Quantum chemical studies of H + $(H_2O)_n$ system as model of chemisorption on icy grain

Y. Osamura

Kanagawa Institute of Technology, Atsugi 243-0292, Japan

The reactions of hydrogen atom with various chemical species on icy grain are important processes on the formation of hydrogenated molecules in interstellar medium. It would be interesting to see the behavior of hydrogen atom both on ice surface and inside ice. The interaction between hydrogen atom and amorphous ice can be modeled as H + $(H_2O)_n$ cluster system in order to explore quantum chemically. We have calculated the structures and interaction energies between hydrogen atom and water clusters with the hybrid density functional method. We have used the B3LYP method with 6-311G(d,p) basis functions to optimize the geometries of H…$(H_2O)_n$ system for n=1~4. Table 1 shows the distance between hydrogen atom and oxygen atom of H_2O and the stabilization energies depending on the number of water molecules. All interaction energies are calculated to be small (1~2 kJ mol^{-1}) and the distance between hydrogen atom and water clusters are shown to be ca. 2.5 Å. This indicates that the interaction between hydrogen atom and water molecule is due to the weak van der Waals attraction. When we look at the dependence of the number of water molecules surrounding to a hydrogen atom, both the binding energies and the distances are found to be nearly the same except the case of water dimer.

If one says that this type of interaction is physisorption, there might be a type of chemisorption between H atom and H_2O molecules. Nevertheless, H_3O radical is energetically high species and spontaneously decompose to H + H_2O. Since the energy of H_3O molecule (69.0 kJ mol^{-1} relative to H + H_2O) is higher than that of the transition state leading to OH + H_2 (42.0 kJ mol^{-1}), the chemical species H_3O cannot be exist not only in gas phase but also in solid or liquid phase. The transition states for hydrogen exchange reactions in H + $(H_2O)_n$ clusters are calculated to be also high in energy.

Table 1. The interaction distances and interaction energies between H atom and H_2O clusters.

n	system	H … O distance (Å)	stabilization energy ΔE (kJ mol^{-1})
1	H_2O…H	2.38	0.9
2	$(H_2O)_2$…H	2.14	2.2
3	$(H_2O)_3$…H	2.49	1.1
4	$(H_2O)_4$…H	2.50	0.9