

Effects of ion adsorption on surface structure of amorphous ice

Norifumi Hara, Riku Togashi, Yu Kumagai, and Tomoko Ikeda-Fukazawa

Department of Applied Chemistry, Meiji University, Japan

In interstellar molecular clouds, various molecules (for instance, H₂O, NH₃, CO, CO₂, and so on) are formed from elements such as H, C, O, and N [1]. Most of H₂O exists as a thin shell of amorphous ice around dust grain. The molecules undergo chemical evolutions to organic molecules through various processes on the surface of amorphous ice [2]. Thus, the surface structure of amorphous ice is an important factor to understand the molecular evolution of organic molecules in molecular clouds. To investigate the effects of adsorption of ion on the surface structure of amorphous ice, the molecular dynamics (MD) calculations of amorphous ice with NO₃⁻ and NH₄⁺ were performed.

The MD calculations were performed using an atom-atom potential model, KAWAMURA potential model [3]. The amorphous ice was prepared by quenching of a liquid phase consisting of 2760 water molecules from 280 to 235 K with 2.5 K/fs in cooling rate. After annealing at 235 K, the system was cooled to 10 K. The density of amorphous ice at 10 K was controlled with the time period of the annealing at 235 K. To equilibrate the fundamental cell, the MD code was run for 40 ps at 10 K. Then, an ion (NO₃⁻ or NH₄⁺) was put in a position, such the center of nitrogen in ion was at a distance of 0.5 nm from the outermost hydrogen atom in surface. An infinite surface was simulated by replicating the cell in the directions parallel to the surface using periodic boundary conditions. The pressure was kept at 0.1 MPa. The layer with 0.5 nm in thickness from the outmost atom was analyzed as the surface layer.

The result shows that the atomic displacement parameters (ADP) of oxygen and hydrogen of water molecules in surface layer increase during the adsorption of NO₃⁻ and NH₄⁺. The maximum value of ADP for surface with NH₄⁺ is larger than that with NO₃⁻. The values are diminished with formation of hydrogen bonds with surrounding water molecules, and gradually approach the values of pure amorphous ice without ions. For surface with NO₃⁻, three oxygen atoms of NO₃⁻ form hydrogen bonds with hydrogen atoms in dangling bonds of water on the surface layer. In the case of surface with NH₄⁺, hydrogen atoms form hydrogen bonds with oxygen atoms of water molecule in the surface layer. When an ion is adsorbed, surrounding water molecules rotate to form hydrogen bonds with the ion. Thus, the rearrangement of water molecules occur even at low temperature. The result indicates that the thermal vibrations of water molecules are enhanced with adsorption and diffusion of ions on the surface, and the effects depend on ion species. The effects of ion adsorption might have important implications for surface reaction in interstellar molecular clouds.

References

- [1] A. Kouchi, T. Yamamoto, T. Kuroda, J. M. Greenberg, 1994, *Astron. Astrophys.* 290, 1009.
- [2] N. Watanabe, A. Kouchi, 2008, *Surface Science*, 83, 439.
- [3] N. Kumagai, K. Kawamura, T. Yokokawa, 1994, *Mol. Simul.* 12, 177.