Theoretical Study of the Lowest Energy Structure of the Water Undecamer

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Density functional calculations and *ab initio* calculations have been carried out to study the lowest energy structure of the water $(H_2O)_{11}$. Among five structures suggested by four different groups, the lowest energy structure is found to have the skeletal structure of Prism56 (Pr56-24) that a cyclic pentamer and a cyclic hexamer are fused into a prism-shape with 16 hydrogen-bonds (HBs).

Key Words : Water clusters, Undecamer, Hydrogen bond

Introduction

Small water clusters $(H_2O)_n$ have been extensively studied with tremendous experimental[1,2] and theoretical[3-15] efforts in the recent past. Studies of structures and energetics of water clusters are of importance for understanding various phenomena such as hydration by cations,[16] anions,[17] electrons,[18] and organic/bio-molecules[19] as well as various types of hydrogen bonding.[20]

Theoretically, at the early stage of low-level *ab initio* calculations there were a few studies of the dimer and cyclic water trimer.[3,4] The study of various low-lying energy conformers for water clusters $(H_2O)_{4\text{-}8}$ was first reported using simulated annealing Monte Carlo method employing various *ab initio* derived two-body to four-body interaction potentials and *ab initio* methods.[5] These predicted minimum energy structures have been found to be in excellent agreement with the experimental findings.[2] Owing to the nature of several isoenergetic conformers of the water hexamer and heptamer responsible for the facile structural changes between two dimensional and three dimensional structures, these conformers have been extensively investigated.[6] Very recently, structures of the water dimer to dodecamer based on extensive *ab initio* calculations have been reported.[7,8]

In the case of the undecamer, five global minimum energy structures have been reported by four different groups (Figure 1).[8,13-15] These conformers have different skeletal structures. Since the five structures are different, it is of importance to find the true lowest energy structure.

As for the empirical studies of $(H_2O)_{11}$, Niesse and Mayne,[13] on the basis of TIP3P potential, reported that the lowest energy conformer of $(H_2O)_{11}$ is Pr56-134, a Prism56 skeletal shape fused by cyclic hexamer and pentamer. Wales and Hodges[14] reported that the lowest energy structures based on the TIP4P potential is a Prism56$_B$ structure (which will be defined in our terminology as a fused structure with a pentagonal pentamer and an open-book-shape hexamer) and new lowest-energy conformer Pr56-13 on the TIP3P potential. Sadlej reported another structure (Prism55+1) using Hartee-Fock calculations with 6-31G* basis set.[15] On the other hand, Kim and coworkers reported that the lowest energy structure is Pr56-24 based on various levels of theoretical methods.[8] However, there was no direct comparison between Pr56-24 and Pr55+1. Furthermore, Sobolewski and Domcke in their study of the water undecamer use Sadlej's structure as the lowest energy conformer.[15] Therefore, the structure of $(H_2O)_{11,12}$ is controversial.

Since no direct comparison of the five structures based on reliable *ab initio* energetics has been made yet, here we compare six structures including Prism443 structure, using the density functional theory (DFT) calculations and Møller-Plesset second order perturbation (MP2) calculations.

Calculation Methods

To locate the low-lying energy structures of neutral water undecamer, we employed the Becke-3 parameters exchange and Lee-Yang-Parr correlation functionals (B3LYP) method by geometry optimization. The 6-311++G**(sp) basis set with 5d components was used, where diffuse sp basis function for heavy oxygen atoms was added. These B3LYP calculation methods have been widely used to predict the vibrational frequencies and thermodynamic quantities as

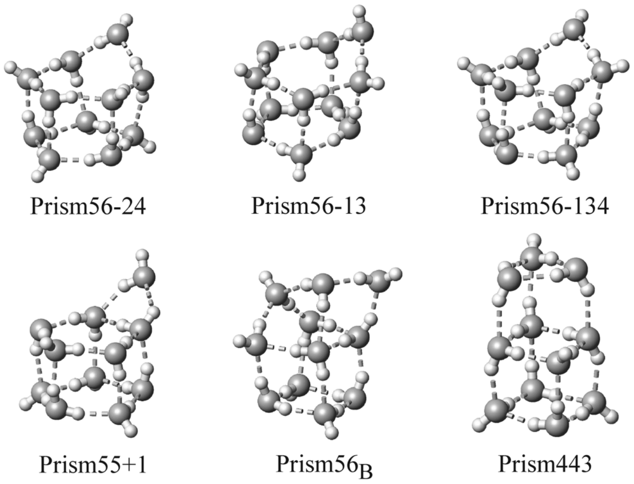
Prism56-24 Prism56-13 Prism56-134
Prism55+1 Prism56$_B$ Prism443

Figure 1. Six structures of neutral water undecamer.

Table 1. Interaction energies and geometrical parameters of neutral water undecamers, $(H_2O)_{11}$

Conf.	$-\Delta E^{B3LYP}$	$-\Delta E^{MP2}$	#HB	#ddaa	$r(OO)_{av}$	$\angle(OOO)_{min}$	A	B	C	μ
Pr56-24	110.81	115.65	16	0	2.788	84.1	0.495	0.446	0.385	2.65
Pr56-13	110.42	115.34	16	0	2.791	82.8	0.498	0.446	0.378	2.43
Pr56-134	110.40	115.32	16	0	2.791	82.3	0.500	0.442	0.383	3.11
Pr55+1	108.77	114.47	17	2	2.820	57.7	0.540	0.402	0.373	2.89
Pr56B	108.74	114.96	17	2	2.809	74.5	0.605	0.412	0.371	3.44
Pr443	105.79	112.47	18	3	2.827	55.1	0.716	0.365	0.363	1.81

Binding energies are in kcal/mol, distances in Å, angles in degree, and dipole moment (μ) in debye (D). #HB is the number of H-bond interactions and #ddaa is the number of “ddaa”-type (double proton donor and double acceptor) water molecules. A, B and C are rotational constants (in GHz).

well as binding energies of many and various aqueous clusters.[6-9,16-20] The B3LYP-predicted vibrational frequencies of water clusters have been especially studied and effectively compared with the experimental outputs. The single point MP2 calculations with the same basis set were done to find a more accurate comparison.

Results and Discussion

Six structures of W11 are shown in Figure 1. Nomenclature of Prism conformers is noted in reference 8. Clusters with skeletons of Prism56-ij (Pr56-ij), Prism56$_B$ (Pr56$_B$), Prism55 +1 (Pr55+1) and Prism443 (Pr443) have 16, 17, 17 and 18 HBs, respectively. These skeletons have different HB-interaction frameworks. The binding energies and geometrical parameters are listed in Table 1. It should be noted that the lowest-energy conformer is Prism56-24 which was predicted by Lee *et al.*[8]

The skeletal shape of Pr56-ij is known to have 20 conformers depending on their H atom orientations.[8] Since the H atoms tend to be less clustered (with dangling H atoms separated), the lowest energy conformer was predicted to be Prism56-24. This is in good agreement in the results in Table 1. Skeletal shapes of Prism56$_B$ and Prism443 are slightly higher in energy than the lowest energy conformer of Prism56-24. Pr56$_B$ and Pr443 conformers have more HBs than Pr56-24 as listed in Table 1, but they should have considerable angular strains. A second lowest energy skeletal structure is Prism56$_B$ where a cyclic pentamer and an open-book hexamer are fused into a prism-shape. Prism56 conformers are stable among undecamers in Table 1, and the next stable conformers are Pr55+1 and Pr56$_B$, which are isoenergetic. Prism443 conformer is the least stable among the four different types of skeletons or among the given six conformers.

The Prism56-24" structure (with same HB helicities for pentagonal and hexagonal rings), which is topologically the same with the most stable W11:Prism56-24 structure (with opposite HB helicities), is nearly isoenergetic to it (within 0.09 kcal/mol in ΔE_e and ΔE_0).[8] These helicities have been discussed in the relative stabilies of other aqueous clusters; neutral water octamer (D_{2d} and S_4), water decamer (Prism55 and Prism55"),[7] dodecamer (Prism444 and Prism444", Prism66 and Prism66"),[8] electron-bound water octamer (Cd and Cd")[18j], and so on.

Table 1 lists the geometric parameters (the average O-O distances of interacting water molecules, the minimum O-O-O angle, and the rotational constants) and dipole moments. In general, the less-HB interaction systems have shorter O-O distances, and vice versa. Especially, Pr55+1 and Pr443 have small O-O-O interaction angles and large O-O interaction distances. Pr56-24 has short O-O interaction distance and large O-O-O interaction angle. The number of “ddaa”-type water molecules (dd: double proton-donor, aa: double proton-acceptor) in Table 1 is related to the characteristic feature representing condensed neutral water in each water molecule is coordinated by four water molecules, resulting in almost all “ddaa: type water molecules in aqueous and solid pahses. Pr55+1, Pr56$_B$ and Pr443 have two, two and three “ddaa”-type water molecules, respectively.

Conclusion

Based on the B3LYP/6-311++G**(sp) and MP2//B3LYP/6-311++G**(sp) calculations, the lowest energy conformer of the undecamer is Prism56-24 (a fused structure by cyclic water pentamer and hexamer), followed by Prism56-24". Thus, this clearly demonstrates that the structures reported by three groups[13-15] are not the lowest energy structure. This information would be very critical when the energy of the neural undecamer is compared with that of the ionized or electron-bound water undecamer. Among the clusters with the same and opposite HB helicities, the latter tends to be slightly more stable. Among the nearly isoenergetic conformers with the same skeleton of Prism56, dangling H atoms tend to be separated as much as possible, and so the structure with less clustered dangling H atoms tend to be more stable. The second low energy skeleton is Prism56$_B$. The important factors for stabilities of water undecamer are more effective and less-strained HB interactions, less clustered dangling H atoms, opposite HB helicities in the same fused frames.

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References

1. (a) Pimental, G. C.; Sederholm, C. H. *J. Chem. Phys.* **1956**, *24*, 639. (b) Fredin, L.; Nelander, B.; Ribbegard, G. *J. Chem. Phys.* **1977**, *66*, 4056. (c) Page, R. H.; Frey, J. G.; Shen, Y.-P.; Lee, Y. T.

Chem. Phys. Lett. **1984**, *106*, 373. (d) Coker, D. F.; Miller, R. E.; Watts, R. O. *J. Chem. Phys*. **1985**, *82*, 3554. (e) Dyke, T. R.; Muenter, J. S. *J. Chem. Phys*. **1972**, *57*, 5011. (f) Curtiss, L. A.; Frurips, D. L.; Blander, M. *Chem. Phys. Lett*. 1978, *54*, 575. (g) Pugliano, N.; Saykally, R. J. *Science* **1992**, *257*, 1937.

2. (a) Liu, K.; Brown, M. G.; Carter, C.; Saykally, R. J.; Gregory, J. K.; Clary, D. C. *Nature* **1996**, *381*, 501. (b) Pribble, R. N.; Zwier, T. S. *Science* **1994**, *265*, 75. (c) Gruenloh, C. J.; Carney, J. R.; Hagemeister, F. C.; Arrington, C. A.; Zwier, T. S. *J. Chem. Phys*. **1998**, *109*, 6601. (d) Huisken, F.; Kaloudis, M.; Kulcke, A. *J. Chem. Phys*. **1996**, *104*, 17. (e) Buck, U.; Ettischer, I.; Melzer, M.; Buch, V.; Sadlej, J. *Phys. Rev. Lett*. **1998**, *80*, 2578. (f) Buck, U.; Huisken, F. *Chem. Rev.* **2000**, *100*, 3863. (g) Nauta, K.; Miller, R. E. *Science* **2000**, *287*, 293.
3. (a) Morokuma, K.; Pederson, L. *J. Chem. Phys*. **1968**, *48*, 3275. (b) Kollman, P. A.; Allen, L. C. *J. Chem. Phys*. **1969**, *51*, 3286.
4. Del Bene, J.; Pople, J. A. *J. Chem. Phys*. **1969**, *4*, 426; *J. Chem. Phys*. **1970**, *52*, 4858.
5. Kim, K. S.; Dupuis, M.; Lie, G. C.; Clementi, E. *Chem. Phys. Lett.* **1986**, *131*, 451.
6. (a) Kim, J.; Kim, K. S. *J. Chem. Phys.* **1998**, *109*, 5886. (b) Kim, J.; Majumdar, D.; Lee, H. M.; Kim, K. S. *J. Chem. Phys.* **1999**, *110*, 9128.
7. Lee, H. M.; Suh, S. B.; Lee, J. Y.; Tarakeshwar, P.; Kim, K. S. *J. Chem. Phys.* **2000**, *112*, 9759; **2001**, *114*, 3343.
8. Lee, H. M.; Suh, S. B.; Kim, K. S. *J. Chem. Phys.* **2001**, *114*, 10749; **2001**, *115*, 7331.
9. (a) Mhin, B. J.; Kim, H. S.; Kim, H. S.; Yoon, J. W.; Kim, K. S. *Chem. Phys. Lett.* **1991**, *176*, 41. (c) Kim, K. S.; Mhin, B. J.; Choi, U.-S.; Lee, K. *J. Chem. Phys.* **1992**, *97*, 6649. (d) Mhin, B. J.; Lee, S. J.; Kim, K. S. *Phys. Rev. A* **1993**, *48*, 3764. (e) Mhin, B. J.; Kim, J.; Lee, S.; Lee, J. Y.; Kim, K. S. *J. Chem. Phys*. **1994**, *100*, 4484. (f) Kim, J.; Mhin, B. J.; Lee, S. J.; Kim, K. S. *Chem. Phys. Lett.* **1994**, *219*, 243. (g) Kim, J.; Lee, J. Y.; Lee, S.; Mhin, B. J.; Kim, K. S. *J. Chem. Phys.* **1995**, *102*, 310.
10. (a) Graf, S.; Mohr, W.; Leutwyler, S. *J. Chem. Phys.* **1999**, *110*, 7893. (b) Kryachko, E. S. *Chem. Phys. Lett.* **1997**, *272*, 132.
11. Franken, K. A.; Jalaie, M.; Dykstra, C. E. *Chem. Phys. Lett*. **1992**, *198*, 59.
12. (a) Fowler, J. E.; Schaefer III, H. F. *J. Am. Chem. Soc*. **1995**, *117*, 446. (b) Klopper, W.; Lüthi, H. P. *Mol. Phys*. **1999**, *96*, 559.
13. Niesse, J. A.; Mayne, H. R. *J. Comp. Chem*. **1997**, *18*, 1233.
14. Wales, D. J.; Hodges, M. P. *Chem. Phys. Lett*. **1998**, *286*, 65.
15. (a) Sadlej, J. *Chem. Phys. Lett*. **2001**, *333*, 485. (b) Sobolewski, A. L.; Domcke, W. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1130.
16. (a) Feller, D.; Glendening, E. D.; Kendall, R. A.; Peterson, K. A. *J. Chem. Phys*. **1994**, *100*, 4981. (b) Glendening, E. D.; Feller, D. *J. Phys. Chem*. **1995**, *99*, 3060. (c) Feller, D.; Glendening, E. D.; Woon, D. E. *J. Chem. Phys.* **1995**, *103*, 3526. (d) Feller, D. *J. Phys. Chem. A* **1997**, *101*, 2723. (e) Kim, J.; Lee, S.; Cho, S. J.; Mhin, B. J.; Kim, K. S. *J. Chem. Phys.* **1995**, *102*, 839. (f) Lee, S.; Kim, J.; Park, J. K.; Kim, K. S. *J. Phys. Chem*. **1996**, *100*, 14329. (g) Lee, H. M.; Kim, J.; Lee, S.; Mhin, B. J.; Kim., K. S. *J. Chem. Phys.* **1999**, *111*, 3995.
17. (a) Robertson, W. H.; Diken, E. G.; Price, E. A.; Shin, J.-W.; Johnson, M. A. *Science* **2003**, *299*, 1367. (b) Baik, J.; Kim, J.; Majumdar, D.; Kim, K. S. *J. Chem. Phys.* **1999**, *110*, 9116. (c) Majumdar, D.; Kim, J.; Kim, K. S. *J. Chem. Phys*. **2000**, *112*, 101. (d) Kim, J.; Lee, H. M.; Suh, S. B.; Majumdar, D.; Kim, K. S. *J. Chem. Phys.* **2000**, *113*, 5259. (e) Lee, H. M.; Kim, K. S. *J. Chem. Phys.* **2001**, *114*, 4461. (f) Lee, H. M.; Kim, D.; Kim, K. S. *J. Chem. Phys*. **2002**, *116*, 5509. (g) Lee, H. M.; Kim, K. S. *Mol. Phys.* **2002**, *100*, 875. (h) Ayotte, P.; Johnson, M. A. *J. Chem. Phys*. **1997**, *106*, 811. (i) Kim, J.; Becker, I.; Cheshnovsky, O.; Johnson, M. A. *Chem. Phys. Lett*. **1998**, *297*, 90. (j) Weber, J. M.; Kim, J.; Woronowicz, E. A.; Weddle, G. H.; Becker, I.; Cheshnovsky, O.; Johnson, M. A. *Chem. Phys. Lett*. **2001**, *339*, 337.
18. (a) Ayotte, P.; Weddle, G. H.; Bailey, C. G.; Johnson, M. A.; Vila, F.; Jordan, K. D. *J. Chem. Phys.* **1999**, *110*, 6268. (b) Bailey, C. G.; Kim, J.; Johnson, M. A. *J. Phys. Chem*. **1996**, *100*, 16782. (c) Ayotte, P.; Bailey, C. G.; Kim, J.; Johnson, M. A. *J. Chem. Phys*. **1998**, *108*, 444. (d) Kim, J.; Park, J. M.; Oh, K. S.; Lee, J. Y.; Lee, S.; Kim, K. S. *J. Chem. Phys.* **1997**, *106*, 10207. (e) Kim, J.; Lee, J. Y.; Oh, K. S.; Park, J. M.; Lee, S.; Kim, K. S. *Phys. Rev. A* **1999**, *59*, R930. (f) Kim, J.; Suh, S. B.; Kim, K. S. *J. Chem. Phys.* **1999**, *111*, 10077. (g) Lee, H. M.; Suh, S. B.; Kim, K. S. *Bull. Korean Chem. Soc.* **2000**, *21*, 555. (h) Suh, S. B.; Lee, H. M.; Kim, J.; Lee, J. Y.; Kim, K. S. *J. Chem. Phys.* **2000**, *113*, 5273. (i) Park, I.; Cho, K.; Lee, S.; Kim, K. S.; Joannopoulos, J. D. *Comput. Materials Sci.* **2001**, *21*, 291. (j) Lee, H. M.; Kim, K. S. *J. Chem. Phys.* **2002**, *117*, 706. (k) Lehr, L.; Zanni, M. T.; Frischkorn, C.; Weinkauf, R.; Neumark, D. M. *Science* **1999**, *284*, 635.
19. (a) Kim, K. S.; Lee, J. Y.; Choi, H. S.; Kim, J.; Jang, J. H. *Chem. Phys. Lett.* **1997**, *265*, 497. (b) Tarakeshwar, P.; Kim, K. S.; Brutschy, B. *J. Chem. Phys.* **2001**, *114*, 1295. (c) Manojkumar, T. K.; Choi, H. S.; Tarakeshwar, P.; Kim, K. S. *J. Chem. Phys.* **2003**, *118*, 8681. (d) Kim, K. S.; Lee, J. Y.; Lee, S. J.; Ha, T.-K.; Kim, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 7399. (e) Oh, K. S.; Lee, C.-W.; Choi, H. S.; Lee, S. J.; Kim, K. S. *Org. Lett.* **2000**, *2*, 2679. (f) Ihm, H.; Yun, S.; Kim, H. G.; Kim, J. K.; Kim, K. S. *Org. Lett.* **2002**, *4*, 2897. (g) Yun, S.; Kim, Y.-O.; Kim, D.; Kim, H. G.; lhm, H.; Kim, J. K.; Lee, C.-W.; Lee, W. J.; Yoon, J.; Oh, K. S.; Yoon, J.; Park, S.-M.; Kim, K. S. *Org. Lett.* **2003**, *5*, 471. (h) Yun, S.; Ihm, H.; Kim, H. G.; Lee, C.-W.; Banyopadhyay, I.; Oh, K. S.; Gong, Y. J.; Lee, J. W.; Yoon, J.; Lee, H. C.; Kim, K. S. *J. Org. Chem.* **2003**, *68*, 2467.
20. (a) Scheiner, S. *Hydrogen Bonding*; Oxford University Press: 1997. (b) Kim, K. S.; Tarakeshwar, P.; Lee, J. Y. *Chem. Rev.* **2000**, *100*, 4145. (c) Tarakeshwar, P.; Lee, H. M.; Kim, K. S. In *Reviews of Modern Quantum Chemistry*; Sen, K. D., Ed.; World Scientific: Singapore, 2002; pp 1642-1683. (d) Kim, K. S.; Suh, S. B.; Kim, J. C.; Hong, B. H.; Lee, E. C.; Yun, S.; Tarakeshwar, P.; Lee, J. Y.; Kim, Y.; Ihm, H.; Kim, H. G.; Lee, J. W.; Kim, J. K.; Lee, H. M.; Kim, D.; Cui, C.; Youn, S. J.; Chung, H. Y.; Choi, H. S.; Lee, C.-W.; Cho, S. J.; Jeong, S.; Cho, J.-H. *J. Am. Chem. Soc.* **2002**, *124*, 14268. (e) Hong, B. H.; Lee, J. Y.; Lee, C.-W.; Kim, J. C.; Bae, S. C.; Kim, K. S. *J. Am. Chem. Soc.* **2001**, *123*, 10748. (f) Hong, B. H.; Bae, S. C.; Lee, C.-W.; Jeong, S.; Kim, K. S. *Science* **2001**, *294*, 348. (g) Kim, K. S.; Oh, K. S.; Lee, J. Y. *Proc. Natl. Acad. Sci. USA* **2000**, *97*, 6373. (h) Oh, K. S.; Cha, S.-S.; Kim, D.-H.; Cho, H.-S.; Ha, N.-C.; Choi, G.; Lee, J. Y.; Tarakeshwar, P.; Son, H. S.; Choi, K. Y.; Oh, B.-H.; Kim, K. S. *Biochemistry* **2000**, *39*, 13891. (i) Kim, K. S.; Kim, D.; Lee, J. Y.; Tarakeshwar, P.; Oh, K. S. *Biochemistry* **2002**, *41*, 5300. (j) Tarakeshwar, P.; Kim, K. S. *J. Mol. Struct.* **2002**, *615*, 227. (k) Tarakeshwar, P.; Choi, H. S.; Kim, K. S. *J. Am. Chem. Soc.* **2001**, *123*, 3323. (l) Lin, J.; Frey, P. A. *J. Am. Chem. Soc.* **2000**, *122*, 11258.
21. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortz, J. V.; Forseman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkely, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Rev. A; Gaussian, Inc.: Pittsburgh, PA, **1995**.