[P3] Geometric isotope effects on small chloride ion water clusters with path integral molecular dynamics simulations

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Introduction:

The understanding of the nature of water has attracted intensive attentions since it is essential for life [1]. The effects of ion on the properties of water are shown to be important both in the bulk and at vapor/water interface [2]. In addition, strong quantum behavior is exhibited for the light atom in hydrogen-bonded systems at low temperature or even at room temperature. The geometric isotope effects are shown to be important for the macroscopic properties of water, such as the melting point and the temperature of maximum density (TMD), which are increased by 3.8K and 7.2K in D2O compared with H2O, respectively [3]. From the microscopic point of view, the neutron diffraction experiments show that intramolecular r(O-D) distance is shorter than r(O-H) by about 0.5% [4]. However, up to now, there is little work with respect to the geometrical isotope effects on the ionic hydrogen-bonded Cl-(H2O)n clusters with respect to the single and multi shell structures, respectively.

Methodology and conclusions:

The thermal structures of Cl-(H2O)1-4 clusters are obtained by using standard imaginary-time PIMD simulations on PM6-DH+ potential energy surface. In the path-integral formalism, a cyclic polymer chain consisting of classical quasi particles is utilized to describe the quantum character of nuclei. Thermal averages are calculated from time averages over fictitious molecular dynamics trajectories, which are generated from the equation of motions described in the normal mode coordinate representation. The system temperature was controlled with a massive Nóse–Hoover chain technique.

The geometric isotope effects on the structures of Cl-(H2O)n clusters were explored by carrying out path integral molecular dynamic simulations. First, an outer shell coordinate rl(Cl…O) is selected to display the rearrangement of single and multi hydration shell structures. Next, to show the competition between intramolecular and intermolecular nuclear quantum effects, the proton transfer and ion-water stretching motions are studied for single and multi shell structures, respectively.

The results indicate that the intermolecular nuclear quantum effects stabilize the ionic hydrogen bonds in single shell structures, however, they are destabilized through the competition with intramolecular nuclear quantum effects in multi shell structures. In addition, the correlations between ion-water stretching and the proton transfer motion are discussed. The results indicate that the intermolecular nuclear quantum effects on the cluster structures are strongly related to the cooperation of the water-water hydrogen bond interactions. The detail results will be shown in the poster.

Bibliography

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