Effects of Density on Surface Structure of Amorphous Ice

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In interstellar molecular clouds, various molecules (for instance, H_2O, NH_3, CO, CO_2, and so on) are formed from elements such as H, C, O, and N by deposition on dust grains [1]. Most of H_2O exists as a thin shell of amorphous ice around dust grain. The deposited molecules undergo chemical evolutions to organic molecule through various processes [2]. The structure of amorphous ice surface is an important factor to understand the molecular evolution in molecular clouds.
Amorphous ice is formed by vapor deposition of H_2O gases [3] or compression of crystalline ice [4]. The structure of amorphous ice depends on formation processes and is classified into two types: high-density amorphous (HDA) and low-density amorphous (LDA) ices [4]. To investigate the effects of internal structure on surface structure, the molecular dynamics (MD) calculations of amorphous ice were performed.
The KAWAMURA potential model [5] was used for the MD calculations. The amorphous ice was prepared by quenching 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 was controlled with the time period of the annealing at 235 K. 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 5 Åin thickness from the outmost atom was analyzed as the surface layer.
The calculations show that the density of amorphous ice at 10 K depends on the temperature history before the cooling to 10 K. In the case that the time period of annealing at 235 K was 1400 ps, for instance, the formed amorphous has the minimum density of 0.962 g/cm^3 at 10 K. For the case that the system was directly quenched from 300 to 10K without annealing at 235 K, the density reaches its maximum value of 1.095 g/cm^3. Because a significant change of density was observed at 235 K, we controlled the density of internal part of amorphous ice with time period of the annealing at 235 K.
The result shows that the density of the surface layer is smaller than that of the internal part, and increases as the density of the internal part increases. The decrease in molecular density observed in the surface layer is attributed to the uneven structure and large amplitude of the thermal vibrations of water molecules. To investigate the contribution of the uneven structure, the radical distribution function (RDF) was calculated. The position of the second peak, which is observed at around 4.1 Å, of surface layer is about 0.3 Ålarge than that of internal part. This suggests that the surface layer has a lower density even if there is no unevenness. The amplitude of the thermal vibration is measured by the atomic displacement parameter (ADP). The calculation indicates that ADP of surface layer is larger than that of internal part, and depends on internal density. This result is consistent with the calculation of RDF. In the RDF result the broadening of peaks was observed for surface layer. It is concluded that the structure of surface layer is affected by density of internal part. This effect of internal structure on surface structure of amorphous ice might have important implications for molecular evolution in molecular clouds.
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