



Emission of ionic water clusters from water ice films bombarded by energetic projectiles

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Abstract

Emission of water clusters $M^{\pm}(H_2O)_n$, where M^{\pm} denotes positive alkali metal ions, Li^+ , Na^+ , Cs^+ or negative halogen ions, Cl^- , Br^- , I^- from ice films frozen on metal substrates bombarded by energetic particles was studied by a molecular dynamics (MD) technique and by ToF-secondary ion mass spectrometry (SIMS) experiments. In the experiment, different concentrations of the salts NaCl, NaBr, and NaI were dissolved in water before freezing. The influence of ion charge and concentration on ion signal was investigated. Due to the different solvation structures of cations and anions in water, cationic clusters were demonstrated to eject more effectively than anionic clusters in both the simulations and experiments. The dependence of the absolute ion yield on the salt concentration is discussed in terms of ion pairing and clustering in the original solution and during emission.

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1. Introduction

This study presents the initial step of the theoretical and experimental investigation of ion formation of ejected molecular species in energetic particle bombardment, or secondary ion mass spectrometry (SIMS) experiments. We consider attachment of ions already present in the sample to parent molecules. This mechanism appears to be a universal way of forming secondary ions, almost independent of the molecule

being investigated [1]. The parent molecules can associate with ions of both charges, such as positive ions Na^+ , K^+ , Cs^+ , or Ag^+ , and negative ions such as F^- , Cl^- , I^- , or Au^- . The ion concentration and the motion of ions in the collision cascade region determine the probability of the association. Thus, we focus on answering the questions of how readily these ions eject and attach to the parent molecules and how the probability of emission depends on ion charge and concentration.

As a realistic model system for theoretical and experimental studies, we have chosen water ice. It is a natural matrix in SIMS experiments on biological cells [2]. Pre-formed ions can be made by adding simple salts in which case the mass spectra show peaks corresponding to clusters such as $M^{\pm}(H_2O)_n$.

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The molecular dynamics (MD) method is used for studying the dynamics as it has been shown to be effective in describing the motion of the atoms in energetic particle bombardment experiments [3]. Interaction potentials for water and ions with water, an essential input to the MD approach, are well established. Specifically, in this initial work, we performed molecular dynamics calculations of emission of ionic water clusters $M^{\pm}(\text{H}_2\text{O})_n$, where M^{\pm} denotes the ions, Li^+ , Na^+ , Cs^+ , Cl^- , Br^- , and I^- , from an ice film, deposited on an Au(1 1 1) surface, under bombardment by 300 eV Ar atoms. To complement the MD simulations, ToF-SIMS experiments were performed with solutions of NaCl, NaBr, and NaI at different concentrations in ice. The solutions were frozen on a silver substrate and exposed to a beam of 20 keV C_{60}^+ ions.

Different solvation structures of cations and anions in water lead to larger absolute yields of $M^+(\text{H}_2\text{O})_n$ clusters as compared to $M^-(\text{H}_2\text{O})_n$ clusters. This finding is supported by the experimental data. An effect of salt concentration in the original sample on the experimental ion yield is discussed in terms of ion pairing and clustering.

2. MD simulations

The system investigated is a film of water ice adsorbed on a Au{1 1 1} substrate. The metal substrate assists in confining the projectile energy in the surface region and reflecting this energy toward the vacuum [4]. All the details of $\text{H}_2\text{O}-\text{H}_2\text{O}$, $\text{H}_2\text{O}-\text{Au}$ and $\text{Au}-\text{Au}$ interaction potentials including the potential parameters were described earlier [5]. The ions are represented by a point charge having a Lennard–Jones center on it [6]. Ion–ion interactions used in the calculations of the highly concentrated NaCl solution are described by the Huggins–Mayer potential for the non-Coulombic part of the interaction

$$U(r) = A \exp(-Br) - \frac{C}{r^6} \quad (1)$$

with parameters taken from [7].

The target includes an amorphous ice film at 77 K consisting of 1056 water molecules with one ion near the surface, representing infinite dilution. A total of eight Na^+ and eight Cl^- ions were

incorporated for the 1 M Na–Cl calculation. The water film was placed on the {1 1 1} surface of a nine-layer crystallite of 1980 Au atoms. No periodic boundary conditions were applied during the calculation of ion emission.

Since we are only interested in the formation of hydrated alkali and halide cluster ions, the water molecules are not allowed to dissociate during the collision cascade. We have used a low energy, 300 eV, for the incident primary Ar particle. Higher energies cause the larger emission, and the sample size should be increased correspondingly. The Ar particle is aimed along the surface normal within a rectangular area ($\sim 65 \text{ \AA}^2$) around the ion for a given set of trials. For each ion, 450 trajectories were performed. Each trajectory lasted over 7 ps. All emitted clusters, however, were traced over the next 250 ps to consider their unimolecular fragmentation.

The velocity Verlet algorithm along with the RATTLE [8] constraint technique were used to integrate the classical equations of motion as described previously [5,8]. These techniques allow us to keep fixed O–H bond lengths in water molecules as well as a fixed H–O–H bond angle.

The same protocol for heating/cooling the system as in [5] was used. To prepare the sample, 12 layers of a hexagonal ice were placed on the metal surface. The system was heated up to 300 K and equilibrated over 50 ps at this temperature. An ion was then placed on the top of the film. Following a 20 ps equilibration at 300 K, the system with the ion was cooled down to 77 K. After this procedure, the ion remained within one to two surface layers of the ice. For preparation of the 1 M solution of NaCl, eight ion pairs were added to the ice. The system was equilibrated over 100 ps at 300 K followed by a fast cooling down to 77 K. Periodic boundary conditions in the directions parallel to the surface were applied for all sample preparation procedures.

2.1. Experimental

Positive and negative SIMS spectra were acquired with a ToF-SIMS apparatus described in detail elsewhere [9]. The samples were prepared by spreading 2 μl of each salt solution onto silver substrates. The sample and substrate were quickly immersed into liquid nitrogen while affixed to a copper sample block.

The sample was transferred to the analysis chamber and loaded onto a sample stage sufficiently cooled with liquid nitrogen. Samples of NaI, NaCl, and NaBr were investigated at 0.0001, 0.01, and 1 M concentrations. The samples were mounted in the spectrometer at the same time and the data were taken on the same day. The analysis chamber has been modified slightly to accommodate the fitting of both a Ga^+ and C_{60}^+ ion source [10]. In principle, to compare with the calculations, the experiments should be performed with monoatomic projectiles. The Ga^+ source, however, causes considerable sample charging and reliable spectra could not be obtained. The use of an electron flood gun did not solve this problem. The C_{60}^+ beam does not produce as much surface charging as atomic projectiles because it seems to produce a sum of positive secondary ions approaching unity—in effect making a more electrically balanced surface after C_{60}^+ bombardment in comparison to the atomic projectile bombardment. Thus, the C_{60}^+ ion source was used to produce a focused 0.6 nA beam of 20 keV C_{60}^+ ions. A total time of 10–20 s of primary beam dc sputtering was needed to remove a water overlayer acquired from sample transfer, and to reveal a fresh salt solution surface for analysis. Charge compensation using low energy electrons was needed to see the signal for negative SIMS spectra. The reasons for the increased effectiveness of the C_{60}^+ source over the Ga^+ source are being investigated in our laboratory for a plethora of systems. For alkali and halide ions of low concentration, which were incorporated into the sample before the measurements, the increase of the signal is associated with an increase of the total emission yield. We will demonstrate below that the relative “ability” for cations and anions to escape the sample is due to the ion–water interaction. It justifies a qualitative comparison of the ion yields of cations versus anions, calculated with Ar atoms and measured with C_{60}^+ for low concentrations. For higher concentration, however, the picture is more complex. A polyatomic projectile causes a more intensive particle mixing around the impact site than a monoatomic particle does, stimulating recombination of the opposite charge ions and thereby decreasing the ion signal. Some general trends only can be discussed in any comparison of results of the calculations involving Ar projectiles with experiments performed using C_{60} clusters.

3. Results and discussion

3.1. Cation versus anion effect

The calculated total sputtering yields for ionic clusters (the ratio of the total ion yield to the number of trajectories) emitted from the infinite dilution samples are given in Table 1. The main observation is that cationic water clusters are emitted quite effectively relative to the emission of the anionic water clusters.

The trend of more effective emission of cations versus anions can be explained by the different solvation structure of positive and negative ions in water. Both MD and ab initio calculations of the ion solvation structure in water indicate that cations interact strongly with neighboring water molecules via cation–oxygen attraction, while the interaction of an anion with nearest water molecules is weaker [11,12]. This cation–water interaction results in re-orientation of water dipoles in the vicinity of the ion, thus disrupting the hydrogen bond network. Consequently, the local structure can be characterized as an almost pre-formed solvated ion with weak bonding to the remaining liquid. An anion in water does not introduce a large perturbation and the hydrogen bond network retains its structural identity near the negative ion [12]. The net effect is that even though the interaction of the anion with water is locally weaker than the cation with water, the interaction of the anion and its solvation structure with the whole medium is stronger than that for cations.

Our calculations [13] reveal that the interaction energy of the Na^+ –water complexes with the remaining system is weaker than that for the analogous Cl^- –water complexes, while the bare Na^+ is more

Table 1
Sputtering yields for ionic water clusters for 450 trajectories of 300 eV Ar atoms hitting the ice water film with one ion, frozen on a Au(1 1 1) substrate. The fractions include bare ions as well as water solvated ions.

Ions	Total sputtering yield
Li^+	0.22
Na^+	0.21
Cs^+	0.18
F^-	0.04
Cl^-	0.02
I^-	0.04

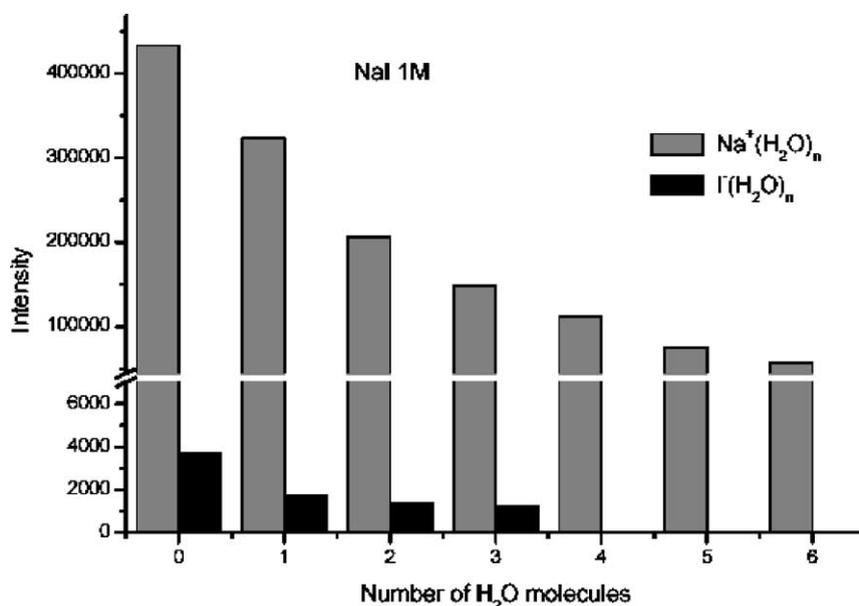


Fig. 1. Size distributions of clusters of $\text{Na}^+(\text{H}_2\text{O})_n$ and $\text{I}^-(\text{H}_2\text{O})_n$ sputtered from the 1 M solution of NaI by 20 keV C_{60}^+ projectiles.

strongly bonded to its nearest neighbors than the Cl^- ion. Desorption of a cation along with its first solvation shell requires, therefore, less energy than desorption of an anion with its solvation shell. The detailed analysis of sputtering trajectories shows that the water molecules initially adjacent to the cation mainly accompany it in the ejection event. We can also conclude that the contribution of bare cations to the ion yield at low concentrations should be smaller as compared to the contribution of cluster ions.

To check the theoretical findings, the ionic clusters $\text{Na}^+(\text{H}_2\text{O})_n$ and $\text{I}^-(\text{H}_2\text{O})_n$ were measured in ToF-SIMS experiments. Fig. 1 presents the yields of these clusters emitted from the 1 M solution of NaI. Emission of positive ions is noticeably more effective than emission of anion-containing clusters. This trend is consistent for all three salts (NaBr, NaCl, NaI), and for all concentrations.

3.2. Concentration effect

The salt concentration effect can be examined from the experimental data in Fig. 2, where the size distributions of $\text{Na}^+(\text{H}_2\text{O})_n$ clusters for NaCl, NaBr and NaI are displayed. Even though the concentrations differ by four orders of magnitude, the ion yield for the 1 M concentration is greater than that for 0.0001 M by

less than a factor of 10. Another observed feature is that the distributions for the 1 M solutions exhibit a relatively higher yield of the bare ions, i.e., Na^+ .

The deficiency in cluster ion intensities for the high concentration is presumably due to clustering of the ion pairs either in the initial sample or during the collision cascade. These ion clusters can and do have intervening water molecules, but are recognizable as localized entities. As the density in the collision cascade region decreases during the sputtering process, the amount of clustering of opposite charge ions increases because there is less water to stabilize individual solute ions. The number of surviving ions, therefore, is not reflective of the initial concentration.

The other trend shown in the data is the large number of bare ions present for the 1 M experiments. The presence of clusters of ions without full solvation shells for each ion in the initial solution could result in more bare ions being ejected or at least shifting the distribution towards smaller clusters. To check this picture, we performed sputtering calculations of a 1 M NaCl ice film. The results display the decrease in sputtering yield for $\text{Na}^+(\text{H}_2\text{O})_n$ species from 0.2 at the infinite dilution to 0.07 at 1 M solution. Even though the total ion yield decreases with concentration, the number of bare ions such as Na^+ increases by a factor of three over the infinitely dilute sample.

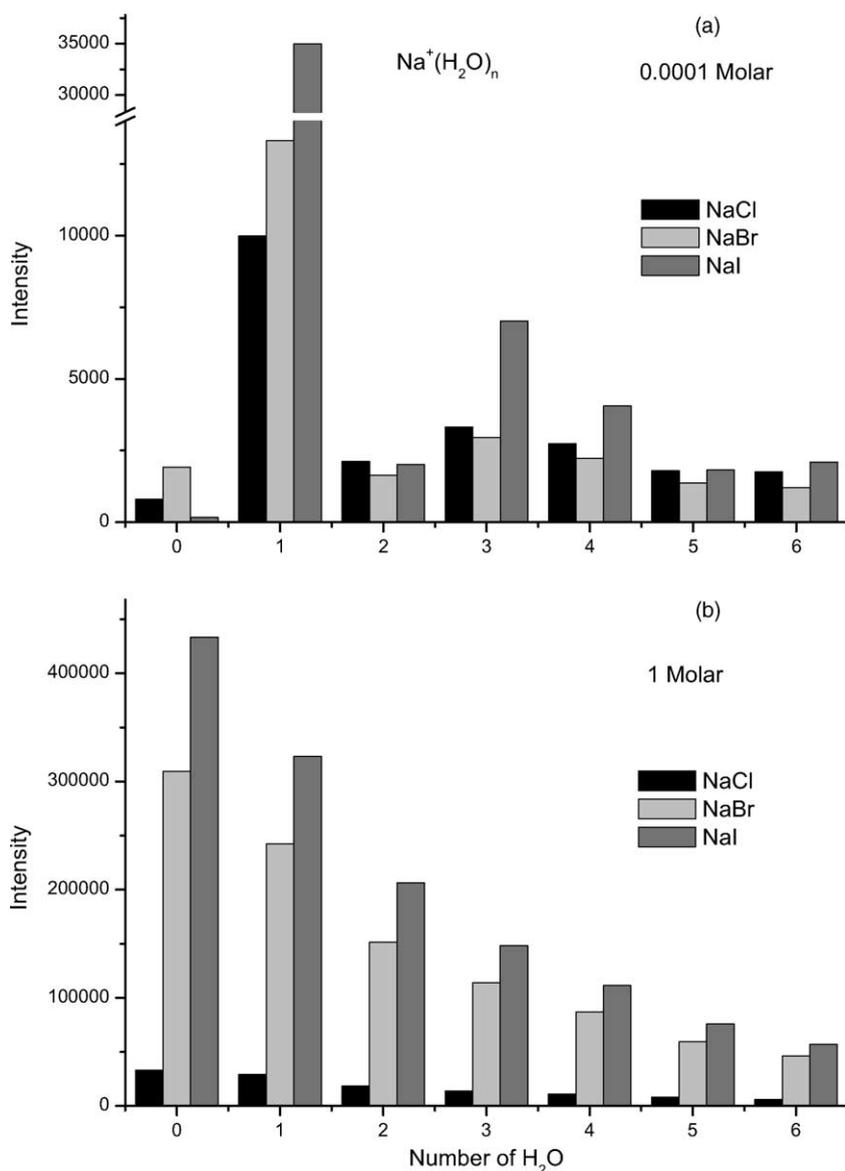


Fig. 2. Size distributions of $\text{Na}^+(\text{H}_2\text{O})_n$ clusters emitted from the solutions of NaCl, NaBr and NaI by 20 keV C_{60}^+ projectiles for two concentrations: (a) 0.0001 M; (b) 1 M.

4. Conclusions

Experiments on C_{60}^+ bombardment of frozen salt solutions support the theoretical finding that cation-water clusters are sputtered much more effectively than anion-water clusters. The experimental effect that signals are not linear with concentration can be qualitatively explained using MD calculations for a 1 M

solution of NaCl. Ion recombination, stemming from the collision cascade, limits the ion yield. Complexes of like ions, such as Na^+-Na^+ , which can exist in water, become unstable during the emission. As a result, bare ions can more readily be emitted from these environments.

As a next step in our project, we plan to investigate the emission of $\text{H}^+(\text{H}_2\text{O})_n$ and $\text{OH}^-(\text{H}_2\text{O})_n$ ions.

Hydronium and hydroxyl ions can form in the process of collisional dissociation of water molecules. A corresponding water model should be included in the simulations to consider this process. A semiclassical approach for proton transport, developed in [14], will be used to describe proton motion.

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