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Stability of the Pentagon Structure of Water Cluster

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A hexagonal hexamer of water cluster is optimized by *ab initio* method using the 4-31G basis set. At this geometry the nonadditive many-body interactions are calculated. The *ab initio* calculation with large basis set [T. H. Dunning, *J. Chem. Phys.*, **53**, 2823 (1970); **54**, 3958 (1971)] shows that a pentagonal unit is rather stable among several kinds of clustering units of water molecules.

Introduction

Due to the characteristic bent \angle HOH bond angle and the strong hydrogen bonds (H-bonds), water molecules form various shapes of clusters. The binding energy of H-bonds per molecule increases with the increase of the cluster size. Any structure of unique large water cluster has not been experimentally found in the liquid state of water. However the anomalous properties of water have been explained theoretically assuming small water clusters, especially in order to explain the properties related to the volume of liquid water in the mixture models^{1,2}. Among the clusters, five-membered ring structures are proposed as high density species that would have a small molar volume². Molecular dynamics studies indicate pentagon units^{3,4}. Speedy and Mezei⁵ also considered that the anomalies of water may be related to the self-replicating propensity of pentagons. In the results of Speedy *et al.*, the concentrations of five-membered rings increase as the temperature decreases. On the other hand, we proposed that the concentration-ratio of five- to six-membered rings (as, maybe, fractures of low density ice having large molar volume) increases with the increase of temperature. According to the ring-analysis from the results of molecular dynamic simulation of Belch and Rice⁶, the concentration of five-membered ring decreases as the temperature increases, but the rate of decrease is much less than that reported by Speedy *et al.* (only a factor of 1.1 as the temper-

ature drops from 313 to 273 K). However their analysis supports that the ratio of five- to six-membered ring increases with temperature rise. Besides the five- and six-membered rings in the simulation of Belch *et al.*, the concentrations of seven- and eight-membered rings are also high compared with those of six- and five-membered rings. The conformations of local minima of water clusters optimized with two-body plus three- and four- body interactions have many four-membered ring structures which have more H-bonded OH-bonds.⁷ In the molecular dynamics simulation of Speedy *et al.*, the total number of heptagon is the largest, but the pentagon and hexagon are dominant as "primitive" polygons⁸. However the result does not show any regular pattern of the temperature dependancy of the ratio of pentagon to hexagon. A different analysis was done by Geiger and Stanley⁹ from the results of molecular dynamic simulations of Stillinger and Rahman¹⁰ using ST2 potential. According to their analysis, the hydrogen-bonded network includes tiny spatially correlated patches of four-bonded molecules, and the local density near a patch is lower than the global density. The four-bonded patches are essentially tetrahedrally bonded and do not like a ring shape. The hydrogen-bonded structures depend very much on the potential functions. The structure and stability of water pentamers were also investigated using molecular dynamics of small clusters¹¹.

It is, however, difficult to determine the shapes and binding energies of clusters in the liquid state, and thus calcula-

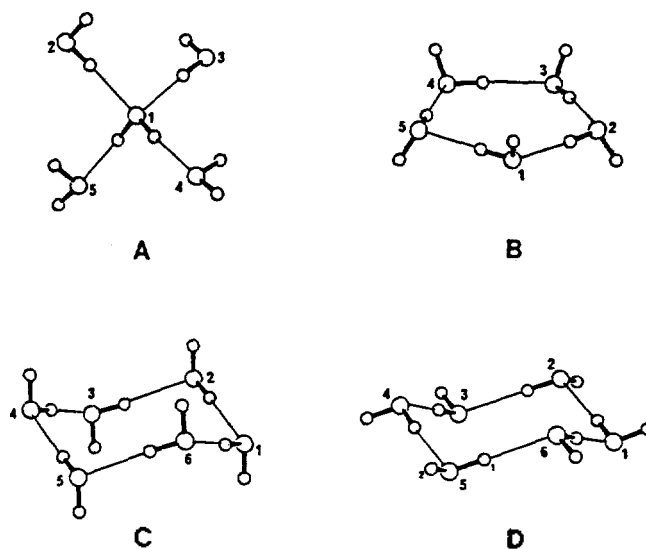
Table 1. The Geometry and Nonadditive Many-Body Interactions of Hexagonal Hexamer Optimized with 4-31G Basis

$R_{OO} = 2.63 \text{ \AA}$	
$R_{OH1} = 0.977 \text{ \AA}$	
$R_{OH2} = 0.948 \text{ \AA}$	
$\angle HOH = 112.3^\circ$	
$\Delta E_{12}^2 = -7.531$	
$\Delta E_{13}^2 = -1.504$	total ^a
$\Delta E_{14}^2 = -0.720$	-56.366
$\Delta E_{123}^3 = -2.356$	
$\Delta E_{124}^3 = -0.376$	
$\Delta E_{125}^3 = -0.376$	
$\Delta E_{126}^3 = -0.069$	-18.786
$\Delta E_{1234}^4 = -0.191$	
$\Delta E_{1235}^4 = -0.011$	
$\Delta E_{1245}^4 = -0.027$	-1.296
$\Delta E_{12345}^5 = -0.128$	-0.766
$\Delta E_{123456}^6 = +0.188$	+0.188
BE^b	34.89(5.81) ^c

^aValues in this column pertain to the total energy of n-body interactions where n=2-6. For example, $\Delta E_{total}^2 = 6\Delta E_{12}^2 + 6\Delta E_{13}^2 + 3\Delta E_{14}^2$. ^b $BE = -1/2\Delta E_{total}^2 - 1/3\Delta E_{total}^3 - 1/4\Delta E_{total}^4 - 1/5\Delta E_{total}^5 - 1/6\Delta E_{total}^6$. ^cThe binding energy per molecule. Refer Figure 1 for the subscripts of ΔE . And refer the text for R_{OH1} and R_{OH2} . Energies are in kcal/mol.

tions are often carried out for several kinds of cluster units, *i.e.*, isolated single clusters in gaseous state. There have been energy optimization studies of several kinds of water clusters with potential function method^{7,12-14} and with *ab initio* method¹⁵⁻²⁰. Both methods have the following weak points: (1) When we use potential functions, whether they are empirically parameterized or are based on *ab initio* results, it is very difficult to find the dependence of H-bond energies on orientations unless otherwise there exist very good reliable potential functions. The semiempirical AM1 parametrization leads to questionable results for H-bonding²¹. Most calculations using potential functions are usually limited to pairwise two-body interactions neglecting the many-body effects. The three- and four-body model functions for water-water interaction have made a little improvement in the radial distribution functions^{22,23}. (2) In *ab initio* calculations, small basis sets (*e.g.*, usually split-valence basis set) have been used for optimizations. These calculations also had the limitations because of the poor representation of H-bond energies. It sometimes overestimates H-bond energies with much deformed water molecules. The *ab initio* optimizations have hardly been carried out with large basis sets. The optimized geometries and energies of water clusters also depend on the basis sets¹⁹.

In this study, we present the optimized hexagonal hexamer of water cluster with 4-31G basis set and nonadditive many-body interactions are calculated in order to examine the order of magnitude of many-body interactions. Next, several different units of water clusters are chosen. Then *ab initio* calculations are carried out at fixed positions to calculate *ab initio* two-body and three-body interactions with large basis set (in section III). It is shown that a pentagon unit is fairly stable among the several kinds of clusters.

**Figure 1.** Structures of water clusters. A: Tetrahedral pentamer (TP), B: pentagonal pentamer (PP), C: axial hexamer (AH), D: equatorial hexamer (EH).

Many Body Interactions and Distortion of Monomer Geometry in the Water Hexamer Optimized With Small Basis Set *ab initio* Calculation

In this section we present the qualitative magnitudes of many-body interactions of water cluster optimized with small basis set using GAUSSIAN program²⁴. Table 1 shows the optimized geometry of hexagonal hexamer (HH) with the split valence basis set (4-31G) keeping symmetry S_6 . Starting with an axial hexamer (AH), the optimized one is the equatorial hexamer (EH). In Table 1, R_{OH1} is the OH bond length along O-O axis and is somewhat stretched with respect to the monomer geometry. R_{OH2} is the bond off the axis. The subscripts under ΔE indicate the atoms of EH in Figure 1. The total nonadditive multi-body interaction energies become smaller in the sequence of two-, three-, and four-body *etc.*, and the six-body interaction is positive probably due to ring closure. Total four-body interaction is about one tenth of total three-body interaction. The total four-body interactions in the optimized water clusters with model functions are about the half of the total three-body interactions⁷. The too much distorted monomer geometry and too short R_{OO} distance in Table 1 indicate the poor basis set to represent H-bond energy. Therefore the quantitative comparison of stability of water clusters with this basis set is not satisfactory.

Two-And Three-Body Interactions in Water Clusters by Large Basis Set *ab initio* Calculations

Molecular orbital (MO) calculations were carried out in this section with the Dunning's basis set²⁵. This basis is large enough to give a small basis set superposition error and gives a correct dipole moment to reproduce good long range interactions²⁶. We have examined only several typical water clusters. These are tetrahedral pentamer (TP), two hexagonal hexamers (*i.e.*, EH and AH), and pentagonal pentamer (PP).

Table 2. Energies per Molecule of The Selected Water Clusters Based on *ab initio* Calculations

		R_{OH}		TP		AH		EH		PP	
		R_{OO}		0.9572	1.0072	0.9572	1.0072	0.9572	1.0072	0.9572	1.0072
ΔE^2	NN ^a	2.74		-2.29	-2.61	-2.86	-3.26	-2.86	-3.26	-3.16	-3.56
		2.98		-3.28	-3.61	-4.09	-4.51	-4.09	-4.51	-4.32	-4.74
	NNN	2.74		-0.65	-0.70	-1.04	-1.14	-0.89	-0.97	-1.01	-1.10
		2.98		-0.46	-0.49	-0.72	-0.79	-0.63	-0.69	-0.71	-0.78
ΔE^3	NN	2.74		-0.66	-0.89	-1.03	-1.43	-1.19	-1.63	-1.16	-1.61
		2.98		-0.39	-0.51	-0.57	-0.90	-0.65	-0.86	-0.67	-0.86
	NNN	2.74	^b	+0.49	+0.53	+0.05	+0.002	-0.76	-0.91	-0.39	-0.46
		2.98		+0.35	+0.39	+0.07	+0.052	-0.45	-0.54	-0.25	-0.28
BE/n ^d		2.74		1.53	1.77	2.12	2.68	2.53	2.96	2.60	3.02
		2.98		1.88	2.09	2.41	2.98	2.73	3.06	2.82	3.13

^aNN and NNN denote the nearest neighbor and non-nearest neighbor interactions, respectively. ^bn is the number of molecules of the cluster. Energies are in kcal/mol and distances are in Å.

These are too large to be optimized by *ab initio* method with the aforementioned basis set. Even a single point calculations at one geometry is not easy. Instead of optimizing, therefore, we perform the *ab initio* calculations only at four different geometries. At these geometries, the two- and three-body interactions are studied. The four geometries have two different R_{OO} distances (2.98 and 2.74 Å) and two R_{OH} distances (0.9572 and 1.0072 Å) with fixed $\angle HOH$ angle of 104.52°. These four points are selected as a succession the previous work²⁷. We did not calculate many-body interactions higher than the three-body, since they are found to be small in the previous section and the calculations are very time-consuming with the Dunning's basis set. Since we have not optimized the structures such O-O skeletons for TP, EH and AH were chosen that TP has an exact tetrahedral framework and EH and AH have a chair form with tetrahedral angle for $\angle O-O-O$. The chair form is more symmetric than the boat form. Since the cyclic structure have the more H-bonds than non-cyclic or bifurcated ones, other non-cyclic clusters than TP are not considered. Besides five- or six-membered cyclic clusters, other membered ones have not been considered assuming rather smaller binding energies per molecule. The main purpose of this work is to compare the stabilities of hexagon units and pentagon units of water clusters. If the oxygen skeleton is optimized for the selected clusters, the tetrahedral skeleton would not be stable. However, in large clusters which consist of several hexagonal units, the ice-I-like (with tetrahedral angles between oxygen atoms) would be acceptable. The flat pentagon is chosen because of no knowledge about the optimized oxygen skeleton. Another reason for the preference of flatness of pentagon is discussed in the next section. However high symmetries are given for O-O skeleton, the hydrogen atoms reduce the symmetries. The orientation of water molecules is chosen to have the highest symmetries within the given O-O skeleton. TP has symmetry C_2 at best and the dihedral angles (a clockwise angle between uninvolved OH-bond of proton donor in H-bonding and the bisector of $\angle HOH$ angle of proton acceptor; see the water molecules numbered 2 and 1 in Figure 1A) are given with 120°. Walrafen²⁸ has used this symmetrized TP to explain the lattice vibration of liquid water. The hydrogen atoms in HH's are positioned to make cyclic

head-to-tail H-bondings (Consider a central water molecule of H-bonded trimer, "head" is proton acceptor and "tail" is a proton donor), and the symmetry is then S_6 . The pentagon loses all symmetry due to the orientations of hydrogen atoms and has the symmetry C_1 .

The two-body interactions (ΔE^2) are obtained by choosing two molecules in an n-numbered cluster. There are nC_2 two-body combinations. The ΔE^2 is given by,

$$\Delta E^2 = E_{AB}(\text{dimer}) - (E_A + E_B) \quad (1)$$

The are nC_3 three-body interactions (ΔE^3) and is given by,

$$\Delta E^3 = E_{ABC} - (E_{AB} + E_{BC} + E_{CA}) + (E_A + E_B + E_C) \quad (2)$$

When we consider only up to the three-body interactions, the binding energy (BE) is defined as follows,

$$BE = -(1/2 \sum \Delta E^2 + 1/3 \sum \Delta E^3) \quad (3)$$

The results are in Table 2 which shows separately two- and three-body interactions. The non-nearest terms indicate that any of H-bonds is intact. PP is the most stable in total BE per molecule at four geometrical points. This is caused mainly by the nearest two-body interactions having the dependence of $(1 + \cos \theta)$ on the dihedral angle θ at the same R_{OO} distance. This flat pentagon has four 180° and one 60° dihedral angles, i.e., the average value, $\cos^{-1} [(4 \cos 180^\circ + \cos 60^\circ)/5]$, is 134.4°. On the other hand, the hexagons have all six 120° in dihedral angles. AH is more stable than EH only if we consider two-body interactions, however AH has the repulsive non-nearest three-body interactions. But EH can have the only two-dimensionally infinite planar replicability. An ice-I-like cluster has a mixed combination of axial and equatorial orientations including boat form of oxygen skeleton. Our result indicates that a pentagon unit of water cluster is more (or not less) stable than a hexagon unit. But there remain the following arguments: (i) In case of three-body interactions, the energy per molecule for EH is the largest. This shows the tendency that the hexamer has stronger many-body interactions than the pentagon. However, according to the calculation in the previous section, the four-body interactions are small of the order of one tenth

of the three-body interactions. (ii) These comparisons are made upon the unoptimized structures. Thus our results are not appropriate for the exact comparison of the stabilities of clusters at optimized structures. However, we can predict the optimized structures from the results in Table 2; The minimum of R_{OO} distance of the nearest neighbor two-body interaction is around 2.98 Å. The non-nearest neighbor two-body and total three-body interactions shrink the R_{OO} distance. BE's increase by stretching OH-bond distances. Therefore the energy minima will be located on the crossing points of the four geometrical points, when we apply the monomer-destabilization energy using the function of Carney *et al.*²⁶ which gives a very reliable description of force constants and potential surfaces for monomer. The destabilization energy of water monomer increases quadratically by stretching OH-bonds²⁷. Therefore, the difference in BE between hexagon and pentagon at their minima would be similar to those at four geometrical points.

Consequently, the pentagon would have larger BE even at this minimum.

Conclusion

The geometry of hexagonal hexamer optimized with 4-31G basis set shows that the monomer geometry is too much distorted. At this geometry, the total nonadditive many-body interactions higher than four-body are quite small. Comparing the energies of pentagon and hexagon as single units of water clusters, the pentagon is more stable than the hexagon. However the hexagonal unit can have an infinite network while the pentagonal unit can make only a finite size of clusters. When the size of cluster becomes large, many-body interactions contribute to the total binding energy. Thus the hexagonal units is more stable in large ordered clusters or in ices. However in liquid phases where small water clusters are preferable, the ratio of pentagon to hexagon increases with temperature rise. Water clusters with pentagonal units have less molar volume than those composed of hexagonal units assuming the same R_{OO} distance.

Acknowledgement. The authors are grateful to Professor Keiji Morokuma for discussions and support for BJY. The numerical calculations were carried out at the Institute for Molecular Science in Japan. BJY thanks for the support from the Korea Science and Engineering Foundations (891-0303-030-2) and BJY's stay at IMS was also supported by the IMS Japan-Korean Cooperative Program.

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