2B3b H-bond pattern of water octamer at finite temperature

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Introduction

In a water cluster, the hydrogen bond (H-bond) network plays an important role in stability and various properties. The H-bond pattern represents the whole H-bond network of the water cluster and a subset of configuration space. Though the H-bond pattern has only information about the H-bond network, the distributions of H-bond patterns imply the structure distributions of the water cluster[1].

Water octamer $(H_2O)_8$ is the first cluster which forms the cube structure by H-bond bonds, and there are 14 possible cubic H-bond networks, in which the corresponding local minima structures exist. The potential energies for the two isomers D_{2d} and S_4 of the 14 structures are almost isoenergetic and lower than the others. Many noncubic octamers also exist as local minima with higher potential energies than the D_{2d} and S_4 cubic isomers.

In this study, we evaluate the distributions of H-bond patterns of water octamer at finite temperature.

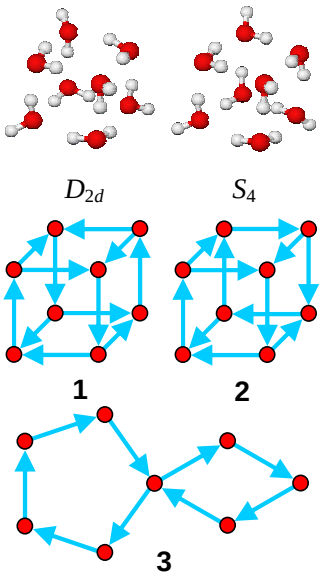

Fig. 1. Cubic octamer structures and H-bond patterns in digraph representation.

Method

We created the NVT ensemble of water octamer by the Monte Carlo (MC) simulation, where temperature is set to 200 K or 300K, and density is fixed to 0.1 mol/L. We used TTM2-R potential function[2] with the additional repulsion term for energy calculation. 10^9 configurations sampled in the emsemble are divided into the H-bond patterns. The relative molar Helmholtz energy between H-bond patterns i and j is evaluated by, $\Delta A_{ij} = -RT\ln(N_i/N_j)$ where N_i/N_j is the ratio of the numbers of configurations belonging to the H-bond patterns i and j. To represent H-bond patterns we use digraph composed of vertices and arcs, which mean water molecules and H-bonds, respectively.

Results

18586 and 37978 H-bond patterns, in which all molecules are connected to the H-bond network, are obtained from 10^9 configurations at 200 K and 300 K, respectively. At 200 K, the cubic pattern **2**, in which the S_4 isomer is classified, is the H-bond pattern with the lowest free energy and the lowest internal energy. At 300 K, on the other hand, the free energy of H-bond pattern **3** is the lowest. It is found that the order of free energy and the distributions of H-bond patterns considerably depend on temperature because of the entropic contribution. It is also found that the cluster dipole moment is characterized by H-bond pattern.

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[2] C. J. Burnham and S. S. Xantheas, *J. Chem. Phys.*, **116**, 1500 (2002).