11568 J. Am. Chem. Soc. **1994,** *116,* 11568−11569

Low-Energy Structures and Vibrational Frequencies of the Water Hexamer: Comparison with Benzene−$(H_2O)_6$

Kyungsun Kim,[†] Kenneth D. Jordan,[*,†] and
Timothy S. Zwier[*,‡]

Departments of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260
Purdue University, West Lafayette, Indiana 47907

Received July 11, 1994

Small water clusters have been the subject of numerous experimental and theoretical studies. The lowest energy structures of the water dimer and trimer are well established from experiment, but larger clusters have so far resisted structural characterization. There is now general agreement from calculations that the global minima of the water trimer and tetramer are simple ring structures[1−4] and that the octamer and larger clusters prefer three-dimensional structures.[5,6] It also appears that the pentamer and heptamer prefer respectively cyclic and three-dimensional structures.[1,7] The situation regarding the hexamer is less clear cut. The hexamer has a large number of low-energy structures.[1,3,8−13] Hartree−Fock (HF) calculations,[8,11] second-order many-body perturbation theory (MP2) calculations using HF-optimized geometries,[11] and density functional calculations[12,14,15] all predict the global minimum to be a ring species. On the other hand, MP2 calculations using flexible basis sets and MP2-optimized geometries indicate that structures **I** and **II**, shown in Figure 1, are several tenths of a kcal/mol below the ring structure (**III**).[13,14] Several studies using model potentials also have predicted various three-dimensional structures to be more stable than the ring structure.[1,3,4,8,9,11]

Although there is no experimental work that bears directly on the relative stability of different forms of the water hexamer, the recently measured vibrational spectrum of the benzene−$(H_2O)_6$ cluster is consistent with a structure in which benzene is π-hydrogen-bonded to the surface of a three-dimensional water cluster, containing either two or three double-donor water molecules.[16] This conclusion is based on the observation that the OH stretching frequencies associated with the three types of OH groups in the cluster—double-donor OH groups and single-donor and free OH groups of the single-donor molecules—fall in different frequency ranges. Force field calculations using the MMC method[17] also support the picture that the benzene molecule is bound to the surface of the $(H_2O)_6$ cluster.[18]

In this work we calculate at the MP2[19] level of theory the harmonic OH stretching vibrational frequencies of structures **I**,

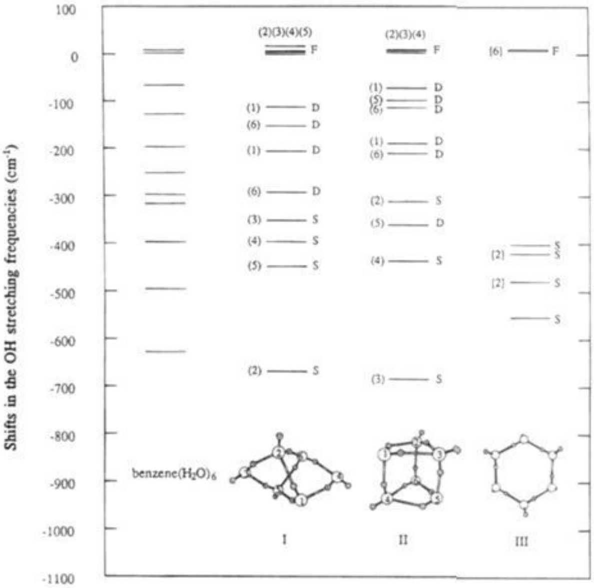

Figure 1. Shifts (cm^{-1}) in the OH stretching frequencies measured for benzene−$(H_2O)_6$ (ref 16) and calculated for structures **I**, **II**, and **III** of the water hexamer. The shifts are reported relative to the mean of the two OH stretching frequencies of the water monomer. The OH stretching modes are labeled by F, S, and D to denote their parentage as free OH, single-donor OH, and double-donor OH stretching modes, respectively. For **I** and **II**, the water molecule on which a particular vibration is localized is indicated in parentheses. Doubly degenerate modes of **III** are indicated by [2].

II, and **III** (shown in Figure 1) of $(H_2O)_6$ and compare these with the measured frequencies of benzene−$(H_2O)_6$ with the goal of establishing the nature of the water portion of the complex. **III** is a cyclic species of S_6 symmetry, and **I** and **II** are low-energy "three-dimensional" forms of the hexamer. The frequencies are calculated using analytic second derivatives evaluated at the MP2-optimized geometries and using a 6-31+G(2d,p) contracted Gaussian basis set, formed by adding to the 6-31+G basis set[20] the two oxygen d functions and the tight hydrogen p function from the aug-cc-pVDZ basis set.[21] MP2 calculations with the 6-31+G(2d,p) basis set give for the water monomer and dimer geometries and vibrational frequencies very close to those obtained using the more flexible aug-cc-pVDZ basis set. Moreover, for the $(H_2O)_6$ structures considered, the MP2 geometries obtained using the 6-31+G-(2d,p) basis set are in excellent agreement with those obtained using the more flexible aug-cc-pVDZ* basis set (formed by deleting the diffuse hydrogenic p functions from the aug-cc-pVDZ basis set).[13] All calculations are carried out with the Gaussian 92 program[22] using the frozen-core approximation.

Before discussing the vibrational frequencies, we first consider the energetics of **I**, **II**, and **III**. The MP2 calculations with the 6-31+G(2d,p) basis set predict **I** and **II** to be energetically more stable than the ring structure, **III**, by 0.93 and 1.12 kcal/mol, respectively. These relative stabilities are

---

[†] University of Pittsburgh.

[‡] Purdue University.

(1) Tsai, C. J.; Jordan, K. D. *J. Phys. Chem.* **1993**, *97*, 5208.

(2) Mo, O.; Yanez, M.; Elguero, J. *J. Chem. Phys.* **1993**, *97*, 6628.

(3) Vegiri, A.; Farrantos, S. C. *J. Chem. Phys.* **1993**, *98*, 4059.

(4) Schroder, K. *Chem. Phys.* **1988**, *123*, 91.

(5) Kim, K. S.; Dupuis, M.; Lie, G. L.; Clementi, E. *Chem. Phys. Lett.* **1986**, *131*, 451.

(6) Tsai, C. J.; Jordan, K. D. *J. Chem. Phys.* **1991**, *95*, 3850.

(7) Tsai, C. J.; Jordan, K. D., unpublished results.

(8) Mhin, B. J.; Kim, H. S.; Kim, H. S.; Yoon, C. W.; Kim, K. S. *Chem. Phys. Lett.* **1991**, *176*, 41.

(9) Franken, K. A.; Jalaie, M.; Dykstra, C. E. *Chem. Phys. Lett.* **1992**, *198*, 59.

(10) Belford, D.; Campbell, E. S. *J. Chem. Phys.* **1987**, *86*, 7013.

(11) Mhin, B. J.; Kim, J.; Lee, S.; Kim, K. S. *J. Chem. Phys.* **1994**, *100*, 4484.

(12) Lee, C.; Chen, H.; Fitzgerald, G. *J. Chem. Phys.* **1994**, *101*, 4472.

(13) Tsai, C. J.; Jordan, K. D. *Chem. Phys. Lett.* **1993**, *213*, 181.

(14) Kim, K.; Jordan, K. D., in preparation.

(15) Laasonen, K.; Parinello, M.; Car, R.; Lee, C.; Vanderbilt, D. *Chem. Phys. Lett.* **1993**, *207*, 208.

(16) Pribble, R. N.; Zwier, T. S. *Science* **1994**, *265*, 75.

(17) Dykstra, C. E. *J. Chem. Phys.* **1989**, *91*, 6472.

(18) Augspurger, J. D.; Dykstra, C. E.; Zwier, T. S. *J. Phys. Chem.* **1993**, *97*, 980.

(19) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91. Bartlett, R. J. *Annu. Rev. Phys. Chem.* **1981**, *32*, 359.

(20) Clark, T. J.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294. Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(21) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6794.

(22) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN 92*; Gaussian, Inc.: Pittsburgh, PA, 1992.

0002-7863/94/1516-11568$04.50/0

Table 1. Hydrogen Bonding Arrangements, O−O Distances (Å), and Vibrational Frequency Shifts (cm^{-1}) in Structures **I** and **II** of the Water Hexamer

	structure **I**			structure **II**		
water molecule[a]	H-bond[b]	OH stretching frequency shift[c]	O−O distance	H-bond[b]	OH stretching frequency shift[c]	O−O distance
1	ADD	−113/−208	2.967/2.927	ADD	−73/−191	2.965/2.880
2	AAD	−670	2.677	AAD	−314	2.778
		−2	free		+8	free
3	AD	−352	2.760	AAD	−685	2.667
		+5	free		+2	free
4	AD	−397	2.769	AAD	−439	2.754
		+16	free		+6	free
5	AAD	−450	2.731	ADD	−100/−362	2.900/2.794
		+6	free			
6	ADD	−154/204	2.920/2.793	ADD	−116/−212	2.933/2.921

[a] The numbering of the water molecules is indicated in Figure 1. [b] A, hydrogen-bond acceptor; D, hydrogen bond donor. [c] In wavenumbers, relative to the mean of the symmetric and antisymmetric O−H stretches in the free water monomer calculated at the same level.

close to those obtained from MP2/aug-cc-pVDZ* calculations, which predict **I** and **II** to be more stable than **III** by 0.72 and 0.93 kcal/mol, respectively.[13] MP2 calculations with the more flexible aug-cc-pVTZ′ basis set (which retains the [5s4p3d/4s3p] portion of the aug-cc-pVTZ basis set[21]) predict **I** to be 1.04 kcal/mol more stable than **III** and also to be slightly (0.02 kcal/mol) more stable than **II**. Corrections for zero-point vibrational energies and basis set superposition errors (BSSEs)[23] destabilize **I** and **II** relative to **III**. Using the unscaled MP2 frequencies calculated in this study, we find that zero-point energy corrections destabilize **I** and **II** relative to **III** by 0.73 and 0.81 kcal/mol, respectively. The inclusion of corrections for BSSE destabilizes **I** and **II** relative to **III** by 0.29 and 0.46 kcal/mol, respectively, in the calculations with the aug-cc-pVDZ* basis set.[13] (Similar corrections are obtained with the aug-cc-pVTZ′ basis set.) This analysis leads to the predictions that the zero-point levels of **I** and **III** are nearly isoenergetic (*i.e.*, falling within 0.1 kcal/mol of one another) and that of **II** is only slightly higher. Calculations with still larger basis sets than those considered here and including also higher-order electron correlation effects[14] indicate that the zero-point level of **I** may be slightly lower in energy than the zero-point levels of **II** and **III**.

In analyzing the trends in the OH stretching frequencies, it is convenient to focus on the shifts in the frequencies relative to the mean of the frequencies of the two OH stretching modes of the water monomer.[24] For the hexamer, the shifts are reported relative to the mean of the MP2/6-31+G(2d,p) OH stretching frequencies of the monomer, whereas for benzene−$(H_2O)_6$ they are reported relative to the mean of the experimental OH stretching frequencies of the monomer. Table 1 summarizes the calculated frequency shifts for **I**, **II**, and **III** as well as the measured shifts for benzene−$(H_2O)_6$. The various water molecules are labeled as AD, AAD, and ADD to indicate the number of acceptor (A) and donor (D) hydrogen bonds. For the $(H_2O)_6$ clusters, the frequency shifts calculated for the free OH groups range from 2 to 16 cm^{-1}, those for the single-donor OH groups range from −314 to −700 cm^{-1}, and those for the double-donor OH groups range from −70 to −362 cm^{-1}.

Figure 1 presents an energy level diagram of the OH stretching frequencies of structures **I**, **II**, and **III** as well as benzene−$(H_2O)_6$. The energy level diagram of **III** is fundamentally different from those of **I** and **II**. In **III**, the modes associated with the free OH groups and those associated with the single-donor OH groups are highly delocalized, and there is an energy gap of over 400 cm^{-1} between the group of six nearly degenerate free OH stretching frequencies and the group of single-donor OH stretching frequencies. By contrast, the OH stretching vibrations in the noncyclic structures **I** and **II** are highly localized, being associated for the most part with single OH groups. This localization is due to the inequivalent environments of the different water monomers in these clusters.

The measured infrared spectrum of benzene−$(H_2O)_6$ shows an unresolved set of two or more free OH stretching transitions shifted by 0−20 cm^{-1}, attributed to free OH groups, a transition shifted by −67 cm^{-1}, due to the OH group bonded to the benzene ring, and eight transitions shifted by −128 to −628 cm^{-1}, due to double-donor and single-donor OH groups.[16] Of the latter eight transitions, those shifted by −128, −198, and −253 cm^{-1} are most likely due to double-donor OH groups, and those shifted by −398, −496, and −628 cm^{-1} are most likely due to single-donor OH groups. The remaining two transitions, shifted by −298 and −317 cm^{-1}, could be due to either double-donor or single-donor OH groups.

The presence of several transitions in the double-donor region rules out a cyclic water structure (**III**) as the isomer producing the experimental infrared spectrum in benzene−$(H_2O)_6$. Species **I** and **II** appear to be the lowest energy structures of the hexamer containing two and three double-donor molecules, respectively. As such, they are prime candidates for the $(H_2O)_6$ portion of the observed vibrational spectrum of the benzene−$(H_2O)_6$ complex. While a firm assignment of the structure of water hexamer in benzene−$(H_2O)_6$ will require further work, comparison of the experimental vibrational frequencies with those calculated for **I** and **II** shows a better match with **I** than with **II** (Figure 1). Furthermore, the number of observed transitions in the double-donor region is more consistent with two rather than three double-donor molecules. Given the congestion and breadth of the free OH absorption (spread over about 20 cm^{-1}), it seems most likely that there are three free OH transitions contributing to this band, consistent with there being two double-donor water molecules in benzene−$(H_2O)_6$. One of the transitions (−298, −317 cm^{-1}), then, is nominally a double-donor band, while the other is tentatively assigned as a single-donor band.

Assuming that the measured spectrum indeed derives from a complex between benzene and **I**, one anticipates that the OH stretching transitions might be affected by interactions with the benzene molecule. Examination of the form of the normal modes and the trends in the geometrical parameters (specifically, the O−O distances, given in Table 1) reveals that the shifts in both single-donor and double-donor OH stretching frequencies increase in magnitude with decreasing distance between the O atom of the OH group and the acceptor O atom involved in the hydrogen bond. We expect that the changes in the OH stretching frequencies that occur upon formation of the complex with benzene reflect primarily these changes in the associated OO distances of the water cluster.

In summary, comparison of the theoretical vibrational frequencies of structures **I**, **II**, and **III** of $(H_2O)_6$ with those of benzene−$(H_2O)_6$ shows convincingly that the water portion of the complex is not cyclic and favors a structure containing four single-donor and two double-donor water molecules. The most likely candidate for the water portion of benzene−$(H_2O)_6$ is **I**, which also appears to be the most stable form of $(H_2O)_6$.[14]

Acknowledgment. This research was supported by grants from the National Science Foundation. Time on the Cray C90 at the Pittsburgh Supercomputing Center was provided through a Metacenter Grand Challenge grant. We thank Professor David Pratt for helpful suggestions.

---

(23) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
(24) Knochenmuss, R.; Leutwyler, S. *J. Chem. Phys.* **1992**, *96*, 5233.