Water clusters - a speculation

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Abstract

A $3 \times 3 \times 3$ cubic grid of oxygen atoms has 54 internal bonds and this can be an idealised model of a completely hydrogen bonded water cluster $(H_2O)_{27}$. A combinatorial study gave 456 distinct isomers of such ideal structures, each of which should have similar energies.

Computer simulation of $(H_2O)_{27}$ with a realistic intermolecular potential has produced such structures with energies of -237 kcal/mol. Similar cubic structures, but with a few external O-H bonds have also been found and these have the lower energy of -241 kcal/mol.

1 Completely Hydrogen Bonded Clusters

Recent studies of the structures and classical dynamics of small water molecules [1] using intermolecular potentials led to the result that the most stable tetramer has a square arrangement of oxygen atoms and the most stable octamer a cubic arrangement of oxygen atoms. In each case the O-O bonds are linked by unsymmetrical hydrogen bonds, with each oxygen having two long and two short O-H bonds. The result is surprising because ice structures are all based on six-membered puckered rings of oxygen atoms but such rings were not found as either the global or low-energy local minima of the hexamer.

These calculations were made with a recent water potential of Cieplak, Kollman and Lybrand [2] which is a 4-site model with charges placed on the hydrogen atoms and on the bisector of the HOH angle at a distance of 0.491 au from the oxygen (q=-1.2e). It assumes a rigid geometry for the water molecules but has independent atom-centred polarizability terms to produce an inductive stabilization; this gives a non pair-additive potential. However, other potentials give a similar oxygen framework for the octamer [3] although there are differences about the disposition of the hydrogen atoms; S_4 or D_{2d} arrangements having very similar energies. For other clusters (e.g. the hexamer) the optimum structure appears to be much more potential dependent [1,3], some potentials giving six-membered rings.

The final point to make about the tetramer and octamer is that there is a relatively large energy gap from the global minimum to metastable structures. The pentamer and hexamer, in contrast have several structures with different oxygen frameworks close to the global minimum; these are very floppy structures.

Calculations on clusters with up to 18 molecules [4] and even 20 [5] show again low-energy cubic lattices, although for the latter a more compact structure with face-sharing pentagonal prisms was found. Stable tetramers and octamers may be relevant to liquid water following a model due to Benson and Siebert [6] in which an equilibrium between these two clusters was used to account for the anomalous heat capacity of water between 0^oC and 100^oC.

One of us (SCF) speculating about the wider existence of cubic arrays in large water clusters [7] carried out energy minimisation studies on $(H_2O)_{64}$. Whilst it is impossible to be sure that for such a large cluster one has found the global minimum, the only minima found by an energy quenching molecular dynamics technique were for structures with very low symmetry for the oxygen framework and, at the most, only local cubic arrays. A cubic 4 x 4 x 4 grid of oxygen atoms did not give low-energy structures. In consequence of the above results we were moved to study $(H_2O)_{27}$ with a 3 x 3 x 3 cubic grid of oxygen atoms. The interesting point about this structure is that it has 54 O-O bonds, so that, in principle, there can be one hydrogen atom in each of these, thus forming Completely Hydrogen Bonded Clusters (CHBC).

However, our first thought was that it may not be possible to dispose of the hydrogen atoms, one in each bond, so that each oxygen has only two short O-H bonds and these are in orthogonal directions (not colinear), an essential requirement for any low-energy structure of a water cluster. In contrast, a 4 x 4 x 4 grid of oxygen atoms has 144 O-O bonds but there are insufficient hydrogen atoms in $(H_2O)_{64}$ to have one atom per bond, so there is a simple reason why such large clusters do not have a wholly cubic array of oxygen atoms; nor indeed why any ice structure has a cubic array.

It was not difficult to find an arrangement of hydrogen atoms to satisfy our rule, but a bigger challenge was to find the number of all symmetry distinct structures that satisfied the rule. The answer is 456, surprisingly large; but small in comparison with 54!, the total number of ways of arranging hydrogen atoms in the bonds (counting symmetry equivalent arrangements).

The task was tackled in two ways. The first was to consider the number of arrangements of a 3 x 3 grid with 12 hydrogens disposed in the O-O bonds and the other six either all on one side of the plane (for the top and bottom layer) or three on one side and three on the other (for the middle layer). For the bottom layer only rotationally distinct arrangements were taken. Each of these arrangements was combined with matching middle layers and finally with matching top layers.

To remove configurations from the above set which are rotationally equivalent, each was rotated so that the central O-H short bonds were along +x, +y. This procedure gave 456 distinct configurations in 228 enantiomeric pairs.

The second procedure was to start by fixing directions for the central O-H short bonds (along +x and +y). This imposes a restriction on the short bonds at the atoms which are face-centred in these directions; each of these must have at least one short bond along the z direction. We see immediately that this removes all planes of symmetry from the resulting structure and indeed the only remaining element of symmetry is a 2-fold axis along the vector (1,1,0). Of the 228 enantiomeric pairs mentioned above, only 8 pairs have this symmetry axis.

The next part of the strategy was to find the complete set of corner atom arrangements consistent with the central bonds and the face centred arrangements already mentioned, and finally to find each of the remaining face-centred arrangements consistent with all of these. Tests for consistency, and indeed a description of any allowed structure can be obtained through a connection matrix linking edge-centred with corner and face-centred atoms. If we number the sites as in figure 1, then the connection matrix with elements (i,j) is as shown in table 1. If we now insert the element 1 for a short O-H bond and -1 for a long O-H bond, the following rules must be satisfied:

1. The sum of each column must be zero.

2. The sum of elements in each of rows 13–20 must be 1.

3. The sum of elements in each of rows 21 and 22 must be zero.

4. The sum of elements in each of rows 23–26 must be -2.

5. The partial sum $\sum_{i=13}^{20}(i,j)$ of elements in each column j cannot be -2; this implies (from rule 1) that the partial sum $\sum_{i=21}^{26}(i,j)$ cannot be +2

   Finally, for rows 21 and 22, to disallow colinear bonds:

6. The element pairs (21,1) and (21,9), (21,5) and (21,8), (22,1) and (22,3), (22,2) and (22,4) cannot have the same signatures (+1 or -1).

These rules create chains of allowed signature through the matrix. For example, if (13,1) is -1 then (13,4), (13,8) and (14,1) must all be +1. Figure 1 shows a typical structure obeying the above rules.

2 Minimum energy conformations of $(H_2O)_{27}$

The above conclusions are based on combinatorial arguments considering the oxygen atoms of the 27 water molecules occupying the grid points of a cubic lattice. Thus, a question is raised about the existence of such Completely Hydrogen Bonded Clusters (CHBC).

We have carried out a search for minimum energy conformations of the $(H_2O)_{27}$ cluster in the same fashion as in our previous studies of water clusters [1,4,7]. The water molecules have been treated as rigid rotors, and with three Cartesian coordinates describing the position of the center of mass, and three Euler angles for the orientation of each molecule with respect to a space-fixed coordinate system. Molecular dynamics techniques were used to explore the phase space and the minima were located by quenching the kinetic energy at regular time intervals. Trajectories were integrated using four quaternions instead of the three Eulerian angles in order to avoid the well known singularities inherent in the Euler angle representation [8,9].

The potential function employed is the pair-additive part of the Cieplak, Kollman and Lybrand potential. Examination of the many-body polarization terms in previous work [1,4] showed that they contribute about 14% to the total energy but had little effect on the geometry of the minimum energy structure.

Initial conditions for the quenching process were taken as a cubic lattice of the centers of mass and random orientations of the hydrogen atoms. Usually, these configurations are of high energy. One initial condition is shown in Figure 2 which has an energy of -5.5 kcal/mol.

Numerous irregular quenched conformations were found in the range of energies from -240 to -230 kcal/mol. However, after a few minimization searches cubic-type arrangements of oxygen atoms indeed appeared with two or more free hydrogen atoms, i.e. atoms which do not participate in hydrogen bonds. One such structure is shown in Figure 3 with energy -241 kcal/mol and three dangling O-H bonds. The fact that these structures appeared after a random search indicates that they are quite abundant in configuration space.

A very large number of minima are expected for the $(H_2O)_{27}$ cluster and the chance to locate one of the 456 CHBC structures is very small. However, by systematically rearranging the hydrogen atoms in a manner guided by Figure 1, and minimizing the energy after each rearrangement, we located the configuration shown in Figure 4. The energy of this structure is -237.13 kcal/mol which is a little higher than the energy of the minimum shown in Figure 3, implying that the CHBC are not necessarily the most stable structures; such structures can rearrange to similar ones having a few dangling bonds and the activation energy for this is only a few kcal/mol.

In the study of $(H_2O)_{64}$ it was shown that the distribution of the O-O bond lengths $n(R)$ in an N molecule cluster,

$$n(R) = \frac{2}{N(N-1)} \sum_{i<j} \delta(R - R_{ij}), \tag{1}$$

had a characteristic pattern for cubic-type conformations.

Figure 5 shows the number distribution function $n(R)$ of the CHBC which we have found by our MD simulation; the three characteristic peaks at 5.5, 8, and 12 a_0 can be seen. The first and second peaks are in very close proximity to the first and second peaks of the oxygen-oxygen radial distribution function found for liquid water. This plus the fact that the cubic-type geometries guarantee for some molecules a coordination number larger than four, as is found in liquid water [10], has encouraged some speculation about the existence of cubic-type clusters in liquid water [7]. Definitely, the size of the studied clusters does not allow an immediate comparison with the liquid phase. Thus, our speculation about the importance of cubic structures in water clusters and liquid water still remains to be established experimentally.

References

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Figure Legends

1. A cubic model structure for a Completely Hydrogen Bonded Cluster (CHBC).

2. A starting arrangement of the water molecules for the minimization process.

3. A cubic-type minimum energy structure with three dangling hydrogen bonds. The energy of the cluster is -241.0 kcal/mol.

4. A completely hydrogen bonded cluster consistent with the pattern of Figure 1. The energy of the cluster is -237.1 kcal/mol.

5. The distribution function of the O-O bond lengths for the cluster shown in Figure 4. The O-O distances are in atomic units (1 au = 0.5292 Å).