# Emission of Water Clusters from Ice Films

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*Abstract*— **This study presents the initial step of the theoretical 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.  Emission of water clusters $M(H_2O)n$ , where M denotes positive alkali metal ion, $Na^+$ from ice films frozen on metal substrates bombarded by energetic particles was studied by a molecular dynamics (MD) technique. The influence of ion charge and concentration on ion signal was investigated. Due to the different salvation structures of cations and anions in water, cationic clusters were demonstrated to eject more effectively than anionic clusters in the simulations. 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.**

*Keywords—computer simulation; klaster; sputtering;*

## I. INTRODUCTION

Secondary ion mass spectrometry (SIMS) is a wonderful technique for providing mass spectrometric information of molecules on surfaces [1]. Theoretical studies of the keV bombardment of organic films on metallic surfaces have contributed to our understanding of the mechanisms governing these processes. Many experiments of keV bombardment, however, are performed both the thick and thin targets [2].

"Water clusters", groups of water molecules held together by hydrogen bonds, have been the subject one of a number of intense experimental and theoretical investigations because of their importance in understanding cloud and ice formation, solution chemistry, and a large number of biochemical processes[3,4]. The recent observation of isolated charged water clusters have focused new attention on this fundamental process[5].

The sputtering from water film at 30-140K by $H^+$ and $Ne^+$ ions of 0.5-6.0 keV was studied experimentally[6]. The sputtering of water molecules was found to be temperature-independent over the whole temperature range. Neon ions deposit their energy in the ice by nuclear collisions, while for protons the energy deposition mechanism shifts gradually from predominantly nuclear collisions to predominantly electronic processes from 0.5 to 6.0 keV. The existing theory of nuclear sputtering predicts very well the yield of ejected water molecules and the experimental results in the region of electronic processes agree well with the experimental results.

In this paper, we present molecular dynamics (MD) simulations aimed at obtaining such a microscopic picture and mass spectrum of sputtering particles. Because of the importance of solvent $H_2O$ in many of the experiments, we have chosen it as our system. Water is also attractive as a system because of the extensive literature available on its physical properties. The interaction potentials available for MD simulations of $H_2O$ are sufficiently reliable such that a quantitative analysis of the simulation results can be directly related to the parameters of water. From the variety of substrate materials used in different experiments, we have chosen to perform our simulations using Au. This substance is chosen to match preliminary experiments with the selective killing of cells by inserted Au nanoparticles and because of the availability of good interaction potentials for gold.

We believe that the model presented here provides the basis for understanding of the molecular-level processes leading to the sputtering of a ionic $H_2O$ film from metallic substrate.

## II. COMPUTATIONAL METHOD

The MD approach involves integrating the classical equations of motion for all the particles in the solid [7]. The results of the simulation provide the positions and

velocities of all the atoms in the system as a function of time. From the final velocities, measurable quantities such as energy, angular distributions and mass spectrum can be calculated. From the time development of the atomic positions, a microscopic picture of the important motions can be visualized. In addition, the microscopic mechanisms can be identified with specific quantities that can be measured. The MD approach needs as input a force field or interaction potential among the atoms. A great advance in the past decade has been the development of many-body potentials for describing extended systems [8].

Below we give our choices for the interaction potentials for the $H_2O$-$H_2O$, Au-Au, and Au-$H_2O$ components of the system. The interaction potential employed to describe the $H_2O$-$H_2O$ interaction is the simple-point-charge (SPC) water potential developed by Berendsen et al.[9]. This potential has been used extensively to study the properties of $H_2O$ as a solid[10,11]. It has been shown that the SPC potential is able to reproduce many of the properties of bulk $H_2O$ [12]. In the SPC model, the molecular interaction potential $U_{inter}$ consists of an electrostatic component $U_{electrostatic}$ describing the charge-charge interaction between pairs of atoms in the two molecules. In order to describe the dispersion and repulsive interactions between the two oxygen sites, a Lennard- Jones function $U_{LJ}$ is included. The total interaction potential between molecules $i$ and $j$ is given as:

$$U_{inter}=U_{LJ}+U_{electrostatic}=$$

$$4\in\left[\left(\frac{\sigma}{r_{ij}}\right)^{12}-\left(\frac{\sigma}{r_{ij}}\right)^{6}\right]+\sum_{i=1}^{3}\sum_{k=1}^{3}\frac{q_{ik}q_{jl}}{4\pi r_{kl}}$$

where $r_{ij}$ is the distance between oxygen atoms and the summation runs over the partial charges $k$ and $l$ of the molecules. All parameters $q_{oxygen=}$ -0.82, $q_{hydrogen}$ = +0.41e, $r_{off}$ =0.85 nm, $\sigma$ = 0.3166 nm, $\in$ 6.7384 x 10$^{-3}$ eV.

The Au-Au interactions are represented by the MD/Monte Carlo corrected effective medium (MD/MC-CEM) potential function for fcc metals[13]. For metal-water systems has been developed a potential by Spohr[14]. The Spohr potential consist a Morse function combined with a corrugation term defining various surface sites for the oxygen-surface interaction and a repulsive term for the hydrogen – surface interaction. For our calculation we used modified Spohr function. Because we need the metal atoms to move and interact the water molecules, we have modified the Spohr function so that the interactions are pair wise additive between the O and H atoms in the $H_2O$ molecule and the metal atoms.

At the system a face centred cubic crystallite composed of 1980 Au atoms arranged in 9 layers of 220 atoms each is used in all of the simulation. The periodic boundary condition has been used. Initial water films are constructed based on a hexagonal arrangement of O atoms as in the Ih ice structure. The

molecules in the first layer, just above the Au(111) surface, are oriented so that the angles between the surface normal and both OH bonds are about 109$^0$ (Fig.1.). The $H_2O$ molecules in the second layer are arranged as if each molecule has one H atom oriented to form a hydrogen bond with the O atom in the first layer and one H atom oriented to form a hydrogen bond with the O atom in the second layer. The water layer molecules in subsequent pairs of layers repeat the orientation patterns of those in the first and second layers.

Since we are only interested in the formation of cluster ion, the water molecules are not allowed to dissociate during the collision cascade. To make this approximation reasonable, we have used a low energy, 700 eV, for the incident primary Ar particle. The Ar particle is aimed along the surface normal within a rectangular area (~ 65Å$^2$ ) around the ion for a given set of trials. For each ion, 450 trajectories were performed. Each trajectory lasted over 7 ps.

The velocity Verlet algorithm along with the RATTLE constraint technique[15]. These techniques allow us to keep fixed O-H bond lengths in water molecules as well as a fixed H-O-H bond angle.
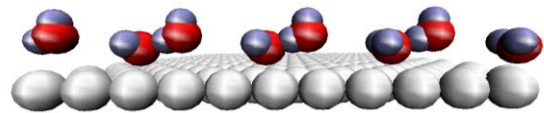


Figure.1.The structure of water molecules on the Au(111) surface. The water molecules in subsequent pairs of layers repeat the orientation patterns of those in the first and second layers.

## III. RESULT AND DISCUSSIONS

In this section we will present the computational results sputtering of ionic water clusters from water film covered on Au(111) surface. The Na$^+$ -water complexes with the remaining system is weaker than that for the Cl$^-$ -water complexes, while the bare Na$^+$ is more strongly bonded to the solution than the Cl$^-$ ion. In this paper we will discuss only sputtering of positive ionic water clusters. The sputtering of negative ionic clusters not discussed in this paper.

This ion-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 almost be characterized as a pre-formed ion with the weak bonding to the remaining liquid forms.

When on the surface are present atoms as Na, K and Li, they form with analyte by molecules quasi-ions. Imaging of MALDI samples shows that the position of analyte molecules and alkali ions highly correlated. The information of alkali attached ions is additionally dependent on the chemical structure of anylite molecule. We have chosen 4 layers of water

with atom Na. This system equilibrated 20 ps. The first case when atom Na is on the surface, and the second one between layers 2-3.

On the Fig.2. illustrates two case of position of $Na^+$ ions why located in the structure. In the first case (Fig.2a), the $Na^+$ ions located on top of water crystal. The $Na^+$ ions formed bond with water molecules. And the second case(Fig 2b), when $Na^+$ formed bonds between first and second layers of ice crystal. The $Na^+$ ions formed bonds with water molecules in the both case.
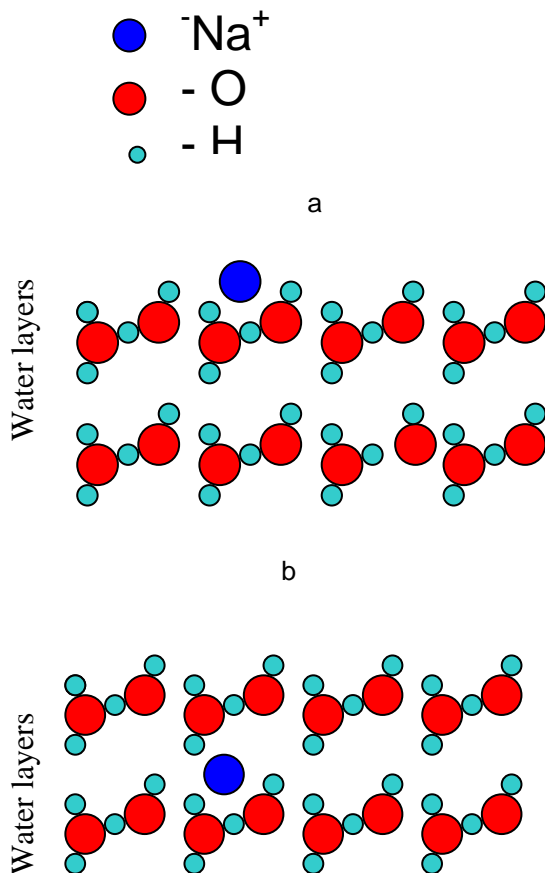


a



b



Figure 2. The presence of $Na^+$ ions both on the surface water layers (a) and interface of water layers (b)

On the Fig.3. represents the energy spectrum of sputtering of water molecules, ionic water molecules and Au atoms from water over layers on Au(111) surface at the bombardment by $Ar^+$ with $E_0=0,7$ keV, at the normal incidence.

The computational results show that on the mass spectrum a few intensive peaks are observed. At the mass spectrum are observed high intensive peak corresponds to molecule $H_2O$. In the mass spectrum also observed peaks which corresponded to the water clusters and Au atoms. The water clusters are consists $2<n<9$ water molecules. The next pick came from ionic water clusters. This is a case when ions $Na^+$ located on the top of water molecules which are shown in Fig.2a. In this cluster Na ions formed bonds

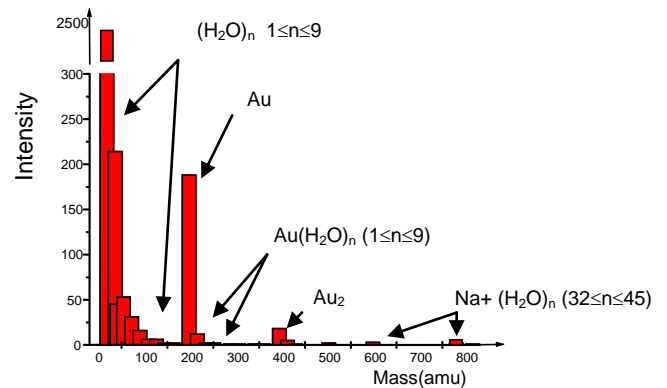with H atoms. And cluster consist 32-45 water molecules.



Figure.3 Mass spectra both water molecules and water clusters sputtered from water over layers on the Au(111) at bombardment by $Ar^+$ ions by $E_0=0,7$keV.

The next step of our study was about the state of large ionic clusters formed at the bombardment. The feature of the ion-water clusters is illustrated in Figure 4, where the interaction of the sphere of a given radius including the ion in the centre and sur-rounding water molecules. The ion position is the centre of cluster. As we shown on the above this paper, we use two cases of location $Na^+$ in water crystal(Fig.2.). And our results shows, different results for this two cases.
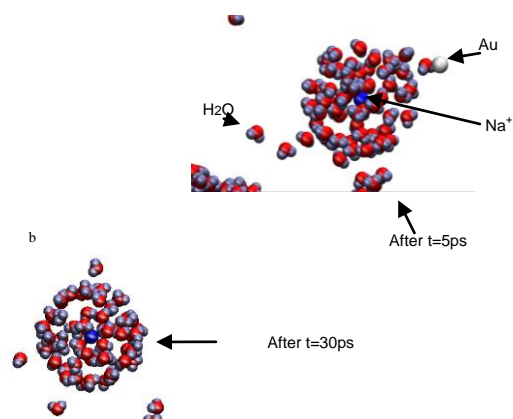


Figure.4. Primary hydration shell of $Na^+$ ion in ionic water cluster.

When bombardment the target in the case of $Na^+$ ion located top of ice crystal, formed a cluster which consists 45 molecules. In the case the $Na^+$ ions located between the layers formed a large cluster which consist 65 molecules. In this case, the Na ions bonded with water molecules before bombardment. And during the bombardment the ion will sputtered

with your neighbours which formed chemical bonds as a large ionic cluster.

In our calculation we not allows the influence of target to the cluster when a large ionic cluster so far from target. And ionic cluster were traced over the next 30 ps to consider their unimolecular fragmentation. As shown in Fig.4a, from the ionic cluster still removed some water molecules during 5ps. After 30ps we will receive more a stable ionic water cluster (Fig.4b).

### IV. Conclusions

The process of sputtering ionic water molecules from the metal surface have been investigated by computer simulation. The receiving mass spectrum consists of peaks corresponding to the water molecules, clusters and ionic water molecules. On the mass spectrum the peaks of gold atoms are also observed.

Our results shows that the preferred orientation of water molecules around a central cation, however, is similar to the orientation around a central water molecule, i.e., the cation in water does not introduce a large perturbation and the hydrogen bond network retains its structural identity near the cation.

These results are interesting for mass spectrometry of molecules, study of surfaces and biological molecules.

### V. References

[1]. B.J.Garrison, A.D.Delcorte, K.D.Krantzman. Acc.Chem.Res.33(2000) 69.

[2].H.Aulich,B.Baron,P.Delahay,R.lugo.J.Chem. Phys. 58,4438(1973).

[3]. H.Haberland,H.G.Schindler,D.R.Workshop. Ber Bunsenges.Phys.Chem.88,270(1984).

[4]. B.J.Garrison. Molecular Dynamics Simulations of Surface Chemical Reactions. Chem. Soc. Rev. 1992, 155-162.

[5]. A.Bur-Nur,G.Herman, M.L.Rappaport, Yu.Makler. Sputtering of water ice at 30-140 K by 0.5-6 keV H$^+$ and Ne$^+$ ions . Ices in the solar system; Proceedings of the Advanced Research Workshop, Nice, France, January 16-19, 1984 (A86-23051 09-91).

[6]. B.J.Garrison. Molecular Dynamics Simulations of Surface Chemical Reactions//Chem. Soc. Rev. 1992, 155-162.

[7]. B.J.Garrison, D.Srivastava, P.B.S.Kodali. Modelling of Surface Processes as Exemplified by Hydrocarbon Reactions. Chem. Rev. 1996, 96, 1327-1341.

[8]. B.J.Garrison, D.Srivastava. Potential Energy Surfaces for Chemical Reactions at Solid Surfaces. Annu. Rev. Phys. Chem. 1995, 46, 373-394.S.H.A. Begemann, A.L. Boers, Surf. Sci. 30 (1972) 134.

[9]. H. J. C.Berendsen, J. P. M., Postma, W. F.van Gunsteren, J.Hermans. in Intermolecular Forces; Pullman, B., Ed.; Reidel: Dordrecht, The Netherlands, 1981.

[10]. R. W.Impey, M.L.Klein, T.S. Tse. J. Chem. Phys. 1984, 81,8406.

[11]. M.Lombardero,C. Martin, S.Jorge, F.Lado, E.Lomba. J. Chem.Phys. 1999, *110*, 1148.

[12]. A.Wallqvist, O. Teleman. Mol. Phys. 1991, *74*, 515.

[13]. Wallqvist, A.; Teleman, O. Mol. Phys. 1991, *74*, 515.

[14]. E.Spohr. J. Mol. Liq. 1995, 64, 91.

[15]. R.M. Braun, P. Blenkinsopp, S. Mullock, C. Corlett, K.F. Willey, J. C. Vickerman, N.Winograd, Rapid Commun.Mass Spectrum., 12 (1998) 1246