

Cube to cage transitions in $(\text{H}_2\text{O})_n$ ($n=12, 16, \text{ and } 20$)

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Molecular dynamics computer simulations were performed for $(\text{H}_2\text{O})_n$ ($n=12, 16, \text{ and } 20$) followed by systematic quenching under a polarizable and a nonpolarizable model to determine the minimum energy structures each favored. *Ab initio* calculations were done on several minima for $(\text{H}_2\text{O})_{12}$ to determine their relative energies. The polarizable model prefers cagelike structures for all cluster sizes, whereas the nonpolarizable model predicts minima of fused cubes for $(\text{H}_2\text{O})_{12}$ and $(\text{H}_2\text{O})_{16}$ but makes the transition to a cagelike minimum at $(\text{H}_2\text{O})_{20}$. © 1996 American Institute of Physics. [S0021-9606(96)50131-5]

I. INTRODUCTION

The importance of including many-body effects in the theoretical description of small water clusters has been intensely studied in the past¹⁻⁴ and recently emphasized by Xantheas⁵ in high level *ab initio* calculations. He found for small clusters that the error in the energy for pair-wise additive potentials is as high as 30%. Two and three-body terms together catch 99% of the Hartree-Fock energy for clusters with five and six water monomers. In classical molecular dynamics calculations, we found good agreement in energy between theory and experiment for water clusters with one halide anion if many-body potentials were used.⁶ In light of these results, we want to explore many-body effects on larger sized homogeneous water clusters and compare them to the same clusters of water under a corresponding potential without explicit polarization.

Minimum energy structures of small water clusters have been reported by several groups using a variety of methods.⁷⁻¹² For the $(\text{H}_2\text{O})_8$ case there has been little ambiguity. Different molecular dynamics simulations agree that the cubes of either S_4 or D_{2d} symmetry are nearly isoenergetic with the latter slightly lower in energy, depending on the model.^{10,12-14} A notable exception is the study of Stillinger and David where their polarizable potential predicted a minimum energy structure which is a fragment of the hexagonal ice structure.¹⁵ *Ab initio* calculations^{11,12} found the D_{2d} cube to be the minimum. For larger water clusters there is not as much agreement as to whether these cubic type structures persist or whether more open cagelike structures are the minima. Most researchers agree that eventually the cagelike structures will prevail over cubes, but the size of the cluster at which this transition occurs is still debated. Does it occur at $(\text{H}_2\text{O})_n$, $n=12, 16, \text{ or } 20$ or even larger?

One comprehensive study of this subject has been done by Tsai and Jordan.¹² They graphically built different confirmations of $(\text{H}_2\text{O})_{12}$, $(\text{H}_2\text{O})_{16}$, and $(\text{H}_2\text{O})_{20}$ clusters and quenched them under the TIP4P model.¹⁶ They found for $(\text{H}_2\text{O})_{12}$ that the model predicts a double cube structure as the minimum. It can be made by fusing two octamers of S_4 symmetry so that they share one face and is denoted as $(S_4)_2$. Another local minimum closeby in energy is a cluster made from two $(\text{H}_2\text{O})_8$ clusters of D_{2d} symmetry sharing

one face [$(D_{2d})_2$]. They calculated energies at the HF level with an augmented, correlation-consistent valence double zeta plus polarization basis set (aug-cc-pVDZ*) and found another $(\text{H}_2\text{O})_{12}$ structure of D_3 symmetry which is lower in energy (by 12.5 kJ/mol), than the $(D_{2d})_2$ double cube. However, if electron correlation was included, the order switched and the $(D_{2d})_2$ became lower in energy (by 7 kJ/mol) relative to the D_3 cluster in qualitative agreement with the simulations. Tsai and Jordan concluded that the HF calculation is inappropriate to use, and that under the TIP4P potential, structures with more hydrogen bonds are energetically favored over structures with fewer hydrogen bonds even though the former have higher ring strain. Both the double cube of $(D_{2d})_2$ symmetry and the one of $(S_4)_2$ symmetry have 20 hydrogen bonds but the simulations predict the latter to be of slightly lower energy. No *ab initio* calculations were done for the $(S_4)_2$ cube to determine its energy relative to the $(D_{2d})_2$ cube.

Farantos *et al.*¹⁷ in their molecular dynamics study using the pair-wise part of the Cieplak, Kollman, and Lybrand (CKL) potential¹⁸ found the same $(\text{H}_2\text{O})_{12}$ cluster of $(S_4)_2$ symmetry to be the minimum energy structure. This structure was never found through quenching from a dynamical run, although other similar double cube structures with different arrangements of hydrogen bonds were found. They confirmed their results with the many-body CKL potential, the MCY potential,¹⁹ and the Niesar, Corongiu, and Clementi (NCC) pair-wise additive potential.²⁰ There is further consensus that this structure is the minimum: Lee *et al.*⁸ found the same result under density functional theory as did Kahn using semiempirical methods.⁹

For $(\text{H}_2\text{O})_{16}$ and $(\text{H}_2\text{O})_{20}$ there is not as much agreement as to which structures are the lowest energy ones. For $(\text{H}_2\text{O})_{16}$, Tsai and Jordan found the fused cubes of $S_4D_{2d}S_4$ symmetry (three octamers of each of those symmetries sharing faces), and for $(\text{H}_2\text{O})_{20}$, the $(D_{2d})_4$ as the minimum.¹² However, also using the TIP4P potential, Wales and Ohmine¹⁰ found an even lower energy structure for $(\text{H}_2\text{O})_{20}$ which consists of three pentagonal prisms sharing three faces. Farantos *et al.*¹⁷ found an interesting $(\text{H}_2\text{O})_{16}$ minimum which is a fused cubic structure where one octamer is stacked onto the double cube fragment, forming an ‘L’ shape. Kahn predicted a cubic type minimum for

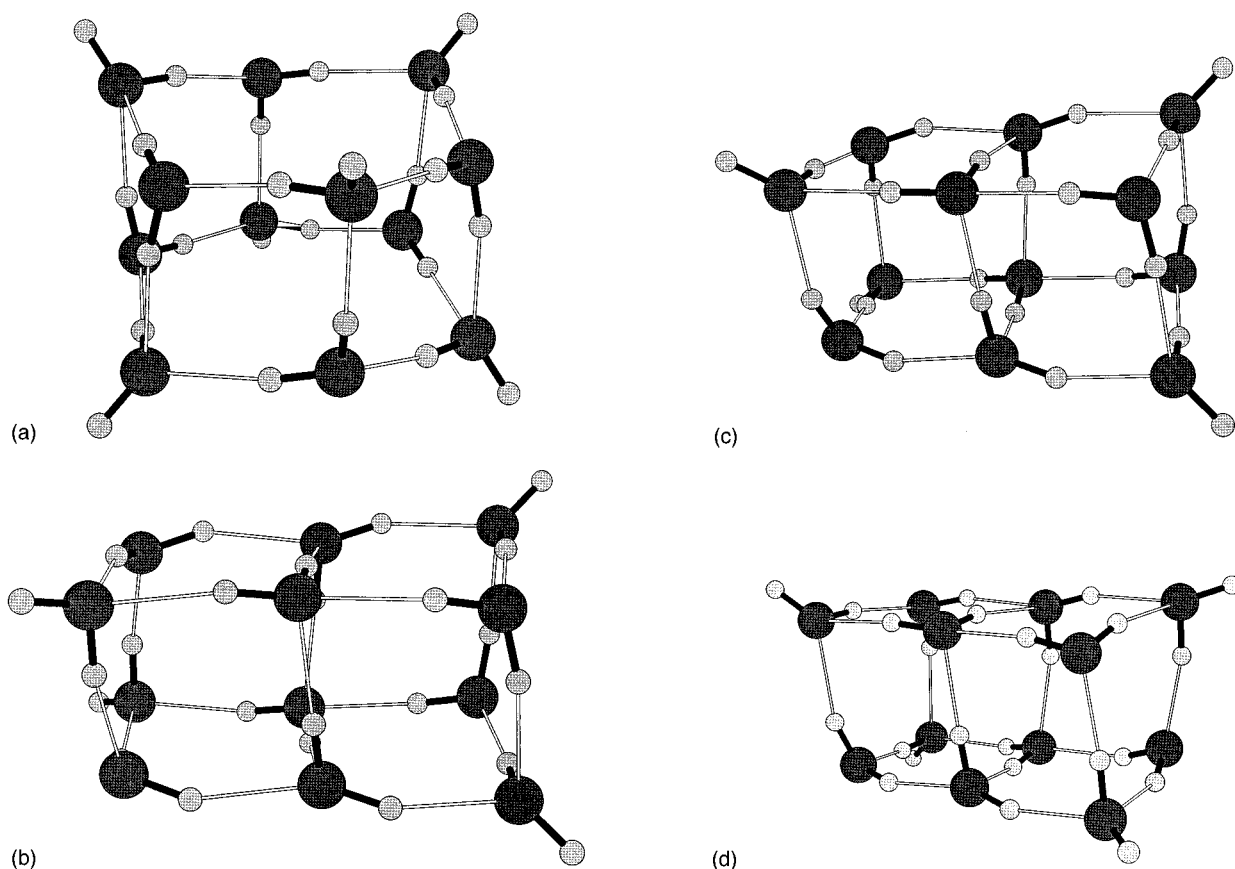


FIG. 1. $(\text{H}_2\text{O})_{12}$ minima. (a) The S_6 geometry which is the minimum for the POL1 model. (b) $(D_{2d})_2$. (c) S_4D_{2d} . (d) $(S_4)_2$.

$(\text{H}_2\text{O})_{16}$ and a distorted icosahedron for $(\text{H}_2\text{O})_{20}$,⁹ and Lee *et al.* find the $(D_{2d})_3$ symmetry as the $(\text{H}_2\text{O})_{16}$ minimum and the one with $(D_{2d})_4$ symmetry for $(\text{H}_2\text{O})_{20}$.⁸

The $(\text{H}_2\text{O})_{12}$ cluster is of special interest to us since when quenching $\text{F}^-(\text{H}_2\text{O})_{11}$ or $\text{Cl}^-(\text{H}_2\text{O})_{11}$ a similar double cube structure is found to be the lowest energy minimum. The 11 oxygens and one ion are each at a vertex of the fused double cube.²¹ To compare the melting patterns of these two clusters, a "reference state" of $(\text{H}_2\text{O})_{12}$ with a similar kind of structure was used. Further quenching of $(\text{H}_2\text{O})_{12}$ under the POL1 model,²²⁻²⁴ which was the model used for the heterogeneous water clusters, revealed another, deeper minimum which can be seen in Fig. 1(a) (all figures herein are produced with the program, Moviemol²⁵). This structure has an overall symmetry of S_6 . It should be noted that the double cube minimum of $(S_4)_2$ symmetry was still used in Ref. 21 since its hydrogen bond arrangement was comparable to that of the heterogeneous clusters.

The purpose of this research was to compare minimum energy structures of $(\text{H}_2\text{O})_n$ ($n=12, 16$, and 20) under POL1, a polarizable model, and under SPC/E,²⁶ a model which accounts for the polarizability in an average way. In addition, the *ab initio* energies of some of these clusters were calculated to compare the energy ordering of different minima. Within the context of the paper we also tried to address the

following questions. What effect does the polarizability have on the structure? How can these structures be thought of as being built up from smaller units, namely tetramers, pentamers, and hexamers? And how do minimum energy structures from molecular dynamics simulations compare with *ab initio* results?

II. METHODS

Two different water potentials were used: SPC/E which is a pair-wise additive potential, and POL1, a polarizable model. The details of these potentials can be found in Refs. 26, 27, and 28. Constant energy molecular dynamics with the Verlet algorithm were used to run trajectories for 1 ns at an average kinetic energy corresponding to 200 K for $(\text{H}_2\text{O})_n$ ($n=12, 16$, and 20). Minimum energy structures were found by quenching configurations from each of the six dynamical runs in intervals of 0.8 ps. Other structures mentioned below were made graphically and then quenched under both models.

MP2 energies were calculated for $(\text{H}_2\text{O})_{12}$ using the GAUSSIAN94 program.²⁹ The reduced form of Dunning's correlation consistent aug-cc-pVDZ* basis set was used.³⁰ As in Ref. 12, we dropped the diffuse p function on the hydrogen (so that the total number of functions on the oxygen and

TABLE I. SPC/E and POL1 minimum energies for (H₂O)₁₂. The *q* refers to structures found through quenching and the *g* to those made graphically. The lowest minimum is in bold face type. Units are in kJ/mol.

| Structure | SPC/E | POL1 |
|---|-----------------------------|-----------------------------|
| <i>S</i> ₆ [noncubic, Fig. 1(a)] | −533.04 (<i>q</i>) | −471.00 (<i>q</i>) |
| (<i>D</i> _{2d}) ₂ [cubic, Fig. 1(b)] | −534.21 (<i>g</i>) | −464.04 (<i>g</i>) |
| <i>S</i> ₄ <i>D</i> _{2d} [cubic, Fig. 1(c)] | −533.94 (<i>q</i>) | −463.95 (<i>g</i>) |
| (<i>S</i> ₄) ₂ [Fig. 1(d)] | −533.45 (<i>g</i>) | −461.90 (<i>g</i>) |

hydrogen are [4*s* 3*p* 2*d*/3*s* 1*p*]). In its reduced form, the uncontracted primitives on the 1*s*, 2*s*, and 2*p* orbitals have been dropped without any effect on the energy.³¹ With this reduction, the number of primitives per water drops to 59 while the number of functions (35 per water) stays the same. The standard MP2 frozen core calculation was used for each cluster. No basis set superposition error calculations were done due to reasons described in Ref. 32 and references therein.

Since the optimized water dimer geometry in quantum calculations³³ is closer to the TIP4P than the SPC/E geometry and in order to compare with previous work, the TIP4P geometry was also used in our quantum calculations. (H₂O)₁₂ clusters at 0 K which had been quenched under the SPC/E potential were requenched after switching the potential to that of TIP4P; oxygen coordinates and relative monomer orientations remained the same, but the OH bond length and HOH angle both decreased to that of the TIP4P geometry. No MP2 calculations have been done for the (H₂O)₁₆ and (H₂O)₂₀ clusters.

III. RESULTS

A. Minimum energy structures from MD

The following sections describe the minimum energy structures found with both potentials. In each case, those found under the POL1 model are presented first in the order in which they appear in Tables, I, II, and III. All energies are quoted in kJ/mol.

B. (H₂O)₁₂

For (H₂O)₁₂ under the POL1 model, the minimum energy structure, found through quenching, is of *S*₆ symmetry and has −471.0 kJ/mol of energy. This structure, shown in Fig. 1(a), is a fusion of two hexamer rings and is separated by ~3.8 kJ/mol from the next quenched minimum energy structure. The next three structures whose energies are listed

TABLE II. SPC/E and POL1 minimum energies for (H₂O)₁₆. The same convention is used as in Table I. Cage refers to a cagelike structure of undetermined or no symmetry.

| Structure | SPC/E | POL1 |
|--|-----------------------------|-----------------------------|
| Cage I [Fig. 2(a)] | −736.57 (<i>g</i>) | −652.09 (<i>q</i>) |
| Cage II [Fig. 2(b)] | −735.47 (<i>q</i>) | −650.57 (<i>g</i>) |
| (<i>D</i> _{2d}) ₃ [Fig. 2(c)] | −736.92 (<i>g</i>) | −643.55 (<i>g</i>) |
| <i>S</i> ₄ <i>D</i> _{2d} <i>S</i> ₄ [Fig. 2(d)] | −736.77 (<i>g</i>) | −643.23 (<i>g</i>) |

TABLE III. SPC/E and POL1 minimum energies for (H₂O)₂₀. The same convention is used as in Table I.

| Structure | SPC/E | POL1 |
|---|-----------------------------|-----------------------------|
| Cage III [Fig. 3(a)] | −947.58 (<i>g</i>) | −845.05 (<i>q</i>) |
| Pentagonal Prism [Fig. 3(b)] | −958.03 (<i>g</i>) | −843.34 (<i>g</i>) |
| Cage IV [Fig. 3(c)] | −946.54 (<i>q</i>) | −842.07 (<i>g</i>) |
| (<i>D</i> _{2d}) ₄ [Fig. 3(d)] | −939.83 (<i>g</i>) | −822.80 (<i>g</i>) |

in Table I are graphically constructed double cube structures. Under the POL1 model, the (*D*_{2d})₂ [Fig. 1(b)] and the *S*₄*D*_{2d} [Fig. 1(c)] confirmations are both 7.0 kJ/mol higher in energy than the *S*₆ one. The third cubic structure considered is the one of (*S*₄)₂ symmetry shown in Fig. 1(d), and is 9.1 kJ/mol less stable than the minimum.

Unlike the POL1 model, the SPC/E model predicts the cubic (*D*_{2d})₂ confirmation as the minimum energy at −534.21 kJ/mol. The next lowest minimum energy structure which happened to be the lowest energy structure found through quenching, is the *S*₄*D*_{2d} cubic structure. It is nearly isoenergetic with the (*D*_{2d})₂ minimum. The other two structures considered in Table I are the *S*₆ and (*S*₄)₂ ones at −533.04 and −533.45 kJ/mol of energy, respectively.

C. (H₂O)₁₆

For (H₂O)₁₆, the POL1 potential predicts (through quenching) a structure which has two pentagons plus one hexagon ring fused together [Cage I in Fig. 2(a)] and an energy of −652.09 kJ/mol. The graphically built (*D*_{2d})₃ [Fig. 2(c)] and *S*₄*D*_{2d}*S*₄ [Fig. 2(d)] confirmations are both around 9 kJ/mol higher than this minimum.

Under the SPC/E model, minimum energy structures are as follows: the (*D*_{2d})₃ triple cube is the minimum at −736.92 kJ/mol. Nearly isoenergetic with the (*D*_{2d})₃ confirmation is the *S*₄*D*_{2d}*S*₄ at −736.77 kJ/mol and the Cage I structure at −736.57 kJ/mol. Through quenching of the selected confirmations from the molecular dynamics, the lowest energy structure [Cage II in Fig. 2(b)] is at −735.47 kJ/mol. This cage structure has the remnants of the double cube in that it has seven tetramers and three pentamers.

D. (H₂O)₂₀

The POL1 model's minimum for (H₂O)₂₀ is Cage III shown in Fig. 3(a) with an energy of −845.0 kJ/mol and was found by quenching. Close in energy and also in topology is the fused pentagonal prism structure [Fig. 3(b)] at −843.34 kJ/mol. The (*D*_{2d})₄ structure [Fig. 3(d)] is highly disfavored under this model, as can be seen in Table III.

The SPC/E model finds the fused pentagonal prism structure for its minimum with an energy −958.03 kJ/mol. Cage III is the next lowest minimum energy structure with −947.58 kJ/mol. This is separated by only 1 kJ/mol from the next lowest minimum which is Cage IV [Fig. 3(c)], a structure found through quenching. The (*D*_{2d})₄ structure is ~18.0 kJ/mol above the minimum.

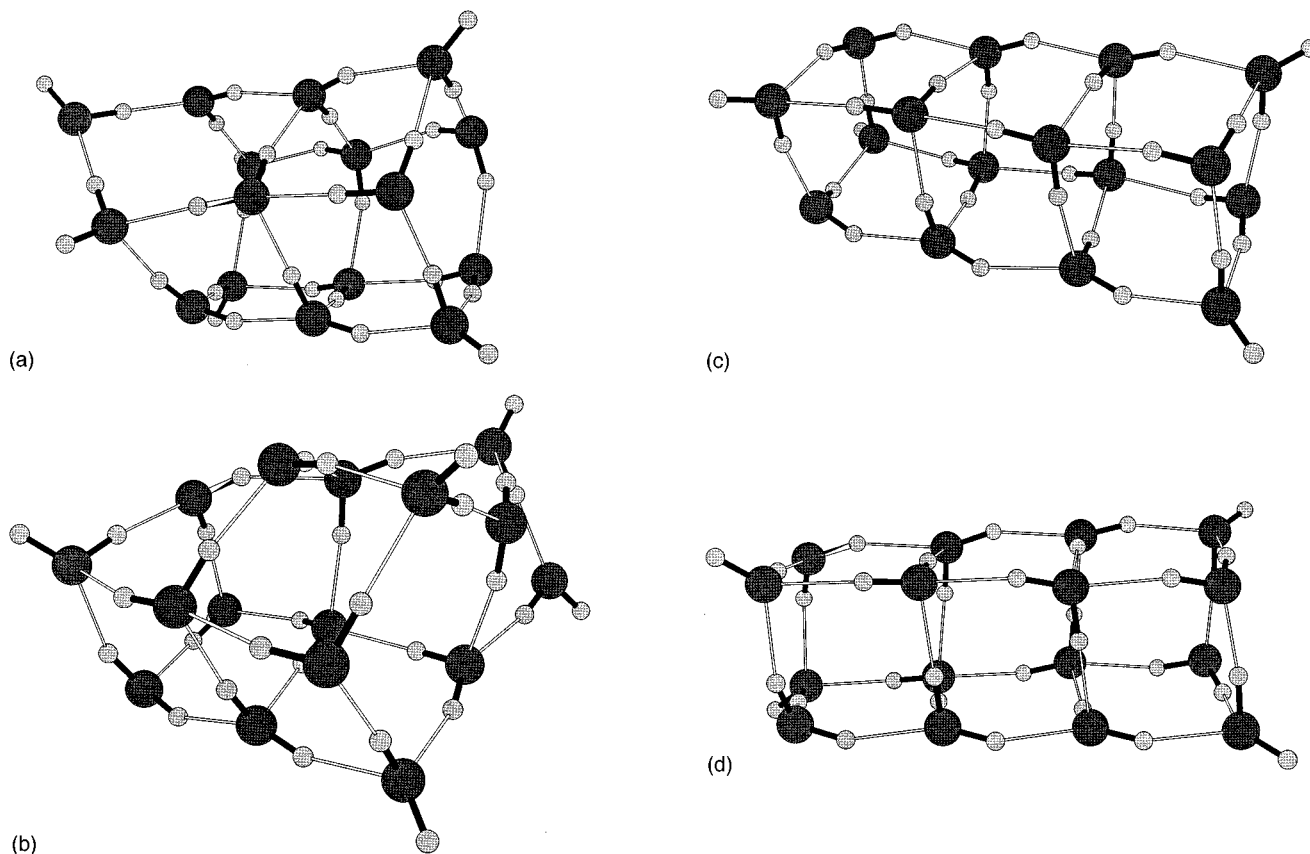


FIG. 2. $(\text{H}_2\text{O})_{16}$ minima. (a) Cage I which is the minimum for the POL1 model. (b) Cage II. (c) $(D_{2d})_3$. (d) $S_4D_{2d}S_4$.

The pentagonal dodecahedron structure gives an even higher energy and is not stable (unless heavy atoms are used, it immediately deforms) under either model.

To summarize these results, both cage- and cubic-type structures were found as the lowest energy structures quenched from an MD production run. For the cluster with 12 waters, the SPC/E model predicts a different minimum from the TIP4P model, although they both turn out to be fused double cubes. The SPC/E energy spacing, however, is very close for cages and cubes at this size cluster. The POL1 model finds the S_6 cluster as the minimum. For $(\text{H}_2\text{O})_{16}$, the SPC/E model finds a cubic-type structure made from three D_{2d} cubes fused together as the minimum and again this is quite close in energy to the cage structures while the POL1 finds as its lowest energy structure two pentagons plus one hexagon fused together. The TIP4P model finds neither of these as its minimum for $(\text{H}_2\text{O})_{16}$. For $(\text{H}_2\text{O})_{20}$, the SPC/E and POL1 potentials' minima are both noncubic, with the SPC/E model sharing the same minimum energy structure as the TIP4P model.

E. *Ab initio* ordering of minimum energy structures of $(\text{H}_2\text{O})_{12}$

It is interesting to explore the energy ordering that *ab initio* calculations predict for different $(\text{H}_2\text{O})_{12}$ structures since both TIP4P and SPC/E models find double cube minima but the polarizable model finds a cluster of S_6 sym-

metry to be favored as the minimum. The structures considered in our MP2 calculations were the three double cube structures of $(D_{2d})_2$, $(S_4)_2$, and S_4D_{2d} symmetries, and the S_6 fused ring structure. [The $(D_{2d})_2$ double cube has already been calculated by Tsai and Jordan¹² with an additional orbital frozen compared to the present calculations.]

The results for the HF and MP2 energies can be seen in Table IV. The HF energy ordering places the $(D_{2d})_2$ cube as the lowest separated by a mere 1.86 kJ/mol from the S_6 double hexamer and by 11.7 and 13.5 kJ/mol from the S_4D_{2d} and the $(S_4)_2$ double cubes, respectively. This order switches when electron correlation is added. The $(D_{2d})_2$ double cube remains the lowest of the four but the S_4D_{2d} and $(S_4)_2$ are now lower in energy relative to the S_6 fused ring confirmation. The difference in energy between these structures is less than 8 kJ/mol overall.

It should be noted that the POL1 potential predicted the same energy minimum that *ab initio* calculations did for $(\text{H}_2\text{O})_8$. This minimum is the cubic D_{2d} structure, and the POL1 model finds the next lowest local minimum to be the cube of S_4 symmetry (see Table V), which is also in agreement with *ab initio* calculations.¹²

IV. CONCLUSION

In comparing the results, the most striking difference between the two models can be seen in the clusters with 12 waters. The POL1 model has the energy levels of the four

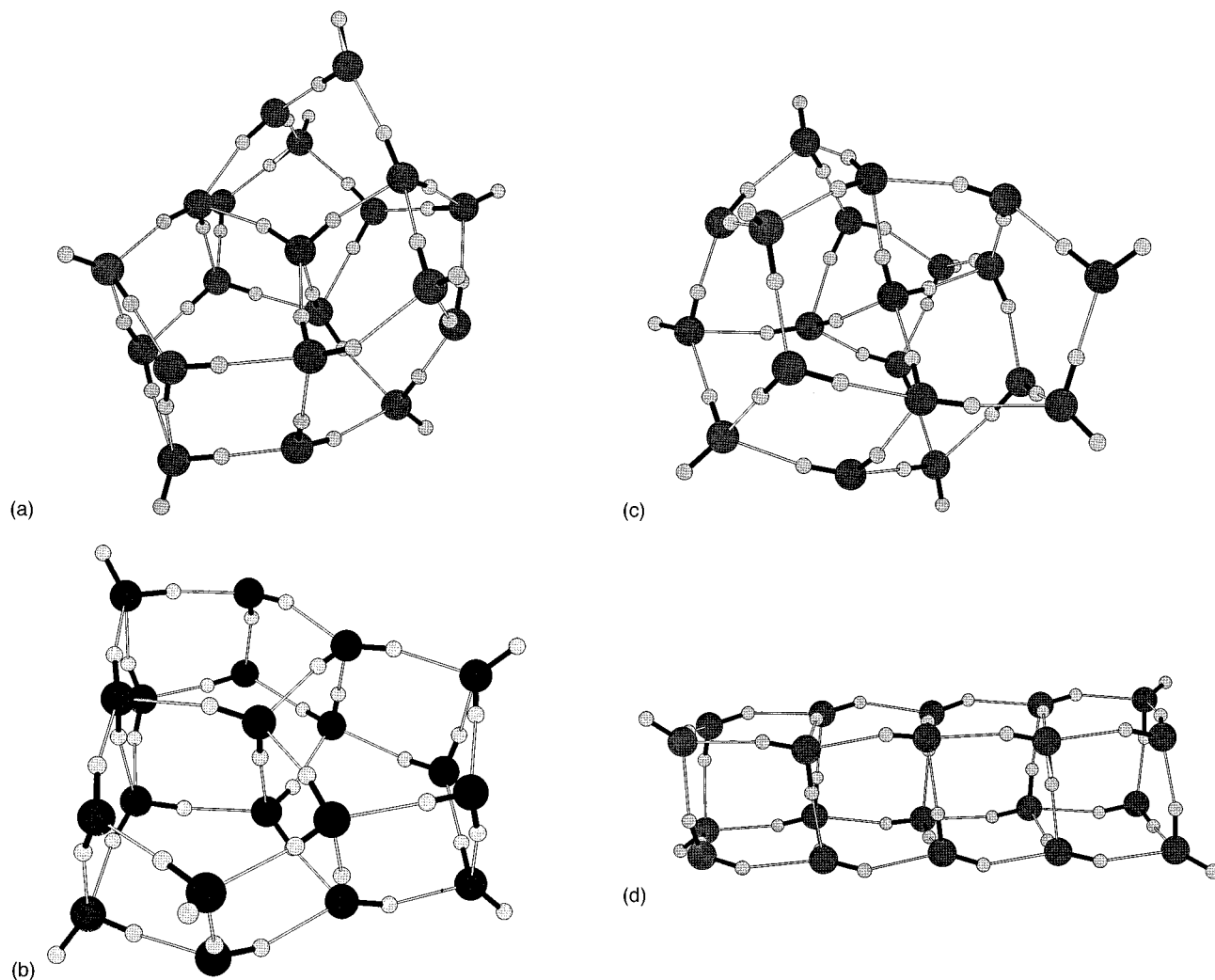


FIG. 3. $(\text{H}_2\text{O})_{20}$ minima. (a) Cage III which is the minimum for the POL1 model. (b) Pentagonal prism which is the minimum for the SPC/E model. (c) Cage IV. (d) $(D_{2d})_4$.

structures that we considered in a different order from that of TIP4P,¹² SPC/E, or MP2 (Table IV). The SPC/E model, on the other hand, does predict the same energy ordering as MP2.

The order of the MP2 energies could change if the cluster geometries were optimized. The relaxation energy, which is the measure of the distortion of water monomers in a cluster relative to the optimal geometry of those monomers in the gas phase, was estimated (not calculated) by Xantheas⁵ at the MP2 level (under the aug-cc-pVDZ basis set) to be as high as 1.26 kJ/mol/monomer in clusters with greater than four

waters. For a cluster with 12 waters, this would correspond to a relaxation energy as high as 15 kJ/mol which is larger than the MP2 energy spacing of the four structures considered, so their ordering could change upon optimization. Tsai and Jordan³² studied the effect of partial optimization in a study of $(\text{H}_2\text{O})_6$, where different configurations were minimized at the MP2 level but with the geometry fixed so that the only changes in geometry were monomer rotations. The energy ordering remained the same as in the unoptimized case. Only after the bond angles and lengths were optimized

TABLE IV. SPC/E, POL1, HF, and MP2 total energies for $(\text{H}_2\text{O})_{12}$ with binding energies in parentheses. SPC/E, POL1, and binding energies are in kJ/mol and the *ab initio* total energies are in hartrees.

| $(\text{H}_2\text{O})_{12}$ symmetry | SPC/E | POL1 | HF (Binding E) | MP2 (Binding E) |
|--------------------------------------|----------------|----------------|-------------------------------|-------------------------------|
| S_6 | -533.05 | -470.99 | -912.610 986 (-312.80) | -915.283 488 (-460.82) |
| S_4D_{2d} | -533.94 | -463.95 | -912.607 245 (-303.00) | -915.286 144 (-467.84) |
| $(S_4)_2$ | -533.45 | -461.90 | -912.606 542 (-301.14) | -915.285 499 (-466.10) |
| $(D_{2d})_2$ | -534.21 | -464.04 | -912.611 699 (-314.66) | -915.286 526 (-468.80) |

TABLE V. SPC/E and POL1 minimum energies for $(\text{H}_2\text{O})_6$ and $(\text{H}_2\text{O})_8$.

| Structure | SPC/E | POL1 |
|--------------------------|-------------|-------------|
| $(\text{H}_2\text{O})_8$ | | |
| S_4 | -331.25 (g) | -284.30 (q) |
| D_{2d} | -331.60 (g) | -284.42 (g) |
| $(\text{H}_2\text{O})_6$ | | |
| Open book (Fig. 4) | -221.73 (q) | -194.83 (q) |
| S_6 | -217.31 (q) | -193.27 (q) |

did the energy ordering of the different configurations change.

How can the transition from cubes to cages be characterized for our water clusters under these models and when does it occur? We find that such a transition occurs at different cluster sizes, depending on the water model. For the SPC/E model this transition occurs for $(\text{H}_2\text{O})_n$ at $n=20$. For the POL1 model, the cage already appears at $n = 12$. In Stillinger and David's polarizable model cubes do not appear even at the $n = 8$ size.¹⁵ Where this transition might occur in MP2 at these (unoptimized) geometries has yet to be seen due to the large amount of time and memory needed for such a calculation.

We observe from our simulation that adding polarizability in an explicit manner has the effect of favoring a reduction in strain energy at the expense of hydrogen bonding for all three sizes. For $(\text{H}_2\text{O})_n$ ($n=12, 16, \text{ and } 20$), the minimum energy structures for POL1 have 18, 26, and 32 hydrogen bonds respectively. (We considered two water molecules to be hydrogen bonded when the distance between a hydrogen and a neighboring water oxygen is less than 2.5 Å and when the $\text{OH}\cdots\text{O}$ angle is greater than 120° where the first O is the covalently bonded oxygen and the second is a neighboring oxygen.) This compares to 20, 28, and 36 hydrogen bonds, respectively, for the corresponding clusters with a cubic geometry. Wales and Ohmine's¹⁰ pentagonal prism $(\text{H}_2\text{O})_{20}$ structure is intermediate between the POL1's Cage III and the cubic $(D_{2d})_4$ in that it has 34 hydrogen bonds. It is possible to rationalize, in part, the minimum energy structures that each potential predicts by considering their dimer bind-

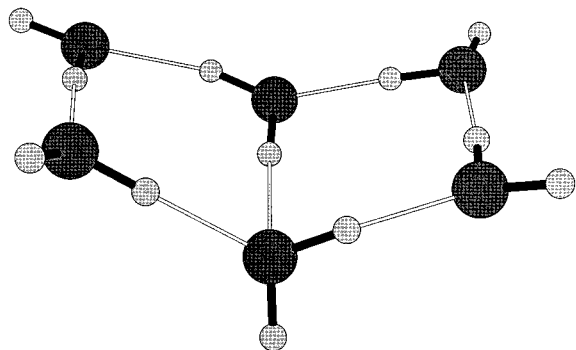


FIG. 4. The geometry of the lowest energy minimum for $(\text{H}_2\text{O})_6$ under the SPC/E and POL1 models.

ing energies. It is known that the TIP4P potential estimates the binding energy of the dimer to be -26 kJ/mol.³² With the aug-cc-pVDZ* basis set and at the same TIP4P dimer geometry, the MP2 energy is -19.4 kJ/mol.³² Both of these results are outside the experimental values of -22.6 ± 2.9 kJ/mol³⁴ or -22.6 ± 0.8 kJ/mol.³⁵ The POL1 model gives a dimer binding energy of -23.5 kJ/mol and the MP2 binding energy given this geometry is -20.7 kJ/mol, both of which are within the ± 2.9 kJ/mol experimental error bar. Thus there is no built in bias to form structures with higher numbers of hydrogen bonds when the POL1 model is used. Hence, it is possible that the $(\text{H}_2\text{O})_{12}$ cluster of S_6 symmetry with two fewer hydrogen bonds than the double cube structures can be lower in energy. In terms of the magnitudes of the binding energies themselves, the POL1 model more closely matches the MP2 binding energies for $(\text{H}_2\text{O})_{12}$ than the SPC/E model does, as can be seen in Table IV.

Rather than viewing the clusters as monomer units connected via hydrogen bonds, they can be viewed as small cluster units fused together to form a larger cluster. The double cube $(\text{H}_2\text{O})_{12}$ clusters, for instance, can be thought of as either a composition of 11 tetramers or two fused octamer units. The symmetry designations of the double cubes reflect the latter. The S_6 structure for $(\text{H}_2\text{O})_{12}$ cluster can likewise be thought of as a fusion of two hexamers and six tetramer units. To better understand the $(\text{H}_2\text{O})_{12}$ cluster with S_6 symmetry, we performed molecular dynamics simulations and quenching of $(\text{H}_2\text{O})_6$ following the same procedure as was outlined in Sec. II. Both the SPC/E and POL1 models predict the same minimum, an "open book" structure (Fig. 4 and Table V) with seven hydrogen bonds. However, the open book structure is only ~ 1 kJ/mol lower in energy than the S_6 hexamer for the POL1 model, and only ~ 4 kJ/mol lower in the case of the SPC/E model. The S_6 hexamer was the minimum energy structure in *ab initio* calculations at the MP2 level with a TIP4P geometry and under the aug-cc-pVDZ* basis set.³² However, when this structure was optimized, it was no longer the lowest in energy relative to other structures considered, which had greater numbers of hydrogen bonds. If the hydrogen bond that forms the "binding" of the open book hexamer is broken, then the S_6 ring structure is obtained. Thus for $(\text{H}_2\text{O})_{12}$, the topology of the double cube and S_6 cagelike structures are very similar if viewed from the perspective of fusing two groups of hexamers. To go from a double cube $(\text{H}_2\text{O})_{12}$ cluster to the S_6 cagelike structure, the two bonds forming the binding of the two "open book" hexamers must be broken.

Breaking hydrogen bonds somewhat destabilizes the structure, but this effect is compensated by a reduction in ring strain. Since in both SPC/E and POL1, the water is modeled as rigid with an (almost) tetrahedral HOH angle of 109.5° , perfect pentamers and hexamers with their angles of 108° and 120° , respectively, allow for better accommodation of the hydrogen bonds than does the tetramer. Indeed, we found that the abundance of pentamers, in particular, increased with increasing cagelike character; for example, irrespective of either (SPC/E or the POL1) model, in going from $(\text{H}_2\text{O})_{12}$ to $(\text{H}_2\text{O})_{20}$, the number of five membered rings

increases from zero to six. There is a balance, therefore, between the numbers of tetramers which result in more hydrogen bonding and the numbers of pentamers and hexamers (only in the case of POL1) which alleviate some ring strain. An increased number of pentamers might be the link to greater bulklike character since different simulations of liquid water show that at a range of temperatures (from supercooled to 360 K), pentagons are the most abundant of polygons ranging in size from three to seven.³⁶⁻³⁸

The polarizable model, though a rigid model, has in a sense some flexibility in the charge distribution since the dipole moments are allowed to change in response to their environment while leaving the charge centers fixed on the atoms. It also does not overestimate the strength of the hydrogen bond. With these many-body effects included in the POL1 model, the order of the minima is quite different and more bulk-like in character compared to nonpolarizable SPC/E and TIP4P models. Does that mean that the transition from cube to cagelike structures for water clusters occurs at $n=12$? The answer can be given only when fully optimized, high quality quantum calculations are done, and more information from experiments is available. At this time, we can only say that both the pair-wise SPC/E and the many-body POL1 potentials predict minimum energy structures that do not consist of fused cubes but rather have a cagelike character for a water cluster with 20 monomers. Finally, we want to mention that the geometry of the lowest minimum cagelike structures can be given only when a method to find the absolute minimum energy structure is found. The problem of finding such a minimum remains unsolved, particularly for water clusters.³⁹

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