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Ab initio MO-SCF Calculation on a Model of Anomalous Water

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Ab initio calculations are carried out on the planar hexamer model of anomalous water using a variety of basis sets. The results are compared to results of similar calculations on free water and water in the ice *I*-like puckered ring configuration.

Es werden *ab initio*-Rechnungen für das planare Hexamer-Modell von anomalem Wasser unter Verwendung mehrerer Basissätze durchgeführt. Die Ergebnisse werden mit Resultaten ähnlicher Rechnungen über freies Wasser und Wasser in der *I*-Eis ähnlichen Konfiguration verzerrter Ringe verglichen.

Calculs *ab initio* sur le modèle hexamérique plan de l'eau anormale en utilisant différentes bases. Les résultats sont comparés à ceux de calculs similaires sur l'eau libre et sur l'eau dans une configuration cyclique compacte analogue à celle de la glace *I*.

Reports by Deryagin [1] in the past few years have indicated that many systems capable of hydrogen bonding may exist in anomalous forms which have properties drastically different from those of the normal states. The reports have precipitated much recent experimental work on these species, and particular attention has been paid to the water system. Many scientists question the existence of such a new and well-defined form of water and it is therefore of obvious importance to investigate the problem theoretically-preferably by *ab initio* techniques. *Ab initio* MO-SCF calculations on cyclic water hexamers are reported here for both an ice *I*-like puckered ring with conventional asymmetric hydrogen bonds and a planar ring with symmetrically placed hydrogens as suggested by Lippincott *et al.* [2]. Calculations have been carried out with three different basis sets: a single Gaussian per atomic orbital, a contracted 7*s*, 3*p* Gaussian set-essentially equivalent to a single exponential (STO) per atomic orbital, and a Hartree-Fock AO set. These three sets all yield a similar pattern of relative atomic charge shifts, and a novel charge distribution is one of the principle features that may be attributed to the symmetrical hydrogen bond model of anomalous water. The question of absolute stability of the hexamer with respect to six monomers and the relative stability of asymmetric to symmetric hydrogen bonds is, however, entirely different for the three basis sets. Neither of the two simpler basis sets are capable of giving correct information on this matter. We consider this to be an important and timely warning-particularly in regard to the intermediate quality basis set, since this set has proved quantitatively useful for a number of problems of chemical interest such as rotational barriers. It turns out that the extremely simple, single Gaussian set produces a somewhat better (but still not adequate) ordering of the relative stabilities than the STO-like intermediate set, but this is entirely fortuitious as it is easy to demonstrate that the single Gaussian set leads to some physically unreasonable results.

The intermediate level calculation is presented first. A slightly modified version of program IBMOL (version 4)[1] was employed with a minimal Gaussian basis set of the type ($7s$, $3p$) contracted to ($2s$, $1p$) for each oxygen [3] and ($3s$) contracted to ($1s$) for each hydrogen [4] was used. A geometry search was carried out for the electronic configurations $(1a_1)^2\,(2a_1)^2\,(1b_1)^2\,(3a_1)^2\,(1b_2)^2$ of the free water molecule and the minimum energy was found for an O–H distance of 1.05 Å and an HOH angle of 104.0° with a total energy of -75.74878 a. u., compared to the experimental value of -76.465 a. u. [5]. Other expectation values compared to experiment [5] were: dipole moment equal to 2.11 D (1.85) stretching and bending force constants equal to 7.97×10^5 dynes/cm (8.35) and 0.857 (0.761) respectively, and first ionization potential 13.25 eV (12.65). A calculation with this same contracted basis set on the asymmetric cyclic hexamer in the C_3 puckered ice I conformation (geometry see Ref. [5]) and electronic configuration $(a_1)^{20}\,(e_1)^{20}\,(e'_1)^{20}$ yields a total energy equal to -454.48480 a.u. and a stability relative to $6\,H_2O$ of 0.09211 a.u. (9.636 kcal/H bond). This value may be compared to the H-bond in water estimated to be $5-7$ kcal [5]. The same contracted basis set was again employed for the D_{6h} planar cyclic hexamer. In-ring hydrogens were placed symmetrically in the O–O bonds, and the out of ring hydrogens were placed such that the H_{in}–O–H_{out} angle was 120° and the O–H_{out} bond distance was 0.99 Å. Calculations were performed for O–O distances of both 2.3 Å and 2.4 Å. The lowest energy configuration was found to be $(a_{1g})^6 (e_{1g})^2\,(e'_{1g})^2\,(e_{2g})^8\,(e'_{2g})^8\,(a_{2u})^2\,(e_{1u})^8\,(e'_{1u})^8\,(b_{1u})^6\,(b_{2u})^2\,(a_{2g})^2\,(e_{2u})^2\,(e'_{2u})^2\,(b_{2g})^2$ and the energies of the 2.3 Å and 2.4 Å were calculated to be -454.59979 a.u. and -454.63812 a.u., respectively. Comparing the total energy to six free water molecules, we find the D_{6h} structure is stabilized by 0.10710 a. u. or 11.20 kcal/H_2O for $R(\text{O–O}) = 2.3$ Å and 0.14543 a. u. or 15.21 kcal/H_2O for $R(\text{O–O}) = 2.4$ Å. The D_{6h} structure is more stable than the puckered C_3 ring by 1.56 kcal/mole and 5.57 kcal/mole for the $R = 2.3$ Å and $R = 2.4$ Å cases, respectively.

Single Gaussian fits to the maxima of Hartree-Fock atomic orbital functions [6] produce a water monomer bond length of 1.12 Å and HOH angle of 96° with a total energy of -68.68721 a.u. The C_3 configuration as given above yields a total energy equal to -411.58580 a.u. A planar cyclic hexamer with $R(\text{O–O}) = 2.35$ Å and external $r(\text{O–H}) = 1.12$ Å gives $E_T = -411.51777$ a.u. Both cyclic hexamers are unstable relative to six monomers. These wave functions and the ones immediately following were constructed by means of digital computer programs written at Princeton and carried out on the IBM 360/91 at the Princeton University Computer Center.

A calculation for the cyclic symmetric planar hexamer yielding a much lower total energy is obtained with an atomic-basis set of essentially Hartree-Fock

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[1] IBMOL was provided by Dr. Enrico Clementi of IBM Research Laboratories, San Jose, California. For a more complete description see: Clementi, E., David, D. R.: J. comput. Physics **1**, 223 (1966).

Table 1. *Atomic charges (number of electrons)*

Basis set	H_2O		$(H_2O)_6$ Asymmetric ice *I*-like ring		$(H_2O)_6$ Symmetric planar ring	
(7, 3, 3)[a]	O	8.52	O	8.62	O	8.68
	H	0.74	H_{int}[b]	0.65	H_{int}	0.59
			H_{ext}	0.73	H_{ext}	0.73
(3, 1, 1)	O	7.78	O	7.88	O	8.03
	H	1.11	H_{int}	1.02	H_{int}	0.92
			H_{ext}	1.10	H_{ext}	1.05
(10, 5, 5)	O	8.73			O	8.84
	H	0.64			H_{int}	0.51
					H_{ext}	0.66

[a] In (X, Y, Z), X = number of Gaussian orbitals employed for oxygen *s* atomic functions, Y = number for oxygen *p*, Z = number of hydrogen. Each basis set is grouped (contracted) to give one function per shell per symmetry type, except that the (3, 1, 1) and (10, 5, 5) have three oxygen *s* groups.

[b] H_{int} = hydrogen (internal) forming part of ring. H_{ext} = hydrogen (external) outside ring.

quality using Whitten's *s* functions [7] and Huzinaga's *p* set [4]. An energy of -455.83392 a.u. is obtained at $R(\text{O–O}) = 2.35$ Å and $r(\text{O–H})$ external $= 0.96$ Å. The energy for the monomer values at the experimental geometry (HOH angle equal to 105° and $r(\text{O–H}) = 0.957$ Å) is -75.97639 a.u. It is seen that this MO-SCF wavefunction is unstable relative to six isolated water molecules by some 2.5 kcal/H_2O. A wavefunction for the asymmetric cyclic hexamer has not been constructed, but it is clear from other work[2] that this structure will be stable relative to six monomers by at least 5 kcal/H-bond[3].

In Table 1 is reported the Mulliken atomic charges for the three levels of calculation. Although it is well-known that the Mulliken population analysis introduces an arbitrary mathematical assumption conceiving the separation of the molecular charge distribution into "atoms" and "bonds", it has proved very useful in the qualitative characterization of many chemical phenomena. From the atomic charges it is immediately apparent that all three basis set levels show a dramatic shift of charge from the hydrogens to the oxygens. This shift is certainly the most unusual feature of the cyclic, symmetric structures and if anomalous water proves to exist in a symmetrically bonded form, this charge distribution will have a major influence on its properties.

In Table 2 the Mulliken bond-orders for the intermediate calculation are presented. Here, the O–H bond in free water is considered to have a bond order of unity, and the numbers reported are relative to this standard. From the table, it is seen that the O–H_{ext} bond order remains quite constant near unity for all the cases reported, while O–H_{int} differs drastically from unity only in the symmetric planar model. This decrease from ~1.0 to ~0.6 would be expected to be reflected in a decreased O–H_{int} stretching force constant on going from the

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[2] Kollman, P. A., Allen, L. C.: J. chem. Physics **51**, 3286 (1969); Janet del Bene and J. A. Pople have carried out calculations on many asymmetric cyclic systems with a basis set giving a slightly higher total energy than our intermediate set, Chem. Physics Letters **4**, 426 (1969).

[3] Further work with high accuracy basis set wavefunctions is to be reported in the J. Amer. chem. Soc. by L. C. Allen and P. A. Kollman.

Table 2. *Relative bond orders for* (7, 3, 3) *basis set*

Case	O–H_{int}	O–H_{ext}
H_2O	1.00	
$(H_2O)_6$-Ice-*I*-like structure	1.01	1.03
$(H_2O)_6$-symmetric planar ring		
$R = 2.3$ Å	0.634	1.04
$R = 2.4$ Å	0.619	1.04

free water or ice *I*-like structure to the planar hexamer, and we would thus expect a significant lowering of the O–H stretching frequency in anomalous water. Such a lowering has indeed been found [2].

Three significant conclusions can be drawn from this work: 1) the frequently useful, intermediate-level, STO-like basis set can yield results very different from those produced by a Hartree-Fock AO basis set in some important cases, 2) considerations beyond those represented by the numbers reported here are required in order to determine the relative stabilities of symmetrically bonded water structures, and 3) the qualitative charge distribution features are preserved in all three levels of the calculations reported here, and they constitute an important characterization of the symmetrically bonded material.

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