

Effects of defects on structure of amorphous ice

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In interstellar molecular clouds, various molecules (e.g., H₂O, NH₃, CO, CO₂, and so on) are formed from elements such as H, C, O, and N [1]. Most of H₂O in interstellar molecular clouds exists as a thin shell of amorphous ice around dust grain. The molecules, which are adsorbed or included in amorphous ice, undergo chemical evolutions to organic molecules through various reaction processes. The photochemical reaction caused by ultraviolet (UV) photon irradiation is one of the dominant reaction processes [2]. Thus, the variation in structure of amorphous ice with UV-irradiation is an important factor to understand the processes of molecular evolutions. Recently, Tachibana *et al.* [3] found that the viscosity of the UV-irradiated amorphous ice decreases at around 50 K, and becomes a lower value than that at the glass transition temperature. The defects formed by UV-irradiation are expected as a cause of the decrease in viscosity. To investigate the effects of defects on the structure of amorphous ice, the molecular dynamics (MD) calculations of amorphous ice including OH and OH⁻ were performed.

The MD calculations were performed using an atom-atom potential model with MXDORTO program [4]. We used an interatomic potential model (KAWAMURA potential model) for the potential parameters of water molecule [5]. The potential parameters of OH and OH⁻ were determined by constraining molecular structure to reproduce the energy surfaces obtained from molecular orbital calculations. The amorphous ice was prepared by quenching of a liquid phase consisting of 360 water molecules from 290 K to 10 K [5]. The system including OH (or OH⁻) with 5% in concentration was prepared by replacing 18 H₂O molecules with 18 OH (or 18 OH⁻) at 10 K. To equilibrate fundamental cell, the MD code was run for 2 ns at 10 K. Then, the system was warmed to 90 K with 2.5×10^{-5} K/fs in rate. The viscosity of amorphous ice was estimated using Stokes–Einstein relation.

The result shows that the density of amorphous ice including OH with 5% in concentration is lower than that of pure amorphous ice, whereas that including OH⁻ is higher. For the viscosity, the amorphous ices including OH and OH⁻ have lower and higher values in comparison with that of pure amorphous ice, respectively. In order to investigate the mechanisms of the variations in density and viscosity with formation of defects, the local structures around the defects were analysed. The results show that the mean coordination number of OH is 1.29, while that of OH⁻ is 4.35. For H₂O, the coordination numbers for both of the states are close to the value of pure amorphous ice. This indicates that the variations in density and viscosity are resulted from the local structures around the defects. The density of amorphous ice decreases as the coordination number decreases. The enhancement of thermal vibrations of OH due to the release from restrictions of surrounded molecules can be a cause of decrease in viscosity.

References

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