Quantum chemical study of water effect for hydrogen abstraction reactions in low temperature

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Hydrogen abstraction reactions and hydrogen transfer reactions are one of important processes of molecular formation and destruction processes of interstellar molecules. We have been studying the molecular processes of these reactions with small water clusters in order to model the chemical reactions on icy grain surfaces in terms of quantum chemical method. In this presentation, we show the differences of the molecular interactions between various chemical species and small water clusters and how water molecules affect the potential energy surfaces of the hydrogen abstraction reactions of hydrocarbons as well as hydrogen transfer reactions.

In order to obtain the interaction energies of various neutral radicals and small water clusters, we have calculated the molecular geometries of $CH_3(H_2O)_n$, $OH(H_2O)_n$, and $H(H_2O)_n$ by using hybrid density functional B3LYP method with 6-311G(d,p) basis functions. Figure 1 shows the optimized structures of CH_3 radical, OH radical and H atom interacting with two water molecules. The binding energies between radicals and water dimer are calculated to be 13, 52, and 2 kJ mol^{-1} for CH_3, OH, and H species, respectively.

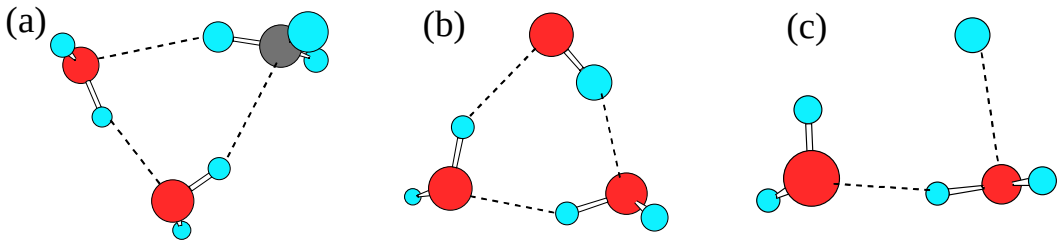

Figure 1. Optimized structures of (a) $CH_3(H_2O)_2$, (b) $OH(H_2O)_2$, and (c) $H(H_2O)_2$ radicals.

The calculated potential energy surface of the chemical reaction of $CH_4 + H \rightarrow CH_3 + H_2$ shows the energy barrier of 25 kJ mol^{-1} and exothermic by 6 kJ mol^{-1}. When single H_2O molecule adds to this system, its energy barrier found to be lower by 3 kJ mol^{-1}. In the case of $CH_4 + OH \rightarrow CH_3 + H_2O$ reaction, the energy barrier 4 kJ mol^{-1} without H_2O molecule is calculated to become 7 kJ mol^{-1} with single H_2O molecule interacting in the $CH_4 + OH$ system. The change of the energy barriers by interacting H_2O molecules depends on which reactant species has strong interaction with H_2O molecules. Figure 2 shows the structures of transition states of two reactions and indicates the difference of the interacting site of H_2O molecule with reacting species.

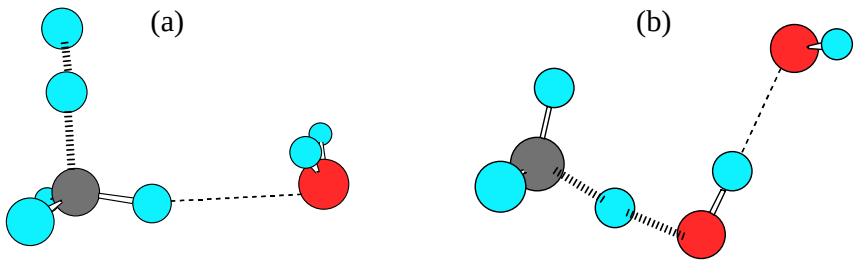

Figure 2: Transition state structures of (a) CH_4 + H and (b) CH_4 + OH interacting with H_2O molecule.