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Ab initio studies of the water hexamer: near degenerate structures

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Ab initio HF-SCF calculations have been performed on several structures of the water hexamers which are expected to have low-lying energies in the potential energy hypersurface. The SCF results with the DZP basis sets show that the hexamer with the global minimum energy has the structure of the cyclic oxygens with the S_6 symmetry. However, the energy of the hexamer with open-book-shaped oxygens is almost as low as that of the cyclic hexamer.

The study of water clusters is directly related to that of liquid water, ice and biomolecular hydration. To study the structures, spectra, energetics, and dynamics of water clusters, a number of experimental studies have been reported [1–3]. Yet, little information for the water clusters is available [4–6] except for the dimer. Just as in experiment, a multitude of theoretical studies have been done on water clusters. However, most calculations have focused on the water dimer [7,8]. Few ab initio studies have been reported for water clusters larger than the dimer [9,10]. This is because these water clusters are very large for theoretical studies.

Since water clusters are stabilized by hydrogen bonding, it is not suitable to use the minimal basis sets for ab initio calculations. Even the double-zeta (DZ) basis set is not suitable, because it predicts a wide bond angle ($\angle$ H–O–H). Therefore, to get reliable results for water clusters, we need to perform ab initio calculations at least at the level of the double-zeta polarization (DZP) basis sets. This situation has discouraged theoretical chemists to perform ab initio calculations on water clusters larger than the dimer. Consequently, no reliable ab initio calculations of the water hexamer have been attempted yet.

As an alternative method, the analytical water–water potential functions have been used to study water clusters [11–17]. According to these studies,

the water trimer, tetramer and pentamer are cyclic, whereas the water clusters larger than the heptamer are not cyclic. It is not clear whether the hexamer is cyclic. The analytical water–water potential functions are not reliable enough to predict correct geometries unless there are large energy differences between different structures. It is because the potential parameters are either empirically derived or analytically fitted to the ab initio water–water interaction potentials calculated at the limited number of geometries. As a simple example, one may note that different potentials predict different structures for the water octamer [15,16]. Nevertheless, the study based on these analytical potential functions has provided basic ideas for the structures and energetics of the water clusters. Further, whenever there have been wrong predictions, potential parameters have been upgraded by adding more parameters; otherwise, new, better or more complicated analytical functions have been devised.

Based on the MCY [18] and CCD [19] potential functions, we previously reported the low-lying energy structures for small water clusters ranging from the tetramer through octamer [11]. For each cluster except for the hexamer, the order of the binding energies for various structures showed a very good consistency between the MCY and CCD potentials. However, for the hexamer, such a consistency was

lost, and the MCY energy order was very different from the CCD energy order.

The six low-lying energy structures for the MCY potential are shown as B through E′ in fig. 1. Structure E is the global minimum for the MCY. The cyclic structure A is not among the six low-lying MCY energy structures, B through E′. The low-lying energy structures for the MCY were searched for with the Monte Carlo method using the Metropolis algorithm. The searching was done by quenching about 100 randomly generated initial structures which were assumed to have a reasonable statistical distribution. We happened to report six hexamer structures whose MCY energies were less than 7.10 kcal/mol monomer. Consequently, the cyclic structure was not reported.

In fig. 1, it is interesting to note the following. There are some similarities between structures B and B′ and between structures E and E′. Structure A has only one 6-membered ring shape with S_6 symmetry, while structures B through E′ have multi-ring shapes. Structures B, C, D and E have a 4-, 4-, and 6-membered ring shape, a 3-, 3-, 4-, 4-, 4-membered ring shape (i.e. a triangular prism shape), a 4-, 5-, 5-membered ring shape, and a 4-, 4-,·4-, 4-membered ring shape, respectively.

The study based on the CCD potential was done only for the potential hypersurfaces near the six low-lying MCY energy structures. Thus, the cyclic structure was not studied with the CCD potential in the previous work. For the CCD potential, structure C in the MCY potential was not stable, but merged into structure B which turned out to have the lowest energy among the remaining five CCD structures (B, B′, D, E, E′). As already mentioned, the CCD energy order is very different from the MCY energy order. Since the low-lying energy structures were searched for based on the MCY potential, one might worry if other low-lying energy structures (such as the cyclic structure) for the CCD potential could be missed.

Belford and Campbell reported that the inclusion of the nonadditive component of the Campbell–Mezei potential seriously altered the energies of the local minima on the potential energy hypersurface [17]. The additive approximation (pairwise energy sum) favored a nearly planar ring, whereas the nonadditive energy preferred a staggered hexagon.

Let us apply Campbell's argument to the MCY and CCD potentials. The MCY potential is only pairwise. The CCD potential includes the nonadditive potential up to the four body interactions in addition to the MCY potential. Therefore, even if the pairwise MCY potential does not include the cyclic stag-
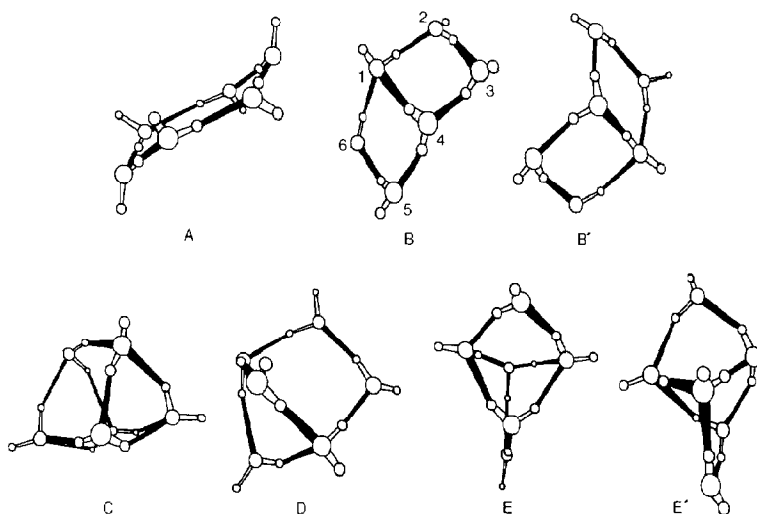

Fig. 1. The low-lying energy structures of the water hexamer. Since the theoretical methods (of the MCY, CCD, SCF) do not significantly alter the structural shapes, the seven structures drawn are based on our most reliable results. We took structure A from the SCF(FOPT)/DZP, B from SCF(COPT)/DZP, B′, C, E, and E′ from CCD, and D from MCY.

gered hexagon structure among the low-lying energy structures, we expect the nonadditive CCD potential may include it.

To study such a possibility, we first checked if the MCY potential may find the cyclic planar structure instead of the cyclic staggered one. But, with the MCY potential, the planar structure is not stable, while the staggered hexagon structure with the O–O–O–O torsional angle of $\pm 38°$ is reasonably stable (-7.03 kcal/mol monomer). This fact is in contradiction with Campbell's argument that the pairwise potential prefers the planar shape. Since the MCY and CCD potentials are very different from the Campbell–Mezei potentials, we may not expect that our system should be consistent with Campbell's. However, his argument needs to be seriously considered in our system in a different way because of the inconsistency between the MCY and CCD energy orders for the hexamer.

To resolve the complexity of the problem for the hexamer, we have performed ab initio calculations for the cyclic structure A as well as the five low-lying energy structures (B, B', D, E, E'). Since ab initio calculations with large basis sets are too costly for very weakly bound 18-atom geometry optimization, we first calculated the SCF energies at the geometries predicted by the CCD potential. The calculations were performed with GAUSSIAN 88 [20]. These results are labeled as SCF(CCD). Therefore, in this case, each monomer in the hexamer has the experimental monomer geometry with the O–H bond distance of 0.9572 Å and the ∠H–O–H bond angle of 104.52°. The SCF minimum energy structures near the CCD minima were determined by energy gradient methods. The SCF geometry optimization was

done as either the full optimization (SCF(FOPT)) of all parameters or the constrained optimization (SCF(COPT)). The SCF(COPT) is denoted for the SCF geometry optimization in which each monomer is constrained to keep the bond lengths and angle equal to the experimental monomer values.

The DZP (we use the Huzinaga/Dunning basis sets [21] with five d orbitals with the exponent 0.8 for the oxygen) gives reasonable values for the water monomer with the bond length of 0.944 Å and the bond angle of 106.7°. On the other hand, the DZ basis sets of the Huzinaga/Dunning type give 112° for the bond angle of the water monomer. Since the angle is too large, the SCF(FOPT) may distort the water cluster structures. Thus, in the DZ case we expect that the SCF(COPT) results will be more reliable than the SCF(FOPT). Indeed, we note from our previous paper [11] that for the predicted energies and geometries there were only small differences between SCF(CCD) and SCF(COPT) methods with the DZ valence (DZV) basis sets, which are similar to, but yet less accurate than the DZ. Therefore, the SCF(CCD) results will be very useful to select the low-lying SCF energy structures which may be possible candidates for the global minimum.

The SCF(CCD)/DZ binding energies of the five low-lying energy structures are shown in table 1. The binding energies of the lowest energy structure B and the next lowest energy structure D are 10.41 and 10.09 kcal/mol monomer, respectively. We note in table 1 that the CCD results are consistent with the SCF(CCD) results, while the MCY results are not. Since the SCF(CCD) result is more reliable than the CCD which in turn is more reliable than the MCY, we expect that the structure B can be a good can-

Table 1

The binding energies of various water hexamer structures (in kcal/mol monomer)

	A	B	B'	C	D	E	E'
MCY	-7.03	-7.16	-7.12	-7.22	-7.18	-7.25	-7.10
CCD	–	-8.52	-8.31	B	-8.45	-8.44	-8.15
SCF(CCD)/DZ	–	-10.41	-9.80		-10.09	-9.91	-9.42
SCD(COPT)/DZ	-11.11	-10.60					
SCF(COPT)DZ/DZP [a]	-6.81	-6.71					
SCF(COPT)/DZP	-7.27	-7.07					
SCF(FOPT)/DZP [b]	-7.15						

[a] The energies at the SCF(COPT)/DZ geometries with the DZP basis sets.

[b] -456.34924 hartree for the SCF energy.

Table 2

The structure and spectra of the cyclic hexamer predicted by SCF(FOPT)/DZP [a]

O–H$_h$	0.957	O–O	2.816	O–H$_h$---O	176.4
O–H$_n$	0.944	∠O-O-O	118.2	O---O–H$_n$	122.9
∠H–O–H	106.7	∠O-O-O-O	±26.4	∠H$_n$–O---O–H$_n$	∓111.4

Sym.	Freq.	1000	Raman	Sym.	Freq.	000	Raman	Sym.	Freq.	000	Raman
a$_g$	4242	0	137	a$_u$	1796	210	0	e$_g$	255	0	0.2
e$_u$	4241	185	0	a$_g$	911	0	1	e$_u$	236	393	0
e$_g$	4240	0	94	e$_u$	828	406	0	e$_u$	187	19	0
a$_u$	4240	295	0	a$_u$	771	713	0	e$_g$	176	0	5
a$_u$	4006	85	0	e$_g$	761	0	2	a$_u$	155	114	0
e$_g$	3993	0	98	e$_g$	434	0	4	a$_g$	143	0	0.2
e$_u$	3958	1670	0	a$_u$	415	46	0	a$_u$	81	3	0
a$_g$	3918	0	358	e$_u$	412	26	0	a$_g$	52	0	1
a$_g$	1824	0	1	a$_g$	386	0	3	e$_g$	45	0	0.2
e$_u$	1814	259	0	a$_u$	281	4	0	e$_u$	31	0.4	0
e$_g$	1800	0	5	a$_g$	278	0	14				

[a] Distances are in Å, and angles in deg. H$_h$ denotes the hydrogen participating in hydrogen bond, and H$_n$ the hydrogen not participating in hydrogen bond. Frequencies, IR intensities and Raman activities are in cm^{-1}, Km/mol and Å^4/amu, respectively.

Table 3

The structure of the open-book-shaped hexamer [a]

	MCY	CCD	SCF(COPT)/DZV
O---O	2.797–2881	2.652–2.744	2.671–2.737
O$_1$---O$_4$	2.960	2.937	3.134
O---H$_h$	1.866–1.942	1.696–1.825	1.723–1.836
O$_1$---H$_{4h}$	2.049	2.059	2.267
	SCF(FOPT)/DZV	SCF(COPT)/DZ	SCF(COPT)/DZP
O---O	2.635–2.722	2.670–2.745	2.819–2.866
O$_1$---O$_4$	3.103	3.140	3.258
O---H$_h$	1.673–1.813	1.861–1.921	1.865–1.969
O$_1$---H$_{4h}$	2.244	2.252	2.358

SCF(COPT)/DZP

∠O$_1$–O$_2$–O$_3$, ∠O$_1$–O$_6$–O$_5$	99, 100	∠O$_1$–O$_2$–O$_3$–O$_4$	7
∠O$_2$–O$_3$–O$_4$, ∠O$_4$–O$_5$–O$_6$	89, 88	∠O$_1$–O$_6$–O$_5$–O$_4$	−11
∠O$_2$–O$_1$–O$_6$	127	∠O$_2$–O$_1$–O$_4$–O$_5$	140
∠O$_3$–O$_4$–O$_5$	146	∠O$_3$–O$_4$–O$_1$–O$_6$	136

[a] Distances are in Å, and angles in deg.

didate for the possible global minimum.

However, according to Campbell's argument, we need to assume that the cyclic staggered hexagon structure can have the lowest energy. Although for the MCY potential the cyclic planar shape is not stable, Campbell's argument for the importance of the nonadditivity term is now strongly supported in that

the results predicted by the MCY and CCD potentials are very different. Therefore, we investigated two structures A and B with the SCF(COPT) using the DZ and DZP basis sets. The results are shown in table 1. In accordance with Campbell's argument, the SCF(COPT)/DZ result shows that the cyclic staggered hexamer (A) is the global energy minimum

structure, the binding energy of which is surprisingly lower than that of the structure B by 0.5 kcal/mol monomer. Therefore, for an adequate study of water clusters and bulk water, it is necessary to take into account the nonadditive potential term.

The DZ results should not be considered to be very reliable for water cluster calculations. Thus, we performed SCF(COPT/DZ)/DZP calculations, which are the SCF/DZP calculations at the SCF(COPT)/DZ geometries. Then, the energy difference between structures A and B is reduced to only 0.10 kcal/mol monomer. Therefore, we performed much more reliable calculations using SCF(COPT)/DZP. The binding energies for structures A and B are 7.27 and 7.07 kcal/mol monomer, respectively. This indicates that the two structures are nearly degenerate.

Finally, we report the structures and spectra of the cyclic water hexamer in table 2, and the structure of the open-book-shaped hexamer in table 3. From table 2, the torsional angle of O–O–O–O for the cyclic hexamer is $\pm 26°$. For the open-book-shaped structure, table 3 shows that for the MCY the distance of O_1–O_4 is small enough to have a strong hydrogen bonding, while for the SCF(COPT)/DZP the distance is rather long. Thus, in the MCY, the open-book-shaped structure is more stable, while in the SCF(COPT)/DZP the cyclic is rather more stable. To confirm whether the structure A is the true global minimum, further research needs to include zero-point energies as well as electron correlation effects.

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