejection of pre-existing ions on surface. In (2), the peak at m/z 153 is due to CsD₂O⁺ and that at m/z 193 is due to CsNaCl⁺. In the last category, two ions are detected, Na⁺ and NaD₂O⁺. The presence of Na⁺ and NaD₂O⁺ are due to the dissolution of NaCl and solvation of the ionic species. It will be shown later in Fig. 2 that the threshold collision energy for Na⁺ ejection is 10–15 eV (lab), which is below the collision energy required for dissociation into ions. Therefore, the ejected Na⁺ follows the dissociation of NaCl in a condensed water matrix. The NaD₂O⁺

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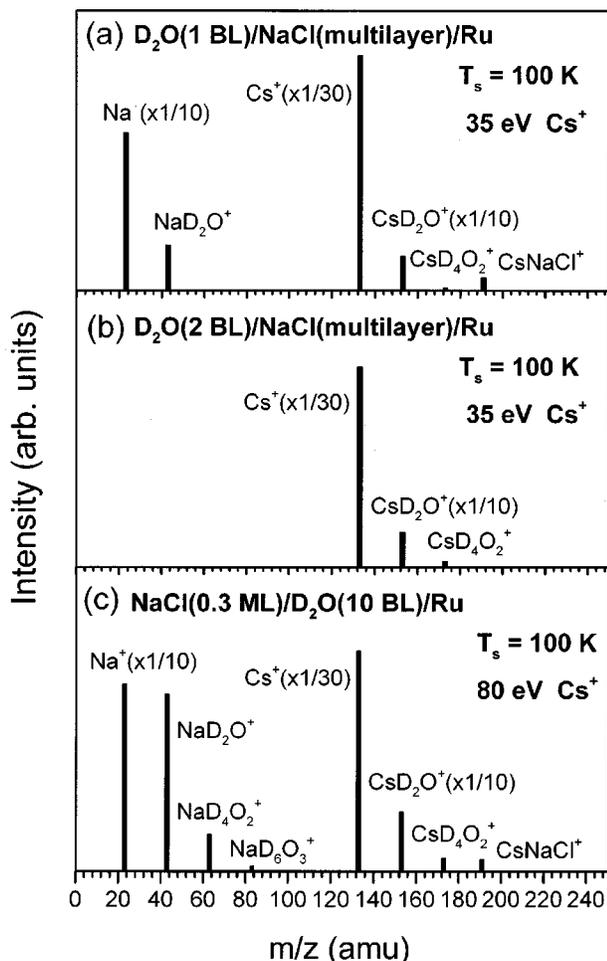


FIG. 1. (a) and (b) Scattered ion mass spectra obtained from a condensed D_2O surface predeposited with NaCl multilayer for D_2O exposures of 1 and 2 BL, respectively. Cs^+ collision energy was 35 eV. (c) Scattered ion spectrum from a 0.3 ML covered NaCl on a predeposited D_2O (10 BL) at a collision energy of 80 eV. Sample temperature was 100 K in all cases.

signal reflects Na^+ hydration by D_2O molecules on the surface. $CsNaCl^+$ signal intensity was much reduced as soon as the water overlayer was added even in a submonolayer coverage, including efficient NaCl ionization due to solvation.⁹ It is important to note that no hydrated NaCl species appear in the spectrum, supporting an earlier study¹⁰ that they do not exist. The experiment reveals that NaCl readily dissociates into ions in the presence of surface water molecules.

The high surface sensitivity of the present technique is evident from spectrum (b), which corresponds to an additional BL of condensed water on the surface. Note that none of the sputtered ions are present in the spectrum, nor the reaction product $CsNaCl^+$. The only ion seen other than Cs^+ is CsD_2O^+ . One BL of D_2O is adequate to stop all the signals due to $CsNaCl^+$, Na^+ , and NaD_2O^+ . Obviously, all the NaCl is covered with D_2O and the species below are not accessible to Cs^+ . The experiment demonstrates that diffusion of Na^+ or beam-induced mixing is insignificant. Thermal desorption experiment on this surface showed D_2O desorption at 190 K and NaCl desorption around 770 K. No desorption of NaD_2O^+ or hydrated forms of NaCl was observed.

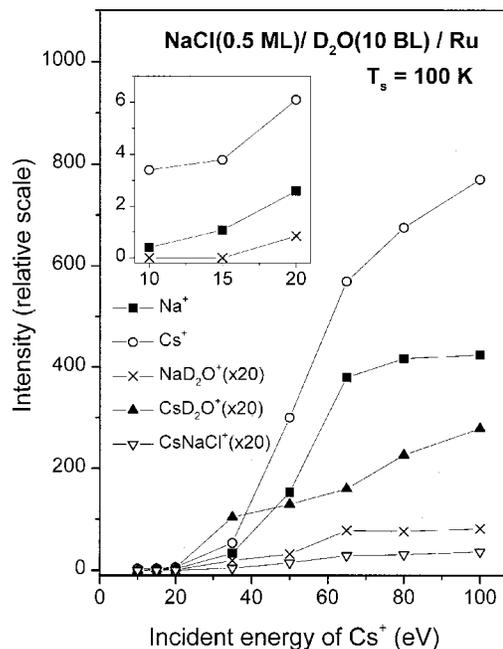


FIG. 2. Variation of ion intensities with collision energy. The sample corresponds to 0.5 ML NaCl deposited on 10 BL D_2O over Ru(001) at 100 K.

As the collision energy is increased, additional peaks appear. In Fig. 1(c) we show the scattered ion mass spectrum upon the impact of 80 eV Cs^+ on a 0.3 monolayer (ML) NaCl covered water surface (10 BL). Water clusters are picked up by Cs^+ , as earlier reported;¹¹ this is an efficient process at higher collision energies. However, no NaCl-water clusters are picked up by Cs^+ . Hydrated forms of Na^+ ions are ejected more efficiently.

Collision energy dependence of the scattered ion intensity was studied (Fig. 2). Care was taken not to deposit Cs^+ for long so that the surface is modified. When exposure exceeded 1 min, fresh surfaces were prepared. The data correspond to 0.5 ML of NaCl deposited on 10 BL D_2O . As mentioned before, the threshold energy of Na^+ is 10–15 eV, and that of NaD_2O^+ is 15–20 eV.¹² It is consistent with the knowledge that cluster ejection from a surface requires higher energy.¹³ The figure shows that Na^+ intensity nearly saturates at high energy. The threshold energies were also examined on differently prepared NaCl surfaces: (1) NaCl multilayer film on Ru(001), (2) NaCl multilayer film on ice, and (3) 0.5 ML water on multilayer NaCl. For cases (1) and (2), Na^+ was not detected up to a collision energy of 40 eV, indicating that Na^+-Cl^- heterolytic bond cleavage does not occur below this energy. On surface (3) the threshold energies were almost similar to the ones in Fig. 2. These experiments confirm that when NaCl and water molecules coexist on the surface, NaCl dissociates to ions and gives rise to the Na^+ signal at low collision energy.¹⁴

Mobility of the ions created by NaCl dissociation is of interest. In Fig. 3, we deposited NaCl on the surface of a D_2O film at 100 K and waited for 120 s before analysis. The Na^+ signal intensity decreased by only 10% over this period, indicating that Na^+ diffusion into sublayers is insignificant. Since Na^+ signal is produced from the top-layer, as demon-

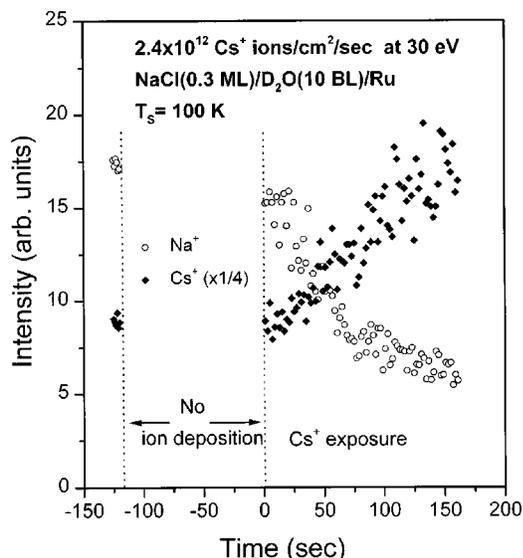


FIG. 3. Variation of Na^+ and Cs^+ signal as a function of Cs^+ exposure time. The data correspond to a sample as in Fig. 2 except for a small change in NaCl coverage. The Cs^+ beam energy was 30 eV and its current was 5.2 nA. The beam was tightly focused onto the surface to give a current density of 2.4×10^{12} ions/cm²/s as measured using a Faraday cup. The initial Na^+ concentration was checked by measuring the sputtered ion intensity 120 s before continuous ion irradiation. After a delay of 120 s during which Na^+ was free to diffuse into the sublayers, continuous ion irradiation was performed.

strated by Fig. 1(b), the result indicates that most of Na^+ species stay on top of the film without diffusing inwards.

The mobility of Na^+ can be affected by the presence of electric fields. In a continuing experiment (Fig. 3), we charged the surface by depositing Cs^+ ions at 30 eV and monitored Na^+ intensity in real-time. The Na^+ signal came down, obviously indicating a decrease of Na^+ concentration at the surface. This reduction is not due to a reduced NaCl quantity in the film, which could be verified after all D_2O was thermally desorbed. In an independent experiment, Cs^+ was deposited on a similarly prepared surface at 3.5 eV collision energy, below the sputtering threshold of Na^+ , in order to accumulate charge on the surface, without additional effects. The collision energy was subsequently increased to 30 eV for surface analysis, and it was found that the Na^+ intensity similarly decreased. This result again verified that reduction in Na^+ intensity in Fig. 3 is not due to the loss of NaCl or Na^+ by sputtering. Apparently, Cs^+ ions accumulated on the surface, force Na^+ species to migrate into the bulk. The voltage generated across the film by Cs^+ is estimated to be about 0.4 V/s at the beam current density of 2.4×10^{12} ions/cm²/s, if we assume that all incident Cs^+ ions remain on top of ice and the dielectric constant of ice film is 3.2.¹⁵ Under this condition, Na^+ intensity decreased by about 60%, which may represent the portion of the migrated species into sublayers. Na^+ apparently migrates faster than Cs^+ resulting in a Cs rich surface. The Cs^+ intensity increased because sputtered Cs^+ signals were added to the scattered Cs^+ flux. An alternate explanation for the observed facts would be collision induced melting of ice film causing burial of Na^+ . This appears to be less likely as seen from Fig. 1(b), where it was shown that an overlayer of water is

adequate to stop all Na^+ signals. If local melting and beam induced mixing was possible, Na^+ should have been observed.

This work showed that NaCl readily dissociates to Na^+ and Cl^- ions on a condensed water surface. The dissociation is almost complete even at temperatures as low as 100 K and regardless of whether NaCl is placed on top of frozen water or water molecules are added over the NaCl film. The chemistry of NaCl aerosols, therefore, should involve solvated ions in the Earth's atmosphere. In contrast to the efficient solvation by water molecules which necessitates their movement at least by a few molecular lengths, Na^+ hardly diffuses through frozen water, for instance, less than a distance of 1 BL of water in several minutes. The immobility of ions is supported by the recent soft-landing experiments of H_3O^+ ions on the ice surface.¹⁵ Charge accumulated on the surface produces strong electric fields which can drive Na^+ ions to migrate inwards. Such charge accumulation might make ionic adsorption more feasible at molecular interfaces contributing to the heterogeneous chemistry of atmospheric, biological, and electrochemical surfaces.

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- ⁸ In all experiments D_2O was introduced into the chamber at 3×10^{-8} Torr (the vacuum gauge was calibrated with water), and the film was grown at 120 K, unless mentioned otherwise. At this temperature, the condensed layer will be nonporous, amorphous ice [D. E. Brown, S. M. George, C. Huang *et al.*, *J. Phys. Chem.* **100**, 4988 (1996)]. The substrate temperature was then changed to the desired value for NaCl deposition.
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- ¹¹ T. H. Shin, S. J. Han, and H. Kang, *Nucl. Instrum. Methods Phys. Res. B* **157**, 191 (1999).
- ¹² If gas-phase association reaction between $\text{Na}^+(\text{g})$ and $\text{D}_2\text{O}(\text{g})$ was contributing significantly to NaD_2O^+ intensity, NaD_2O^+ could have been detected at 15 eV collision energy. Thus a majority of NaD_2O^+ intensity must be due to direct ejection from the surface.
- ¹³ *Sputtering by Particle Bombardment*, edited by R. Behrish (Springer-Verlag, Berlin, 1981).
- ¹⁴ It may be feasible that NaCl molecules dissociate to solvated Na^+ and Cl^- ions during beam-induced local melting of ice. However, it is much less feasible that thus-generated Na^+ ions are further ejected into vacuum during single ion impact at 15 eV. A similar experiment on H_3O^+ -containing ice surfaces showed that an energy of 15 eV is barely above the sputtering

threshold of pre-existing H_3O^+ on surface [H. Kang, T.-H. Shin, S.-C. Park *et al.*, *J. Am. Chem. Soc.* **122**, 9842 (2000)]. When only HCl molecules were present on ice without ionization, the H_3O^+ signal was not detected at 15 eV and its emission intensity was extremely small even at

several tens of eV, indicating that collision-induced HCl ionization was insignificant.

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