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多面体水クラスターの水素結合ネットワーク: 電荷移動項と分散項による解析

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Analysis of Hydrogen Bonded Networks in Polyhedral Water Clusters by Charge-Transfer and Dispersion Terms

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Because a water molecule is capable to have two donating and two accepting hydrogen bonds (HB), clusters of water molecules $(H_2O)_n$ have many isomers. Even with a given configuration of oxygen atoms the number of distinct clusters increases dramatically with *n*. For instance, as were counted by McDonald et al [1], the cubic configuration of eight water molecules has 14 isomers, while the dodecahedron of twenty water molecules has 30026 isomers. Less symmetric configurations of oxygen atoms have much more isomers. The HB networks in polyhedral water clusters are suitable for studying the characteristics of the HB, because the backbone of the oxygen networks is common among all isomers and only the directions of HB are different.

For the cubic (H₂O)₈, the geometries of all of 14 isomers are optimized with the MP2(full)/aug-cc-

pvdz(cart) level of approximation. For dodecahedron $(H_2O)_{20}$, 14 isomers reported in Ref.[2] are studied; their binding energies are close to one another. The theoretical method for the analysis is the locally projected molecular orbital perturbation theory (LPMO PT) developed by one of authors (SI).[3,4] The binding energy is evaluated by eq.(1), and the charge-transfer (CT) terms (2) between molecules are evaluated by the first order PT wave function. The dispersion energy is also evaluated pair-wisely.





Figure 2. The Schlegel diagrams of cube (H_2O)₈. The second number R-s is the label of the isomer, where R is the number of the D2A1 \leftarrow D1A2 type of the hydrogen bonds. The tiny number on each arrow is the CT term.

$$E_{\text{Binde}}^{\text{LPMO SPT+Disp}} = \left(E^{\text{HF}} \left(\Psi^{\text{LPMO}} \right) - \sum_{X} E_{X}^{\text{HF}} \right) + E^{2\&3SPT} + E^{\text{Disp}}$$
(1)
$$E^{2\&3SPT} = \sum_{X,Y} E_{XY}^{\text{CT}}$$
(2)

Figure 1 shows the relative binding energies of the 14 isomers of the cube (H₂O)₈, and Figure 2 is their Schlegel diagram, where square marked molecules are of D1A2 type and triangle ones are of D2A1 type. DnAm implies that the water has n donating OH and m accepting O---H HB. Figure 1 shows that there are four groups of isomers in the relative stability. The most stable isomers (4-1 and 4-2 in Fig.2) have four D2A1←D1A2 HB, and the least stable isomers (0-1 and 0-2) have no such HB. Figure 3 shows the O---O length dependence of the CT and dispersion energies for the cube (H₂O)₈ and dodecahedron (H₂O)₂₀. isomers. All of HB shorter than 2.7Å are D2A1 \leftarrow D1A2 type. The clusters are classified by the number of D2A1←D1A2 HB. All of dodecahedron isomers studied in the current works have 7 D2A1←D1A2, 17 D1A2←D2A1, 3 D2A1←D2A1, and 3 D1A2←D1A2. Their binding energies are within 1.5kJ mol⁻¹. As noticed in Fig. 3, there is a large distribution in the pair-wise interaction energies (CT and dispersion terms) for the same $DnAm \leftarrow Dn'Am'$. The other important finding seen in Figs.1 and 2 are that the first 2 isomers of 2-s are distinctively more stable than the next 4 isomers, and that the first 3 isomers of 1-s are more stable than isomer 1-4. It turns out that these two findings are inter-related to each other. By carefully examining Fig.2, we can notice that in isomers 2-1 and 2-2 there are two separate pairs of $D2A1 \leftarrow D2A1$ ($D1A2 \leftarrow D1A2$), while in slightly less stable 2-3, 2-4, 2-5 and 2-6, there is a chain of D2A1—D2A1—D2A1 (D1A2—D1A2) and an isolated D2A1 (D1A2). This difference might leads to a small but definite change in energy by about 4kJ mol⁻¹ in the binding energy. Also, isomers 1-1, 1-2 and 1-3 have a linear chain of 2A1-D2A1—D2A1—D2A1 (D1A2—D1A2—D1A2—D1A2), and on the other hand, isomer 1-4 has a three-membered chain with a branch, and this isomer is distinctively less stable than the other 1-nisomers.

The above findings imply that the strength of the HB $DnAm \leftarrow Dn'Am'$ is dependent also on the neighboring HB. The adjacent HB can be defined at both donor and acceptor molecules for each HB $DnAm \leftarrow Dn'Am'$. There are (n+m-1) adjacent HB at the hydrogen acceptor (donor) molecule. One of the typical examples is seen in isomer 2-6, where both w5 \leftarrow w6 and w1 \leftarrow w4 are D2A1 \leftarrow D1A2 but their CT terms are -21.2 and -11.4kJ mol⁻¹, respectively, the largest and smallest among the D2A1 \leftarrow D1A2 plots in Fig.3. The two adjacent HBs of w6 are both *from* D1A2 and those of w5 are *to* D2A1. On the other hand, the two adjacent HBs of w4 are *from* D2A1 and those of w1 are *to* D1A2. These difference can be analyzed in terms of the CT (electron-donor-acceptor) theory of Mulliken. The systematic and qualitative analysis leads to accurate model interaction functions for water clusters. [1]McDonald, Ojamäe, Singer, J.Phys.Chem.A (1998) <u>102</u>, 2824; [2]Xantheas, Can.J.Chem.Eng. (2012) 90, 843; [3] Iwata, PCCP (2014) <u>16</u>, 11310; [4]Iwata, Bandyopadhyay, Xantheas, J.Phys.Chem.A.(2013) <u>117</u>, 6641



Figure 3. The O---O length dependence of the CT and dispersion energies for the cube $(H_2O)_8$ and dodecahedron $(H_2O)_{20}$. isomers