

Methanol production via interactions of low-energy CH_3^+ ions with ASW surface: experimental investigation of ion-surface reactions

Y. Nakai¹, H. Hidaka², and N. Watanabe²

¹*RIKEN Nishina Center for Accelerator-Based Science, RIKEN, Japan*

²*Institute of Low Temperature Science, Hokkaido University, Japan*

Various neutral and ion species have been observed in molecular clouds, despite their very low temperatures. To understand how molecules evolve, many chemical processes have been proposed. In gas phase, ion-molecule reactions have been always considered to play an important role. However, the abundances of some molecules such as water and methanol molecules cannot be explained only by the gas-phase reactions. Consequently, reactions between neutral radicals and neutral species on an icy grain surface have been proposed as the other essential pathways and it has been experimentally confirmed that reactions of hydrogen atoms adsorbed on an ice surface are essential for productions of hydrogen, water, methanol, and so on [1, 2]. Besides pure gas-phase and surface reactions, it is reasonably inferred that processes triggered by interactions of gas-phase ions with an ice mantle play some role in molecular evolution. In this context, the experiments of energetic ion bombardment to an ice containing other primordial molecules have been performed for a long time. In contrast, little is known about the interactions between low-energy ions and an ice surface, while molecular cations have been simply considered to recombine with negative charge (electrons) on an ice surface in theoretical models [3, 4]. However, it is not clear how electrons exist on icy grains, and thus it is also unclear if cation-electron recombination immediately occurs or not.

In fact, the reactions of very-low-energy ions with an icy surface have been theoretically proposed as new non-energetic reaction pathways [5, 6]. Since an icy grain can be regarded as a huge molecular cluster, reactions of ions with an icy grain surface would occur without reaction barriers as ion-molecule reactions. For example, the quantum chemical calculation predicted that the reaction of a CH_3^+ ion with a water ice surface spontaneously produces a methanol molecule [5]. Despite recent theoretical progress, no experimental study for low-energy ion reactions with ice surface have been performed due to experimental difficulties in obtaining enough reaction products for their detection using conventional methods such as infrared absorption spectroscopy. Accordingly, we have newly developed an experimental setup to enable us detecting trace amounts of reaction products. Using this setup, we have performed the experiments for production of methanol through the reaction of low-energy CH_3^+ ions with a water ice surface. The CH_3^+ ions with their energies as low as or lower than ~ 10 eV impinged on an amorphous solid water (ASW) prepared on an Al substrate around 10 K. Reaction products by CH_3^+ irradiation were monitored through pick-up reaction method by Cs^+ ions at several tens eV [7, 8]. After CH_3^+ irradiation, methanol molecules on the ASW were observed as the theoretical study suggested.

References

- [1] T. Hama and N. Watanabe, 2013, *Chem. Rev.*, 113, 8783
- [2] N. Watanabe and A. Kouchi, 2008, *Prog. Surf. Sci.*, 83, 439.
- [3] C. Walsh, T. J. Millar, and H. Nomura, 2013, *ApJL* 766, L23.
- [4] A. Rimola, C. Ceccarelli, N. Balucani, and P. Ugliengo, 2021, *frontiers in Astron. Space Sci.*, 8, 655405.
- [5] D. E. Woon, 2011, *ApJ*, 728, 44.
- [6] D. E. Woon, 2021, *Acc. Chem. Res.*, 54, 490.
- [7] H. Kang, 2011, *Bull. Korean Chem. Soc.*, 32, 389.
- [8] A. Ishibashi, *ApJL*, to be published.