

Structure of the Water Hexamer Anion

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Received March 26, 2000

The structures and properties of water clusters^{1,2} and the hydration phenomena of cations,^{3,4} anions,^{5,6} electrons,⁷⁻¹⁰ and aromatic compounds¹¹ have been an active area of research during the last few decades. One of the recent interesting issues is the structure of the anionic water hexamer or electron-bound water hexamer $[e-(\text{H}_2\text{O})_6]$.⁸⁻¹⁰ Bowen and co-workers⁸ reported the vertical electron detachment energies (VDE) for various sizes of clusters $e-(\text{H}_2\text{O})_n$, followed by Johnson and coworkers.⁹ These experiments showed that the anionic water clusters for $n=2, 6, 7,$ and 11 show particularly strong VDE peaks. As yet, this reason has not been explained. Since we have recently reported the structures and properties for $n=2-5$ at high levels of *ab initio* theory,¹² here we report the structure, VDE, and O-H vibrational spectra for $n=6$ at the same level of theory.

We have investigated various structures (based on our previous work on the water hexamer¹³ and the anionic water hexamer¹⁴) using Møller-Plesset second order perturbation theory (MP2) with the aug-cc-pVDZ+diff(2s2p/2s) basis set. The exponents of the diffuse basis set used the scaled values of the outermost exponents by 1/8. The calculations were carried out using a Gaussian 94 suite of programs.¹⁵ The lowest energy structure of the anionic water hexamer is predicted to be a pyramid structure, in contrast to the cage structure^{13,16,17} of the neutral water hexamer (Figure 1). The details of other various low-lying energy structures will be reported elsewhere. Though both pyramid and cage structures have eight hydrogen bonds, their cluster skeletons are quite different. The dipole moment of the anionic pyramid structure is 10.4 debye (which is large enough to have strong $e\dots$ dipole interaction) with four clustered dangling hydrogen atoms along the direction of the dipole moment. On the other hand, the dipole moment of the neutral cage structure is 2.1 debye which is too small to bind an excess electron.¹² Though the hydrogen bonds in the anionic pyramid structure are rather weak compared with those in the neutral cage structure, the strong $e\dots$ dipole interaction in the anionic pyramid structure seems to compensate the weakened hydrogen bond strengths.

The VDE of the pyramid structure is predicted to be 0.43 eV, which is close to the experimental value of 0.48 eV.^{8,9} Since our previous MP2 VDEs for $n=2-5$ were slightly smaller (by $\sim 10\%$) than the VDEs predicted by the coupled cluster method with single, double, and non-interactive triple excitations [CCSD(T)],¹² the 10%-corrected VDE for $n=6$ is

in excellent agreement with the experiment. We have studied the O-H stretching vibrational frequencies using Becke-3-Lee-Yang-Parr (B3LYP) density functional theory (DFT) employing the 6-311++G** basis set due to the limited computing power. As the predicted O-H vibrational spectra of the neutral cage hexamer are in reasonable agreement with the experimental spectra of the water hexamer bound to a benzene monomer,¹⁷ those of the anionic pyramid water hexamer are found to be also in reasonable agreement with the experimental spectra of the anionic water hexamer.⁹ The predicted average value of the symmetric (ν_1) and asymmetric (ν_3) O-H vibrational frequencies of the water monomer (3869 cm^{-1}) needs to be compared with the corresponding experimental value (3706 cm^{-1}) as the reference point of the spectra. Thus, the B3LYP/6-311++G** predicted frequencies should be red-shifted by 163 cm^{-1} for realistic comparison with the experimental frequencies. Then, we note that the spectra of neutral cage structure have peaks near 0 cm^{-1} for the O-H frequencies involving dangling H atoms (H_d) and peaks red-shifted by up to $\sim 600\text{ cm}^{-1}$ for strongly hydrogen bonded O-H. On the other hand, the anionic pyramid structure have no peaks near 0 cm^{-1} , but it has peaks red-shifted by $\sim 100\text{ cm}^{-1}$, since the dangling H atoms involve the $e\dots\text{H}_d$ interactions. The spectra of each molecule in water clusters show signatures of the type of hydrogen bonds: the single proton donor – single proton acceptor type (“da”), the single donor – double acceptor type (“daa”), the double donor – single acceptor type (“dda”), the double acceptor type (“aa”). Two O-H frequencies involving the single donor type of “daa” and “da” are red-shifted by 77 (“da”) and 107 cm^{-1} (“daa”), respectively. Two O-H frequencies involving the dangling H_d atoms of the single donor types of “da” and “daa” are red-shifted by 436 cm^{-1} (ν_3) and 398 cm^{-1} (ν_1). The asymmetric ν_3 mode of the “aa”-type water shows a very strong IR intensity. The O-H frequencies of the “dda”-type water molecule are red-shifted

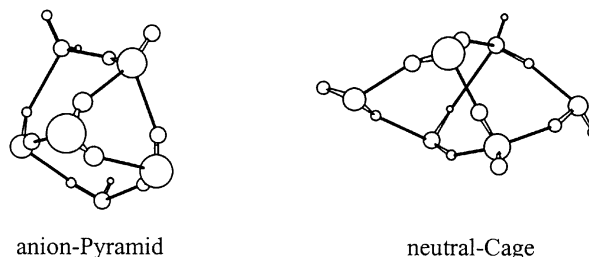


Figure 1. Structures of the anionic Pyramid water hexamer and the neutral Cage water hexamer.

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by 141-209 cm^{-1} for symmetric modes (ν_1) and 260-321 cm^{-1} for asymmetric modes (ν_3). The frequency shifts ($\delta\nu_3$) of the symmetric modes of “da” and “daa”-type water molecules are -474 and -492 cm^{-1} . These O-H stretching frequencies are in good agreement with the experimental spectra. The bending frequencies (ν_2) for the “dda”-, “da”-, and “daa”-type water molecules are blue-shifted by 113-89, 83, and 41 cm^{-1} (relative to the bending frequency of the free water monomer), while that for the “aa”-type is red-shifted by 77 cm^{-1} .

In conclusion, we find that the lowest energy conformer among the anionic water hexamer is the pyramid structure, and its VDE and O-H stretching spectra are in good agreement with the experiments.

Acknowledgment. We thank Drs. J. Kim, J. Y. Lee, P. Tarakeshwar, and S. Lee for helpful discussions. This work was supported by KISTEP (CRI).

References

- (a) Nauta, K.; Miller, R. E. *Science* **2000**, *287*, 293. (b) Brudermann, J. *et al. J. Chem. Phys.* **1999**, *110*, 10649. (c) Liu, K. *et al. Science* **1996**, *271*, 62.
- Lee, H. M. *et al. J. Chem. Phys.* **2000**, (in press); Kim, J. *et al. ibid.* **1999**, *110*, 9118; Kim, J. *et al. ibid.* **1995**, *102*, 310; Kim, K. S. *et al. ibid.* **1992**, *97*, 6649; Mhin, B. J. *et al. Phys. Rev. A* **1993**, *48*, 3764; Kim, J. *et al. Chem. Phys. Lett.* **1994**, *219*, 243.
- (a) Blades, A. T. *et al. J. Chem. Phys.* **1990**, *92*, 5900. (b) Weinheimer, C. J.; Lisy, J. M. *ibid.* **1996**, *105*, 2938.
- (a) Lee, H. M. *et al. J. Chem. Phys.* **1999**, *111*, 3995. (b) Kim, J. *et al. ibid.* **1995**, *102*, 839. (c) Lee, S. *et al. J. Phys. Chem.* **1996**, *100*, 14329.
- (a) Ayotte, P. *et al. J. Phys. Chem. B* **1998**, *102*, 3067. (b) Ayotte, P. *et al. J. Am. Chem. Soc.* **1998**, *120*, 12361. (c) Johnson, M. S. *et al. Chem. Phys. Lett.* **1996**, *260*, 551. (d) Cabarcos, O. M. *J. Chem. Phys.* **1999**, *110*, 5.
- (a) Majumdar, D. *et al. J. Chem. Phys.* **2000**, *112*, 101. (b) Baik, J. *et al. ibid.* **1999**, *110*, 9116.
- (a) Armbruster, M. *et al. Phys. Rev. Lett.* **1981**, *47*, 323. (b) Haberland, H. *et al. J. Chem. Phys.* **1984**, *81*, 3742. (c) Desfrancois, C. *et al. J. Chem. Phys.* **1991**, *95*, 7760. (d) Desfrancois, C.; Lisfi, A.; Schermann, J. P. *Z. Phys. D.* **1992**, *24*, 297. (e) Lehr, L. *et al. Science* **1999**, *284*, 635.
- (a) Coe, J. V. *et al. J. Chem. Phys.* **1990**, *92*, 3980. (b) Lee, G. H. *et al. Z. Phys. D.* **1991**, *20*, 9.
- (a) Bailey, C. G. *et al. J. Phys. Chem.* **1996**, *100*, 16782. (b) Campagnola, P. J. *et al. Chem. Phys. Lett.* **1991**, *181*, 206. (c) Bailey, C. G.; Johnson, M. A. *ibid.* **1997**, *265*, 185. (d) Kim, J. *et al. ibid.* **1998**, *297*, 90. (e) Ayotte, P. *et al. J. Chem. Phys.* **1998**, *108*, 444. (f) Ayotte, P. *et al. ibid.* **1999**, *110*, 6268.
- (a) Smith, D. M. A. *et al. J. Chem. Phys.* **1997**, *107*, 5788; **1999**, *109*, 1238; **1999**, *110*, 3804. (b) Kim, J. *et al. ibid.* **1997**, *106*, 10207. (c) Barnett, R. N. *et al. J. Chem. Phys.* **1988**, *88*, 4421; **1988**, *88*, 4429; *Phys. Rev. Lett.* **1987**, *59*, 811.
- (a) Tarakeshwar, P. *et al. J. Chem. Phys.* **2000**, *112*, 1769. (b) Tarakeshwar, P. *et al. ibid.* **1999**, *111*, 3995. (c) Tarakeshwar, P. *et al. ibid.* **1999**, *110*, 8501. (d) Kim, K. S. *et al. Chem. Phys. Lett.* **1997**, *265*, 497.
- (a) Kim, J. *et al. J. Chem. Phys.* **1999**, *111*, 10077. (b) Kim, J. *et al. Phys. Rev. A* **1999**, *59*, R930.
- (a) Kim, J.; Kim, K. S. *J. Chem. Phys.* **1998**, *109*, 5886. (b) Mhin, B. J. *et al. ibid.* **1994**, *100*, 4484. (c) Mhin, B.-J. *et al. Chem. Phys. Lett.* **1991**, *176*, 41. (d) Kim, K. S. *et al. ibid.* **1986**, *131*, 451. (e) Franken, K. A. *et al. ibid.* **1992**, *198*, 59. (f) Tsai, J.; Jordan, K. D. *ibid.* **1993**, *131*, 451.
- (a) Kim, K. S. *et al. Phys. Rev. Lett.* **1996**, *76*, 956. (b) Lee, S. *et al. ibid.* **1997**, *79*, 2038. (c) Lee, S. *et al. Chem. Phys. Lett.* **1996**, *254*, 128. (d) Kim, K. S. *et al. J. Am. Chem. Soc.* **1997**, *119*, 9329.
- Frisch, M. J. *et al. Gaussian 94*, Rev. A; Gaussian, Inc.: Pittsburgh, PA, 1995.
- (a) Liu, K. *et al. Nature* **1996**, *381*, 501. (b) Gregory, J. K. *et al. Science* **1997**, *275*, 814.
- (a) Pribble, R. N.; Zwier, T. S. *Science* **1994**, *265*, 75. (b) Kim, K.; Jordan, K. D.; Zwier, T. S. *J. Am. Chem. Soc.* **1994**, *116*, 11568.