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Distribution of H-bond patterns and enhancement of molecular dipole moment in water clusters

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Introduction

In water clusters, water molecules are connected by hydrogen bonds and each molecular dipole moment of the constituent molecules is enhanced due to the electric field induced by surrounding molecules. Hydrogen-bond (H-bond) pattern can be represented by digraph having a set of information on the hydrogen bond connectivity between any two of the constituent water molecules of the cluster. In digraph representation, water molecules and hydrogen bonds from hydrogen donor to acceptor are regarded as vertices and arcs, respectively, and free OH bonds and relative configuration of the molecules are neglected. The number of H-bond patterns increases explosively with the cluster size and is far more than that of local minima, because H-bond pattern has no information about whether or not the stationary points exist.

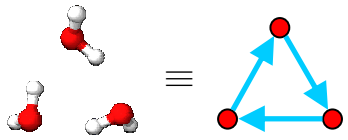

Fig.1. A structure of a hydrogen bonded water cluster and the equivalent digraph representation.

Method

We calculated the distribution of H-bond patterns in water clusters ($(H_2O)_n$, $n \leq 8$). The NVT ensembles of water clusters at temperature T are formed by the MC simulation using TTM-2R potential function [1] with the additional repulsion term. Density is set to be constant (0.1 mol/L for molecule) independent of cluster size. 10^9 configurations are divided into the H-bond patterns. The relative molar Helmholtz energy ΔA_{ij} of water cluster between H-bond patterns i and j is evaluated by $\Delta A_{ij} = -RT \ln\left(N_i / N_j\right)$, where N_i/N_j is the ratio of the numbers of configurations belonging to the H-bond patterns i and j.

Results

A lot of H-bond patterns are observed in the ensemble. At low temperature (T = 200K), the H-bond patterns that have lower molar Helmholtz energies have lower internal energies (i.e., ensemble average of potential energies), and more hydrogen bonds. At high temperature (T = 300K), however, the H-bond patterns favored in Helmholtz energies are different from those observed at 200K, and some of them have isolated water molecules which are not hydrogen-bonded to other molecules. The contribution of minor H-bond patterns increase with cluster size. It is found that molecular dipole moment is mostly influenced by molecules directly connected with hydrogen bond and correlate with the number of hydrogen accepter and donor in hydrogen bonding. The average dipole moment of fully hydrogen-bonded water molecules in clusters approaches to the value for liquid, while the average value for molecules without any hydrogen-bonding is almost equal to the value for monomer in the gas phase.

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