

Clusters of classical water models

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The properties of clusters can be used as tests of models constructed for molecular simulation of water. We searched for configurations with minimal energies for a small number of molecules. We identified topologically different structures close to the absolute energy minimum of the system by calculating overlap integrals and enumerating hydrogen bonds. Starting from the dimer, we found increasing number of topologically different, low-energy arrangements for the trimer(3), the tetramer(6), the pentamer(6), and the hexamer(9). We studied simple models with polarizable point dipole. These were the BSV model [J. Brodholt *et al.*, *Mol. Phys.* **86**, 149 (1995)], the DC model [L. X. Dang and T. M. Chang, *J. Chem. Phys.* **106**, 8149 (1997)], and the GCP model [P. Paricaud *et al.*, *J. Chem. Phys.* **122**, 244511 (2005)]. As an alternative the SWM4-DP and the SWM4-NDP charge-on-spring models [G. Lamoureux *et al.*, *Chem. Phys. Lett.* **418**, 245 (2006)] were also investigated. To study the impact of polarizability restricted to the plane of the molecule we carried out calculations for the SPC-FQ and TIP4P-FQ models, too [S. W. Rick *et al.*, *J. Chem. Phys.* **101**, 6141 (1994)]. In addition to them, justified by their widespread use even for near critical or surface behavior calculations, we identified clusters for five nonpolarizable models of ambient water, SPC/E [H. J. C. Berendsen *et al.*, *J. Phys. Chem.* **91**, 6269 (1987)], TIP4P [W. L. Jorgensen *et al.*, *J. Chem. Phys.* **79**, 926 (1983)], TIP4P-EW [H. W. Horn *et al.*, *J. Chem. Phys.* **120**, 9665 (2004)], and TIP4P/2005 [J. L. F. Abascal and C. Vega, *J. Chem. Phys.* **123**, 234505 (2005)]. The fifth was a five-site model named TIP5P [M. W. Mahoney and W. L. Jorgensen, *J. Chem. Phys.* **112**, 8910 (2000)]. To see the impact of the vibrations we studied the flexible SPC model. [K. Toukan and A. Rahman, *Phys. Rev. B* **31**, 2643 (1985)]. We evaluated the results comparing them with experimental data and quantum chemical calculations. The position of the negative charge in the models plays a crucial role. In this respect models with SPC geometry provided structures different from the TIP4P-type potentials, including polarizable ones. The TIP4P variants form configurations similar to one another. Results for TIP4P-EW and for TIP4P/2005 were especially close to each other in every respect. This is also true for the BSV and the DC pair. The charge-on-spring models (SWM4-DP and SWM4-NDP) are also very similar to each other, despite the sign exchange of charges on the spring particle and the oxygen. The spherical polarization of water is crucial. Due to the planar polarization of the SPC-FQ and the TIP4P-FQ models, they prefer planar arrangements contrary to other polarizable models and quantum chemical calculations. The tetrahedral geometry of TIP5P stabilizes additional clusters with peculiar geometries and small O–O distances. Inclusion of vibrations causes only insignificant changes in the characteristic geometries but decreases the internal energy relative to its reference rigid version. Comparing with quantum mechanical calculations the GCP model provided the best overall results. © 2009 American Institute of Physics. [doi:10.1063/1.3266838]

I. INTRODUCTION

The literature is full with water models suggested during the past four decades.^{1,2} However, none of them is able to fulfill the most important three criteria: to be economic, to be conceptually simple, still physically justifiable, and transferable over a wide range of thermodynamic conditions and environmental peculiarities. This is the reason that the search for better candidates is still an ongoing process in the scientific community.

Most of the models below were devised primarily for the simulation of liquid water. This means that their cluster forming properties do not qualify or disqualify their usage in

bulk liquid. Still it can be very informative during the search for a transferable model, to see how different approaches perform in dilute systems.

First, one must describe a single molecule accurately. The gas phase geometry of water is planar with 0.9572 Å for OH distance and 104.52° for HOH angle.³ The dipole moment⁴ of the molecule is 1.855D, while its quadrupole moments are $Q_{xx} = -0.134$ D Å, $Q_{yy} = 2.626$ D Å, and $Q_{zz} = -2.493$ D Å.⁵ Components of the molecule's gas phase polarizability⁶ are $\alpha_{xx} = 1.4146$ Å³, $\alpha_{yy} = 1.5284$ Å³, and $\alpha_{zz} = 1.4679$ Å³. These are the most important features in the framework of classical electrostatics.

In condensed phases both the average bond length and bond angle might change depending on the surroundings. In

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hexagonal ice the OH distance is longer and the HOH angle is larger.⁷ As for the average dipole and quadrupole moments, there is no experimental evidence.

There are simple, planar, nonpolarizable models with a reasonable success in ambient liquids.¹ Some of these models have the gas phase geometry of water with fixed dipole moments. Such models are the classical TIP4P (Ref. 8) and its modifications. The TIP4P-EW (Ref. 9) model is a systematic reparametrization of the original TIP4P for several liquid properties simultaneously. The TIP4P/2005 is also a recent version to describe the liquid-solid region with a better accuracy.¹⁰ A feature of the above models is that while the positive partial charges rest on the hydrogen atoms the negative charge is positioned on the bisector of the HOH angle in certain distance from the oxygen. The size of the negative charge and its distance from the oxygen determines the dipole moment of the molecule which is assumed to be the average dipole moment in liquid phase.

The SPC/E model¹¹ has 1 Å for its OH bond and a tetrahedral HOH angle (109.47°). The partial charges rest on the atoms. Contrary to the TIP4P-type models, the parametrization of this model takes into account the self-energy term of polarization¹¹ which is a step toward polarizable models.

All the above models provide correct density at ambient condition, a reasonable pair-distance distribution, and internal energy, although none of them is capable to reproduce the correct melting temperature of hexagonal ice.¹² Dipole moment, 2.18D, for the TIP4P model is too small to provide an acceptable estimate for the dielectric constant of ambient water.¹ Since there is a correlation between the dipole moment and the dielectric constant, the other models give better performance in this respect. Surprisingly, the SPC/E model gives a good estimate for the critical point.^{1,13}

In addition to charges on the hydrogens, the TIP5P model puts two point charges on the molecule creating a tetrahedral charge arrangement to represent the nonbonding pairs of the molecule.¹⁴ The original model was to be used without long-ranged interaction. A later reformulation of the Lennard-Jones parameters adapted it for Ewald summation.¹⁵ The TIP5P model is substantially different from the models described above. The negative charges are 0.7 Å from the oxygen. Therefore their value is smaller, it is only 0.241 esu. The model provided good results in condensed phases where the tetrahedral character of intermolecular structure is dominant.

There is a family of polarizable models where a point dipole is added to fixed partial charges to be polarized by the electric field of the surroundings. A closely related alternative is the spring-on-charge model where the point dipole is replaced by a small but finite dipole formed by two charges.

The BSV model¹⁶ has the gas phase geometry of water with three permanent charges and a point dipole to represent polarizability. The -0.998 esu negative charge is 0.2 Å from the oxygen on the main axis of the molecule. The polarizable point dipole is in the center of mass of the molecule. The used polarizability is 1.44 \AA^3 , the Lennard-Jones parameters are 3.20 Å and 0.9 kJ/mol.

The model of Dang and Chang¹⁷ (DC) is very similar to the BSV model. This model also uses the gas phase geom-

etry. The fixed negative charge is 0.215 Å from the oxygen with a value of -1.038 esu. The Lennard-Jones parameters are 3.234 Å and 0.7638 kJ/mol. The polarizable point dipole is placed at the site of the negative charge. The used polarizability is 1.444 \AA^3 .

A more elaborate version is the GCP model¹⁸ because it uses Gaussian functions to represent the distribution of permanent charges. The center of the negative charge is placed 0.27 Å from the oxygen. Instead of the usual Lennard-Jones repulsion it uses a Buckingham exp-6 potential. The polarizable point dipole is placed in the center of mass with 1.444 \AA^3 for polarization.

The approximation of the point dipole is valid strictly for long distances. However, it has been shown by MP4 calculations that for such water models it is a reasonable method for short distances as well.¹⁹

The fourth model is the Drude oscillator potential of water.²⁰ This potential belongs to a different family of simple polarizable models. The polarization of the molecule is expressed in the form of a point charge connected by a classical spring to the oxygen atom. The model contains five charged sites. In the absence of an external polarizing force the spring particle rests on the oxygen, so the net charge on the oxygen is zero. In this case the three remaining sites, similar to the previous polarizable models, rest on the hydrogens and on the bisector of the HOH angle to approximate the quadrupole moment of the molecule. This model has two parametrizations. First, the spring charge was positive and the charge on the oxygen negative (SWM4-DP), then with slight refinement of other parameters the spring charge was set to be negative and the oxygen site positive (SWM4-NDP).²¹

Another charge-on-spring model was devised by Yu and van Gunsteren.²² This model has two versions, termed COS/G2 and COS/G3, with different parameters. The former has TIP4P geometry, the latter has SPC geometry. The essence of both models is that the spring is connected to the negative charge placed on the HOH bisector at a distance of 0.22 or 0.15 Å from the oxygen atom. At this point there is an additional charge with 8.0 esu and a spring charge of -8.0 esu. In this respect, these models with their small dipole vector are very close to the point dipole models.

In terms of the accuracy of quadrupole moments the goodness of the models is as follows: GCP, SWM4, DC, COS, and BSV. Polarizable models above follow identical or, at least, very similar philosophy. A completely different approach was taken by Rick *et al.*²³ when they devised a dynamical fluctuating charge force fields for SPC and TIP4P geometry. The charge, following the impact of the surrounding, moves within the molecule to equalize the electronegativity of the atoms. The weakness of this model is that polarization is restricted to the HOH plane. We studied this model to see the effect of this restriction.

Polarizable models have varying accuracy of predictions. The SWM4 models besides other properties were fitted to the dielectric constant. The other models overestimate this property.²⁰ However, this is closely related to the fact that SWM4 models have the smallest average dipole moment in water (2.456D, 2461D).^{20,21} In addition, SWM4 models use

smaller polarizability (1.04 \AA^3) justifying this with the “energy cost of overlapping electronic clouds in the condense phase due to Pauli’s exclusion principle.”²⁰ This is also true for the COS models,²² their polarizability is 1.25 \AA^3 .

Browsing all the reported properties, the GCP model seems the best.¹⁸ Its dielectric constant at ambient conditions is only slightly larger than the experimental (84.3), but estimates of all the other properties, especially pair-correlation functions and critical behavior, are remarkably accurate. This model has the largest average dipole moment in ambient liquid state, 2.72D. This value is somewhere halfway between the typical classical and quantum chemical estimates.²⁰ On the other hand, this model is the most expensive of the above models.

All the above models are rigid entities. We chose a flexible model to see the impact of vibrations on the arrangements of clusters. The model introduced by Toukan and Rahman²⁴ is based on SPC geometry (termed by us in the following as SPCf).

The hierarchy of water clusters provides the next step to test the quality of the models. While there are such calculations for the SWM4-DP and the DC models,^{17,20} these consider only part of the topologically distinguishable conformations. We used their data as crosscheck of the correctness of our results. For the BSV,¹⁶ the TIP5P,^{14,15} the TIP4P-FQ (Ref. 23) and SPC-FQ,²³ and the SPCf²⁴ we did not find data of cluster calculations. Description of the GCP model¹⁸ reported only about the dimer.

Using the above models, the purpose of this paper is to identify topologically different arrangements of water clusters near their minimum energy and compare the results with experimental and quantum chemical calculations. We study the clusters up to 6 molecules. Although nonpolarizable models cannot give correct results for gas phase cluster calculations, in general, we included them in the study to serve as references to polarizable models. We refer to cluster properties calculated for the TIP3P model⁸ by Tsai and Jordan.^{25,26} Since the authors determined the lowest energy clusters,²² we did not calculate the clusters for the COS models but use their results for comparison.

We discuss the results in three groups. The first contains the nonpolarizable models with three fixed charges. The second shows the point dipole and the Drude oscillator polarizable ones. The third contains the TIP5P, the SPC-FQ, the TIP4P-FQ, and the flexible SPCf models. The first two groups contain closely related models where the comparison emphasizes performance differences caused by parametrizations. The third group collects models different from these two families of potentials. The TIP5P model shows the acceptability of its pronounced tetrahedral character for cluster calculation. The SPC-FQ and TIP4P-FQ models can decide about the importance of spherical polarizability, while the SPCf models test the role of flexibility in cluster determination.

The organization of the paper is as follows. In Sec. II we describe the methods for minimum searching. In Sec. III we describe the methods we used for identifying topologically identical or different structures. In Sec. IV we discuss the results for dimers, where experimental and several quantum

chemical results exist for comparison. In Secs. V–VIII we discuss the trimers, tetramers, pentamers, and hexamers, respectively. In Sec. IX we conclude the paper.

II. SEARCHING FOR ENERGY MINIMA OF CLUSTERS

We used two methods to identify minima: molecular dynamics (MD) simulations of the cluster and the SIMPLEX algorithm.²⁷ We applied the “steepest descent” method in MD by rescaling the velocities of the system to 10^{-5} K in each time step. The starting configurations were generated randomly using the TIP4P model. We compared our results with that of Tsai and Jordan.^{25,26} They used a much more expensive eigenmode following search.²⁵ For the 2–4 molecules we obtained all the minima they found. Out of the 15 smallest energy minima they found for clusters of 5 molecules, we identified 14. In the case of hexamers they found 30, while we identified 27 of them. Still, we found all *topologically* different structures they reported.

In the case of the TIP4P-type rigid potentials (SPC/E, TIP4P-EW, and TIP4P/2005) we started the search randomly from the TIP4P minima using the SIMPLEX algorithm.²⁷ The advantage of this method is that it is sufficient to calculate the energies. There is no need for force calculations. Due to their structural differences separate MD simulations were carried out for the TIP5P and the SPCf potentials.

Since the polarizable models might have different kinds of arrangements, we carried out MD simulations again for the DC, the SWM4-DP, the SPC-FQ, and the TIP4P-FQ models. For the rest of the models, we carried out the search for the minima starting from both the DC and the SWM4-DP arrangements.

The accuracy of our energy calculations is ± 0.002 kJ/mol. Barrier heights are typically in the range of 0.1–1.0 kJ/mol. However, in some cases barriers between two neighboring minima might be practically zero, which means that the search ends up in the common minimum of the two arrangements. In this case only one cluster will be identified connected to the most similar topological group.

III. DEFINING CRITERIA FOR TOPOLOGICALLY EQUIVALENT CLUSTERS

The potential surface of clusters with increasing numbers of molecules contains more and more minima. These minima define different configurations. However, in most of the cases the actual structural differences among the clusters are small. It is useful to group them by their topological similarity and show only that configuration which has the smallest energy in the topologically identical group.

The simplest way to do this is to study hydrogen bonds. To go beyond visual identification it is important to define a criterion for the existence of the bond. However, there is no way to do this unambiguously. We consider two molecules hydrogen bonded to each other if the distance between the donor proton and acceptor oxygen is shorter than 2.6 \AA and the distance between the two oxygens is shorter than 3.15 \AA . Using this definition we can construct simple, visually informative graphs. In Fig. 1 we show graphs representing pentamers with low energy. In Fig. 2 the same is shown for

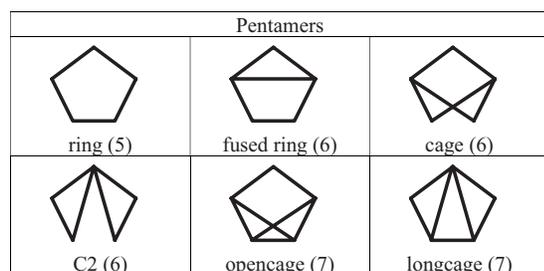


FIG. 1. A schematic view of pentamers identified by the graph of their hydrogen bond network. The trivial name of each cluster is written below the corresponding graph. We are showing in parenthesis the number of hydrogen bonds.

hexamers. The numbers in parenthesis show the number of hydrogen bonds in the structure. The vertices are oxygen atoms, the lines mark hydrogen bonds.

A more elaborate possibility for identifying topological similarity is to calculate overlap integrals between configurations of found minima. We place a three-dimensional Gaussian to each atom of cluster A . The sum of these functions is considered as some kind of structural function S_A . Then the normalized overlap integral below will give the similarity H_{AB} of cluster A relative to cluster B as

$$H_{AB} = \frac{\int S_A(\mathbf{r})S_B(\mathbf{r})d\mathbf{r}}{(\int S_A^2(\mathbf{r})d\mathbf{r})^{1/2}(\int S_B^2(\mathbf{r})d\mathbf{r})^{1/2}} \quad H_{AB} \in [0,1]. \quad (1)$$

The parameters of the Gaussian are chosen to provide optimum results. The method is devised with the ability to assign different weight functions to oxygen and hydrogen atoms in order to provide larger role to oxygen positions. The integration is carried out by fixing the position of cluster A . The center of mass of cluster B is placed into the center of mass of cluster A . Then, keeping the internal structure of clusters fixed, using Euler angles for relative rotation, we look for the largest value of $H_{A,B}$.

We form a matrix of the H_{AB} values. The matrix is arranged to contain the largest H_{AB} values close to the diagonal. Then we choose a number H_{AB}^{\min} as the minimum overlap integral value. Two clusters in a column belong to the same

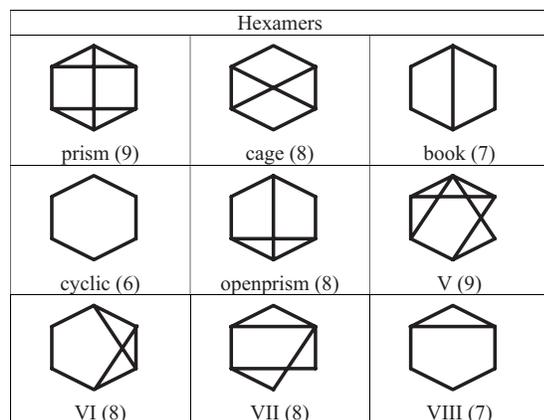


FIG. 2. A schematic view of hexamers identified by the graph of their hydrogen bond network. The trivial name of each cluster is written below the corresponding graph. We are showing in parenthesis the number of hydrogen bonds. Since typically only the cyclic, the cage, the book, and the prism forms are studied, the rest has no trivial name given so far.

topological group if their overlap integral is larger than H_{AB}^{\min} . This choice is surprisingly unambiguous. The typical H_{AB}^{\min} value is ~ 0.7 . Thus, we can mark borders around the diagonal to form the group of topologically similar clusters. We choose from this group the arrangement with the lowest energy as a representative of the group.

The overlap integral in most of the cases only quantified the results obtained by the hydrogen bond enumeration. For a given interaction model separation of groups was unambiguous. However, selecting the structure with the lowest energy of a group, there can be differences between different models with the same topology. This comes from the slightly different shape of the potential energy surface of different models, or it can happen that within the same topological group two models will position themselves in neighboring minima as their absolute minimum.

IV. THE DIMER

The dimer is the most studied entity because for this cluster, in addition to quantum chemical calculations, there is experimental information. The energy content of the arrangement was determined using thermal conductivity data.²⁸ The geometry which is given by the O–O distance, d_{O-O} , and the angle θ° between the OH bond of the donor molecule and the main axis of the acceptor molecule was determined from microwave spectroscopy.²⁹ The equilibrium constant of the dimer as a function of temperature was also determined from spectroscopic data.³⁰

The small size of the cluster invited numerous quantum chemical calculations. These calculations used different methods. In this paper we cite only calculations taking into account electron correlations because HF energy results are 6–6.5 kJ/mol smaller than the experimental value.

In Table I we present the description of calculations carried out for the water dimer. The potential surface of the dimer is quite flat, a change of 0.1 Å in the oxygen-oxygen distance d_{O-O} causes a mere 0.6 kJ/mol difference in intermolecular energy. The geometry of Frisch *et al.*³¹ is 2.911 Å for d_{O-O} and 57.8° for the angle. This geometry was used by subsequent authors (see Table I). The d_{O-O} calculated by Xantheas^{35,36} is 2.907 Å which by applying counterpoise correction becomes 2.933 Å. The d_{O-O} distance by Halkier *et al.*³⁷ at CCSD(T)/aug-cc-pVTZ level is 2.895 Å, at the MP2/aug-cc-pVQZ level it is 2.915 Å. In general it may be stated that there is coherence in the quantum chemical calculations presented in Table I. Different methods obtained very similar results.

Our results are shown in Table II. The most important features to be noticed in Table II are the following. As one might expect the nonpolarizable models gave poor results. Since the dipole moments of the individual molecules in the dimer are somewhere around 2–2.15D, the best results are given by the TIP4P model which has the smallest dipole moment. The poorest estimate is provided by the SPC/E model. A long list of dimer properties is presented in the paper of Yu and van Gunsteren.²² The presented results for the potentials we also calculated are the same.

The best description for these properties was obtained by

TABLE I. Quantum chemical calculations for the water dimer (A: authors; G: method used for geometry optimization; M: method used for energy calculation; E: calculated intermolecular energy; R: remarks about further techniques used) (cbsl=complete basis set limit, CPC=couterpoise correction).

A	G	M	E	R
Frisch <i>et al.</i> ^a	MP2/6-311++G(2d,2p)	MP4/6-311++G(3df,3dp)	-22.34, -18.91	CPC
Feller ^b	Frisch	MP2/aug-cc-pVQZ	-20.71	cbsl, CPC
Feyereisen <i>et al.</i> ^c	Frisch	MP2/aug-cc-pV5Z	-20.92	cbsl, CPC, geom. relax.
Klopper <i>et al.</i> ^d	Frisch	MP2/PW-qz	-20.59	CPC
Xantheas ^{e,f}	MP2/aug-cc-pVTZ	MP2/aug-cc-pV5Z	-20.67	cbsl, CPC
Halkier <i>et al.</i> ^g	CCSD(T)/aug-cc-pVTZ	CCSD(T)/daug-cc-pV5Z	-20.92	cbsl, CPC, geom. relax.

^aReference 31.^bReference 32.^cReference 33.^dReference 34.^eReference 35.^fReference 36.^gReference 37.

the polarizable models of GCP and BSV. Their results are very close to the data of quantum chemical calculations. However, it is a general feature of all of the models calculated by us that the experimental 2.976 Å O–O distance is difficult to reproduce. This is also true for the quantum chemistry results, although they are closer to the experimental value. Not surprisingly, the net dipole of the arrangement is very sensitive to the characteristic angle θ . Larger angles correspond to smaller net dipole moments, smaller angles correspond to larger net dipole moments.

At the end of Table II we present results for group III models. The two sets of parameters of the TIP5P model provided very similar results, therefore here and in the rest of the paper we show only the values obtained by the potential of Rick.¹⁵ This potential also underestimates the intermolecular energy and overestimates the net dipole moment like all nonpolarizable models. However, its d_{O-O} distance is extremely small, the smallest of all the studied models. The FQ models provide the best estimates for the d_{O-O} distance but this happens at the expense of the intermolecular energy which is too high. For these models the characteristic angle is extremely small, for SPC-FQ it is a mere 14.32° which means that the arrangement is very close to linear. This is also true for the SPCf flexible model. When we switched off

the flexibility, the results remained very similar with the difference that the flexibility gave slightly lower energy, shorter d_{O-O} , and larger net dipole moment.

While it is very important to obtain accurate results for the dimer, it cannot ensure the accuracy of the model in the gas phase. There is a fine structure in clusters of 3–6 molecules which can manifest many differences among models because during potential development, typically, there is no fit for larger clusters.

V. THE TRIMER

Contrary to the dimer, there are no detailed experimental data for trimers. The only experimental information is that the three oxygen molecules form a triangle with 2.97, 2.97, and 2.94 Å mutual distances.³⁸ Three oxygens and three hydrogens are in the same plane, while two hydrogens are positioned above, and one is positioned below the plane.

Quantum chemical studies were done by Fowler and Schaefer.³⁹ They used DZP basis set augmented by diffuse functions. The average d_{O-O} they obtained was 2.83 Å, which is substantially smaller than the experimental value. For this geometry at TZ2P+diff/CCSD level they obtained -61.92 kJ/mol intermolecular energy. In addition to the ab-

TABLE II. Properties of the dimer calculated using different models (E: calculated intermolecular energy; d_{O-O} : distance of the oxygen atoms; θ : angle between the OH bond of the donor and the main axis of the acceptor molecule; D_T : the total dipole moment of the arrangement; D_i : the average polarization of the molecules).

Model	E (kJ/mol)	d_{O-O} (Å)	θ	D_T (D)	D_i (D)
Expt.	-22.60	2.976	57	2.64	...
SPC/E	-30.106	2.734	22.28	3.738	0
TIP4P	-26.093	2.748	48.88	2.7131	0
TIP4P/2005	-28.712	2.77	49.02	2.885	0
TIP4P-EW	-28.66	2.753	41.9	3.20	0
BSV	-19.346	2.884	55.19	2.70	0.287
DC	-19.616	2.866	68.58	2.289	0.290
SWM4-DP	-21.68	2.822	70.18	2.087	0.224
SWM4-NDP	-21.548	2.828	70.74	2.063	0.22
GCP	-20.771	2.877	55.28	2.617	0.272
TIP5P	-28.516	2.679	50.19	2.921	...
TIP4P-FQ	-18.43	2.924	27.13	3.432	0.328
SPC-FQ	-18.434	2.943	14.32	3.72	0.348
SPCf	-28.63	2.737	21.91	3.752	...

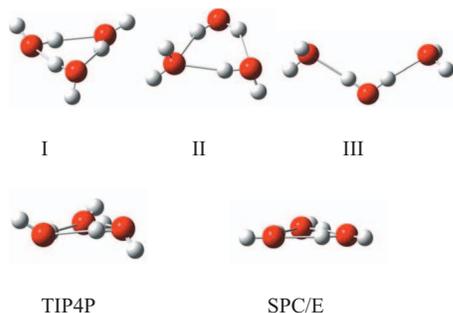


FIG. 3. The first row shows the possible clusters of trimers. Below a TIP4P and a SPC/E cluster is shown. The former is another view of structure I above, while the SPC/E arrangement is completely flat for the same hydrogen bond structure.

solute minimum, M \acute{o} *et al.*⁴⁰ determined the geometry of two further minima and several transition states. The geometries were calculated at MP2/6-311+G(d,p) level, the energies were determined at MP4SDQ/6-31+G(2d,2p) level. The geometries of the three minima are in qualitative agreement with that of classical models. The average d_{O-O} at the absolute minimum is 2.794 Å. The energies of the three minima are -63.88, -41.54, and -37.44 kJ/mol. These two calculations neglected BSSE.

To study the torsional motions close to the absolute minimum, Schütz *et al.*⁴¹ calculated the d_{O-O} which at the level of MP2/6-311++g(d,p) using CP corrections proved to be 2.797 Å with the energy of -58.20 kJ/mol. Trimer calculations at the highest level were carried out by Xantheas and co-workers.⁴² They optimized the geometry at the level of MP2/aug-cc-pV5Z and calculated the energy using aug-cc-pVxZ basis set extrapolating to the CBS limit and taking into account BSSE. Unfortunately, they did not present the geometry obtained. Their calculated energy is -66.1 kJ/mol.

There are three distinct possibilities for three molecules to form a cluster with all the molecules bonding. These forms are shown in the top row of Fig. 3 for the TIP4P model. In Table III we show results for nonpolarizable models. There were small variations in oxygen-oxygen distances but saving the reader from data overflow we present only the average.

Not surprisingly nonpolarizable models underestimate the energy and the average distances, d_{O-O} . Properties of the TIP4P-type models are quite similar. There is, however, a

TABLE III. Results for the trimers using nonpolarizable models [E: total intermolecular energy (kJ/mol); d_{O-O} : average oxygen-oxygen distance (Å); D_T : total dipole moment of the arrangement (D)].

	SPC/E	TIP4P	TIP4P/2005	TIP4P-EW
E	-82.012	-70.008	-76.987	-76.8
d_{O-O} I	2.742	2.761	2.784	2.766
D_T	0.0	0.592	0.654	0.313
E	-57.804	-52.077	-57.466	-56.99
D_{O-O} II	2.837	2.835	2.858	2.841
D_T	5.762	4.868	5.148	5.263
E	-53.787	-47.439	-52.249	-51.56
d_{O-O} III	2.750	2.755	2.777	2.764
D_T	3.158	0.64	0.674	1.212

remarkable behavior of the SPC/E model. This model forms a totally symmetric planar arrangement for the deepest energy minimum. Therefore its net dipole moment is zero (see Table III). This is also true for the SPCf and the SPC-FQ models (see Table V). The TIP4P geometry models including also the polarizable ones do not form planar arrangement for this topology. They look like the TIP4P model in the second row of Fig. 3. (This configuration is just another view of structure I in the row above.) The fact that this behavior is connected to the negative charge being on the oxygen is proved by the fact that the same geometry was obtained by Tsai and Jordan²⁵ for the TIP3P model.

In Table IV we show the results for the polarizable models. Trimers are still small enough clusters that the drastic differences observed for dimers between estimation qualities of polarizable and nonpolarizable models still exist. The energies for the polarizable models are much closer to the quantum chemical results. In fact, the average d_{O-O} 's are quite long for the polarizable models, so they are closer to the experimental value than d_{O-O} 's from quantum chemical results.

The SWM4-DP, the SWM4-NDP, and the GCP potentials do not have configuration II. The barrier between trimer configurations I and II is zero, therefore the iteration could find only the absolute minimum, i.e., configuration I. Such a transformation is quite common among the clusters. When this happens, we will present the trivial name or roman number of that configuration which was reached by the energy minimization procedure instead of the starting topologically different arrangement.

The energies for the COS models²² calculated for structure I are close to the BSV and DC energies with slightly longer d_{O-O} 's (2.94 and 2.95 Å).

In Table V the FQ models, similar to the dimers, have long d_{O-O} 's and high energies. The SPCf model gives very deep energy and short d_{O-O} 's. The most special behavior was found for the TIP5P model. In addition to the three topologically different minimum energy arrangements shown in Fig. 3, this model has two further structures shown schematically in the first row of Fig. 4. We do not show the numerical details of the extra structures of TIP5P but, in general, the calculated energies of these structures are comparable to the energies of the "standard" structures. In the case of trimers, for instance, the energy of structure IV is -61.251 kJ/mol, while for structure V it is -50.182 kJ/mol. The tetrahedral position of the charges stabilizes structures unstable with the three-charged models and not found by quantum chemical calculations.

While the trimer energies determined by quantum chemical calculations vary a lot, the most recent calculation of Xantheas and co-workers⁴² provided considerably lower energy than the polarizable models for structure I. In this respect the GCP was the best. The nonpolarizable models, just like for dimers, underestimated the energy. This tendency will prevail for all larger clusters, but as the average polarization increases for larger number of molecules, the difference will become smaller. The reason that this difference will not disappear for larger clusters is caused by the much smaller repulsion of the rigid models. Looking at Table

TABLE IV. Results for the trimers using polarizable models [E: total intermolecular energy (kJ/mol); d_{O-O} : average oxygen-oxygen distance (Å); D_T : total dipole moment of the arrangement (D); D_i : average induced dipoles (D)].

	BSV	DC	SWM4-DP	SWM4-NDP	GCP
E	-54.472	-55.787	-60.407	-60.018	-60.671
d_{O-O} I	2.879	2.855	2.826	2.832	2.838
D_T	0.813	1.071	1.091	1.107	1.059
D_i	0.469	0.492	0.358	0.358	0.478
E	-39.312	-39.334			
d_{O-O} II	2.981	2.979	I	I	I
D_T	4.595	4.763			
D_i	0.309	0.311			
E	-35.11	-35.90	-40.325	-40.091	-37.98
d_{O-O} III	2.895	2.873	2.826	2.833	2.898
D_T	0.302	0.496	0.059	0.177	0.477
D_i	0.307	0.316	0.247	0.245	0.279

II, one can see an ~ 0.1 Å shorter d_{O-O} for nonpolarizable models than for polarizable ones. This smaller repulsion will be present in each cluster.

The tendency of energies for the three possible structures is correct not only intuitively but also by comparing them with the results of M \acute{o} *et al.*⁴⁰ Gregory *et al.*⁴³ calculated the net dipole of structure I using MP2 theory with aug-cc-VdZ basis set. They got 1.071D which is in good agreement with the DC, the SWM4-DP, the SWM4-NDP, and the GCP potentials (see Table IV). The BSV interaction gives a bit lower value for that. This also indicates that the SPC-type structure I with its zero net dipole moment is less realistic than that for the TIP4P-type models.

VI. THE TETRAMER

There is no experimental result for tetramers. Quantum chemical calculation was carried out by Xantheas *et al.*⁴² They calculated energies at MP2/aug-cc-pV5Z level but did not report geometry for this basis set. The energy they found is -115.48 kJ/mol.

In Table VI we present the results found for nonpolarizable models. The same is shown in Table VII for polarizable models. As it can be seen there are empty rows in both

TABLE V. Results for the trimers of group III models [E: total intermolecular energy (kJ/mol); d_{O-O} : average oxygen-oxygen distance(Å); D_T : total dipole moment of the arrangement (D); D_i : average induced dipoles (D)].

	TIP5P	TIP4P-FQ	SPC-FQ	SPCf
E	-62.728	-52.607	-53.201	-78.869
d_{O-O} I	2.770	2.912	2.920	2.740
D_T	1.074	0.417	0.0	0.0
D_i	...	0.482	0.551	...
E	-52.287			-55.473
d_{O-O} II	2.809	I	I	2.837
D_T	5.165			5.780
D_i
E	-50.138	-31.664	-30.593	-51.06
d_{O-O} III	2.693	2.966	2.997	2.755
D_T	1.529	1.333	3.166	3.308
D_i	...	0.184	0.217	...

tables. For rigid models structure II does not exist, the molecules transform to structure I. Therefore we completely left it out from Table VI. Arrangement I where the nonbonded hydrogens alternating above and below the approximately planar arrangement has the lowest energy and has been cal-

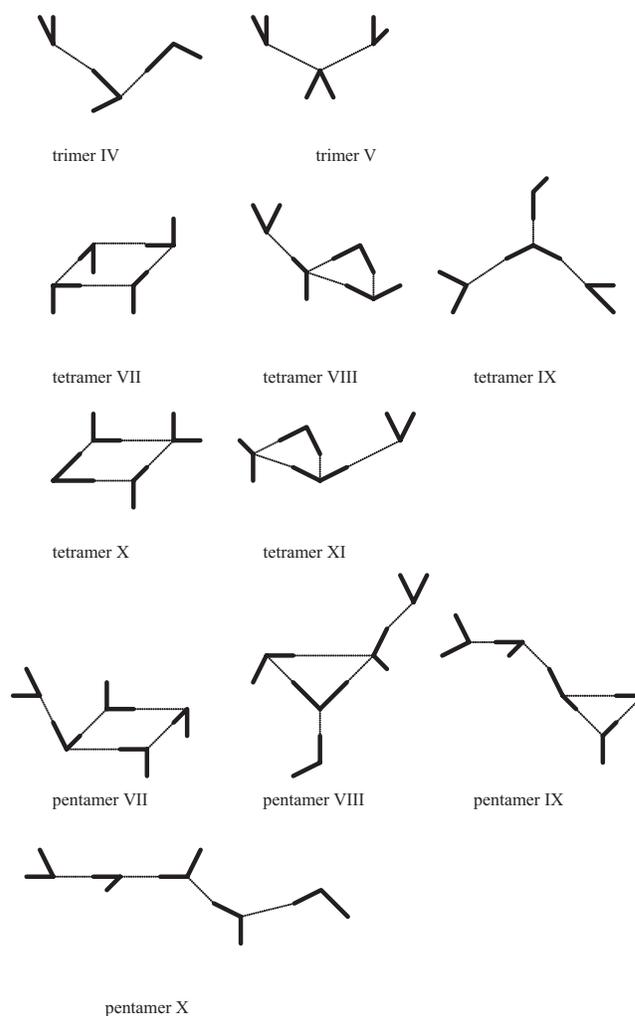


FIG. 4. A schematic picture of the extra structures found for the TIP5P model. Thick lines represent the HOH bonds, thin lines represent the hydrogen bonds.

TABLE VI. Results for the tetramers using nonpolarizable models [E: total intermolecular energy (kJ/mol); d_{O-O} : average oxygen-oxygen distance(Å); D_T : total dipole moment of the arrangement (D)].

	SPC/E	TIP4P	TIP4P/2005	TIP4P-EW
E	-136.60	-116.614	-128.277	-128.42
d_{O-O} I	2.704	2.723	2.745	2.726
D_T	0.0	0.0	0.0	0.0
E	-106.072	-100.525	-110.847	
d_{O-O} III	2.796	2.787	2.810	I
D_T	4.206	3.354	3.556	
E	-110.258	-95.049	-104.619	-104.09
d_{O-O} IV	2.743	2.758	2.779	2.762
D_T	2.573	3.076	3.280	1.948
E	-106.058	-93.695	-103.237	-102.31
d_{O-O} V	2.759	2.765	2.788	2.771
D_T	5.384	4.478	4.739	4.879
E	-95.948	-85.467	-94.241	-93.53
d_{O-O} VI	2.777	2.790	2.812	2.792
D_T	0.0	0.0	0.0	0.0

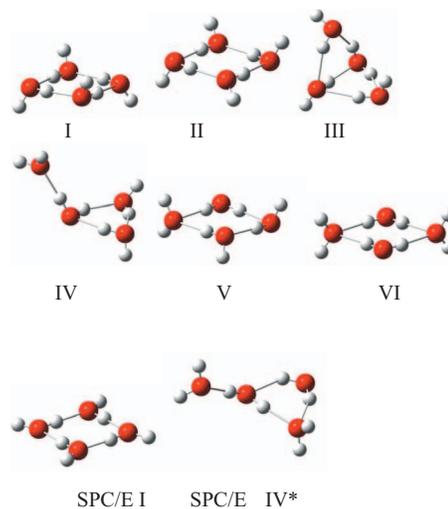


FIG. 5. The six structures for tetramers. Below two structures of the SPC/E models are shown. Structure I of this model is completely flat with zero net dipole. This model has also a variant of structure IV.

culated for the DC,¹⁷ the SWM4-DP,²⁰ and the COS²² models earlier. Energies for the COS/G2 and COS/G3 models are -103.4 and -101.1 kJ/mol, respectively.

In Fig. 5 we presented pictures of tetramer structures for the SWM4-DP model. In the case of structure IV, when this arrangement for this interaction does not exist, we show the structure of TIP4P. The number under the given structure in Fig. 5 determines the order of the data shown in the tables.

There is a possibility for polarizable models to have non-bonded hydrogens positioned, as it is shown by structure II,

and the energy of this arrangement is only slightly smaller than that for structure I. Structure IV with its open character is stable for nonpolarizable models, but unstable for all the polarizable models with the exception of the BSV model. The remaining two clusters (V and VI) exist, but the related energies are considerably higher, especially for polarizable models. The reason for this is that the favorable rectangular shape is distorted by the presence of the HOH angle. Since the symmetric structure VI has two HOH angles, it has higher energies than structure V which has only one HOH angle.

TABLE VII. Results for the tetramers using polarizable models [E: total intermolecular energy (kJ/mol); d_{O-O} : average oxygen-oxygen distance (Å); D_T : total dipole moment of the arrangement (D); D_i : average induced dipoles (D)].

	BSV	DC	SWM4-DP	SWM4-NDP	GCP
E	-98.718	-100.185	-105.485	-105.009	-106.416
d_{O-O} I	2.801	2.781	2.769	2.771	2.773
D_T	0.0	0.0	0.0	0.0	0.0
D_i	0.68	0.697	0.49	0.498	0.649
E	-96.68	-96.984	-102.976	-102.444	-104.281
d_{O-O} II	2.808	2.795	2.776	2.778	2.777
D_T	0.0	0.0	0.0	0.0	0.0
D_i	0.671	0.67	0.488	0.494	0.647
E			-89.33	-88.767	
d_{O-O} III	I	II	2.856	2.864	II
D_T			2.655	2.632	
D_i			0.0352	0.350	
E	-75.675				
d_{O-O} IV	2.872	II	III	III	II
D_T	3.431				
D_i	0.50				
E	-74.645	-75.35	-82.125	-81.595	-83.248
d_{O-O} V	2.878	2.865	2.83	2.836	2.84
D_T	4.215	3.936	3.993	3.98	3.80
D_i	0.0485	0.484	0.362	0.360	0.478
E	-65.023	-64.424	-71.533	-71.037	-68.85
d_{O-O} VI	2.927	2.927	2.877	2.884	2.938
D_T	0.0	0.0	0.0	0.0	0.0
D_i	0.365	0.343	0.288	0.283	0.336

TABLE VIII. Results for group III models [E: total intermolecular energy (kJ/mol); d_{O-O} : average oxygen-oxygen distance(Å); D_T : total dipole moment of the arrangement (D); D_I : average induced dipoles (D)].

	TIP5P	TIP4P-FQ	SPC-FQ	SPCf
E	-119.56	-98.888	-103.229	-132.508
d_{O-O} I	2.675	2.809	2.794	2.698
D_T	0.0	0.0	0.0	0.0
D_I	...	0.772	0.931	...
E	-114.563			
d_{O-O} II	2.686	I	I	I
D_T	0.0			
D_I	...			
E		-75.111	-68.148	-101.649
d_{O-O} III	II	2.948	2.998	2.797
D_T		2.771	2.998	4.069
D_I		0.437	0.454	...
E		-72.779	-72.994	-106.106
d_{O-O} IV	II	2.908	2.92	2.742
D_T		2.352	3.522	2.591
D_I		0.485	0.556	...
E	-95.967			-101.84
d_{O-O} V	2.715	I	I	2.76
D_T	5.212			5.309
D_I
E	-93.133	-60.08	-57.146	-90.972
d_{O-O} VI	2.720	2.977	3.007	2.782
D_T	0.0	0.0	0.0	0.0
D_I	...	0.257	0.299	...

The energy of structure I is higher for the polarizable models than the quantum chemical result.⁴² Due to the symmetry of structure I both quantum chemical calculations⁴³ and the classical models provided a net dipole of 0.0D.

The SPC-type models show peculiar behavior again. Structure I for this model is perfectly flat, all atoms are in the same plane (see Fig. 5). The same is the case for TIP3P.²⁵ The SPC/E model has an additional structure, marked IV* similar to structure IV shown in Fig. 5. This structure has -86.848 kJ/mol energy, 2.809 Å average O-O distance, and 6.61D net dipole moment.

In Table VIII we present the data for group III models. The TIP5P model has numerous additional stable minima with topologically different arrangements. In Fig. 4 we show schematically five additional structures within the energy range of -81-113.5 kJ/mol. There is still an additional conformer for TIP5P which in this simplified graph view is identical with structure V, the difference is that the four oxygen atoms are not in the same plane. The energy of structure VII (-113.524 kJ/mol) is comparable to the energies of structures I and II (-118.955 and -113.945 kJ/mol). Structure I shows its nonbonded hydrogens alternating up and down, while structure II shows two neighboring hydrogens up, the other two pointing down. For the TIP5P model the structure with single hydrogen pointing up and three hydrogens down is also a low energy stable arrangement.

VII. THE PENTAMER

Pentamers have six different structures, as they are shown on simple diagrams of Fig. 1. The quantum chemical

TABLE IX. Results for the pentamers using nonpolarizable models [E: total intermolecular energy (kJ/mol); d_{O-O} : average oxygen-oxygen distance(Å); D_T : total dipole moment of the arrangement (D)].

	SPC/E	TIP4P	TIP4P/2005	TIP4P-EW
E	-178.294	-152.139	-167.325	-168.03
d_{O-O} ring	2.698	2.721	2.743	2.722
D_T	0.31	0.574	0.609	0.56
E	-166.495	-151.118	-166.521	-164.37
d_{O-O} cage	2.748	2.749	2.771	2.756
D_T	4.457	3.481	3.683	3.751
E	-159.7	-148.586	-163.621	-163.22
d_{O-O} fused ring	2.756	2.765	2.787	2.770
D_T	4.342	1.953	2.066	3.087
E	-144.18	-148.989	-164.228	
d_{O-O} open cage	2.81	2.793	2.815	Cage
D_T	4.137	2.066	2.187	
E	-155.457	-137.527	-151.387	-149.44
d_{O-O} C2	2.751	2.757	2.78	2.765
D_T	1.173	0.38	0.384	0.576

result for their energy calculated by Xantheas *et al.*⁴² is -151.88 kJ/mol. Xantheas gave also estimate for the average O-O distance in his earlier paper to be 2.86 Å.³⁵

Our results are shown in Tables IX and X. While the simple diagrams of Fig. 1 create a very understandable inventory about the identifiable arrangements, they show nothing about the nonbonding hydrogens which can influence the structure and the energy of the arrangement. Therefore in Fig. 6 we present the pentamers as they were determined by the GCP potential. These arrangements being complicated structures obtained trivial names. Earlier studies⁴⁴ found perfect C2 symmetry for the last structure; therefore we named it like that, although the perfect C2 symmetry does not hold for our models.

The ring structure has the lowest energy for all models, despite it has the smallest number of hydrogen bonds, 5. In ice phases ice III has five member rings with different d_{O-O} distances.⁷ Without translational symmetry in the gas phase the molecules have much freedom to optimize this arrangement. The polarizable models have all the topologically possible structures.

In Table XI we show results for group III pentamers. The most interesting thing is that the SPC-FQ interaction forms a perfectly symmetric planar ring with zero net dipole. While the net dipole is small for the other SPC-type models as well, the planar polarizability further enhances the realization of a perfectly planar and symmetric arrangement. The long cage arrangement is unstable for both nonpolarizable models and group III models, therefore it is not shown. The starting configurations turn into ring or fused ring structures.

The TIP5P model creates new structures again. In Fig. 4 we show them schematically. The energy of structure VII is -141.13 kJ/mol, while the energy of the other three structures is ~-122-126 kJ/mol. The open chain structure is unique among the clusters.

Unlike in the case of trimers and tetramers, the net dipole of the cyclic pentamer calculated by quantum chemical

TABLE X. Results for the pentamers using polarizable models [E: total intermolecular energy (kJ/mol); d_{O-O} : average oxygen-oxygen distance (Å); D_T : total dipole moment of the arrangement (D); D_I : average induced dipoles (D)].

	BSV	DC	SWM4-DP	SWM4-NDP	GCP
E	-134.247	-133.035	-139.841	-139.075	-142.872
d_{O-O} ring	2.778	2.774	2.758	2.758	2.749
D_T	0.564	0.803	0.628	0.652	0.235
D_I	0.785	0.759	0.556	0.564	0.737
E	-127.424	-129.951	-137.597	-136.89	-138.438
d_{O-O} cage	2.843	2.824	2.804	2.808	2.821
D_T	3.053	3.098	3.074	3.024	1.45
D_I	0.641	0.663	0.46	0.465	0.612
E	-128.008	-128.505	-134.499	-133.702	-137.175
d_{O-O} fused ring	2.846	2.834	2.818	2.822	2.818
D_T	2.134	2.145	2.031	2.033	1.213
D_I	0.7	0.692	0.484	0.488	0.66
E	-124.484	-126.969	-134.314	-133.508	-135.873
d_{O-O} open cage	2.901	2.894	2.857	2.844	2.84
D_T	1.949	2.678	2.254	1.871	1.204
D_I	0.614	0.653	0.444	0.445	0.597
E	-110.677	-115.18	-122.987	-122.56	-123.328
d_{O-O} long cage	2.916	2.8912	2.876	2.885	2.879
D_T	1.069	0.605	0.613	0.652	0.605
D_I	0.534	0.592	0.399	0.402	0.527
E	-109.641	-112.424	-120.494	-118.978	-121.995
d_{O-O} C2	2.867	2.848	2.824	2.828	2.832
D_T	0.581	0.273	0.318	0.606	0.1109
D_I	0.551	0.563	0.405	0.423	0.543

calculations⁴³ is considerably different from the values provided by classical models. The quantum chemical value is 0.927D. The closest is the DC model with 0.803D, the most different is the GCP model with 0.235D.

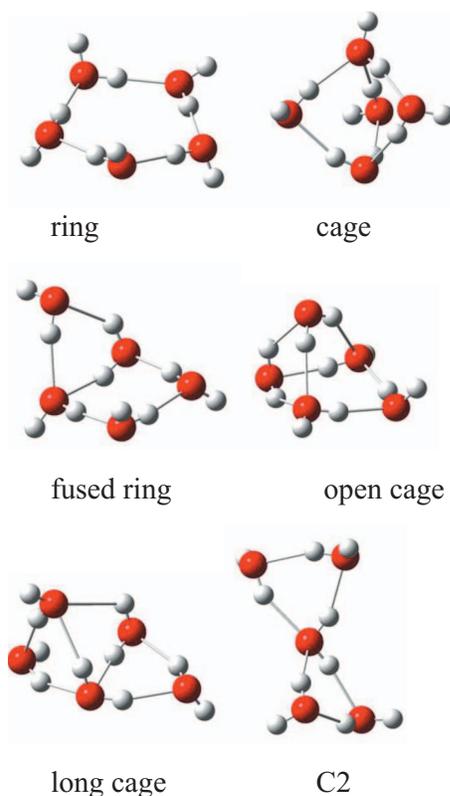


FIG. 6. Picture of pentamer structures.

VIII. THE HEXAMER

Hexamers received large attention in cluster calculations. This can be attributed to the fact that they are the largest clusters to be calculated within a conceivable variability, or they are interesting because water molecules prefer rings consisting of six molecules (e.g., iceIh).

TABLE XI. Results for the pentamers for group III models [E: total intermolecular energy (kJ/mol); d_{O-O} : average oxygen-oxygen distance(Å); D_T : total dipole moment of the arrangement (D); D_I : average induced dipoles (D)].

	TIP5P	TIP4P-FQ	SPC-FQ	SPCf
E	-160.219	-137.836	-147.297	-174.514
d_{O-O} ring	2.659	2.773	2.737	2.69
D_T	1.221	0.401	0.0	0.255
D_I	...	0.935	1.18	...
E	-147.54	-124.538	-120.88	-161.887
d_{O-O} cage	2.731	2.86	2.8805	2.744
D_T	3.518	3.212	3.384	4.338
D_I	...	0.659	0.747	...
E	-149.51	-119.207	-127.09	-154.388
d_{O-O} fused ring	2.736	2.875	2.88	2.755
D_T	2.561	3.085	2.007	4.205
D_I	...	0.665	0.861	...
E		-102.664		-138.188
d_{O-O} open cage	Cage	2.955	Ring	2.811
D_T		4.241		-4.391
D_I		0.407		...
E	-123.745	-107.144	-105.276	-149.578
d_{O-O} C2	2.766	2.888	2.907	2.749
D_T	0.762	0.242	0.65	1.167
D_I	...	0.549	0.618	...

TABLE XII. Results for the hexamers using nonpolarizable models [E: total intermolecular energy (kJ/mol); d_{O-O} : average oxygen-oxygen distance(Å); D_T : total dipole moment of the arrangement (D)].

	SPC/E	TIP4P	TIP4P/2005	TIP4P-EW
E	-217.548	-197.817	-218.005	-215.357
d_{O-O} cage	2.762	2.756	2.779	2.763
D_T	2.225	1.896	1.996	2.072
E	-205.262	-196.326	-216.52	-213.405
d_{O-O} prism	2.799	2.791	2.813	2.795
D_T	2.601	2.695	2.855	2.867
E	-221.593	-193.008	-212.446	-211.261
d_{O-O} book	2.823	2.735	2.757	2.739
D_T	2.439	2.118	2.256	2.249
E	-217.576	-185.709	-204.246	-205.427
d_{O-O} cyclic	2.696	2.721	2.743	2.721
D_T	0.0	0.0	0.0	0.0
E	-215.33	-194.953	-214.486	-212.83
d_{O-O} open prism	2.764	2.763	2.876	2.768
D_T	3.786	2.361	3.47	2.652
E	-202.417	-188.646	-208.148	-202.629
d_{O-O} V	2.773	2.778	2.799	2.784
D_T	4.165	0.519	0.553	3.175
E		-186.681	-205.629	-204.387
d_{O-O} VI	VIII	2.778	2.800	2.784
D_T		1.373	1.471	1.355
E	-202.54	-186.178	-205.24	-201.898
d_{O-O} VII	2.777	2.761	2.784	2.77
D_T	1.08	0.566	0.607	0.482
E	-213.697	-185.287	-203.958	-204.203
d_{O-O} VIII	2.741	2.754	2.776	2.756
D_T	2.228	2.946	3.137	2.94

The large number of structural variations can form topologically different structures with small differences in energy. The first four arrangements have quantum chemical calculations. Xantheas *et al.*⁴² obtained -192.0 , -191.6 , -190.8 , and -187.4 kJ/mol for the prism, the cage, the book, and the cyclic arrangements, respectively. They determined the geometry at MP2/aug-cc-pVTZ level and calculated energy for this geometry with aug-cc-pVxZ basis using CBS limit and taking into account BSSE. Losada and Leutwyler⁴⁵ obtained -178.9 , -182.9 , -181.2 , -183.2 , and -174.3 kJ/mol for the cyclic, the cage, the book, the prism, and the boat conformations. These energies were obtained using MP2(FC)/aug-cc-pVTZ with optimized geometries at the same level and using counterpoise correction. While there is considerable difference between the energies of Xantheas *et al.*⁴² and of Losada and Leutwyler⁴⁵ the hierarchy of the structures is identical: prism < cage < book < cyclic.

Gregory *et al.*⁴³ concluded based on theoretical and electronic calculations that the most stable form is the cage. They claim that “the prism is probably the global minimum on the hexamer electronic potential energy surface (PES),⁴⁶ whereas a smaller vibrational zero-point energy is responsible for the greater stability of the cage.”⁴⁷

Looking at Table XII the SPC/E model has too deep energy for the clusters and an energy hierarchy which is very different from the ones found by quantum chemical calculations (book < cyclic < cage < prism). In this respect the

TIP4P-type models are closer to the energy values and the probable order of structures (cage < prism < book < cyclic).

In Table XIII we see the results for the polarizable models. The energy of the BSV and the DC models seems a bit high relative to quantum chemical results. The suggested quantum chemical hierarchy more or less seems to hold for all polarizable models. The COS models²² have energies similar to the BSV and DC models. The estimates of the GCP model are the best compared with quantum chemical calculations.

In pentamers and hexamers the polarization of molecules is considerable. The polarization vectors in most of the cases are not parallel with the permanent dipole of the molecule, so it is incorrect to simply add them to the gas phase value. The deepness of the intermolecular energy is determined by polarization and the number of possible hydrogen bonds in the structure. In hexamers the cyclic arrangement has the largest average polarization but because its number of hydrogen bonds is only six, it has higher interaction energy than the cage, prism, and book conformations for quantum chemical calculations and the polarizable models of Table XIII.

In Fig. 7 we presented nine topologically different structures we found. The pictures were created using the GCP model. While in theoretical calculations only four-five structures are considered, one can see looking at Tables XII and XIII that in certain cases the other four structures we just termed by numbers V, VI, VII, and VIII can have deeper energy than one of the other four-five arrangements.

In Table XIV we show the results for group III models. For hexamers TIP5P creates no extra structures. The increasing number of atoms makes the tetrahedral hydrogen bonding feasible. In fact, the energies are very close to the quantum chemical results, although the energy hierarchy is very different (cyclic, book, VI, open prism, prism, VIII, and cage). All the standard conformers are stable with the exception of VII which turns into prism.

The TIP-FQ model manifests its general behavior: relatively long O–O distances and high energies. The energy hierarchy is also different from the quantum chemical. The reason of this is that the model favors the planar structures. The cyclic arrangement is planar, it has the smallest energy for the two FQ models and for the TIP5P model, too. The book structure is also favored because it is an opened up version of the prism and the cage. In the case of SPC-FQ where both the SPC-type geometry and the polarizability favor planar arrangements all the cross-bonded structures transform into open topology (see Fig. 7). For the SPCf model the book has the lowest energy, but the cyclic is the second lowest.

IX. CONCLUSIONS

We carried out an extensive calculation of clusters formed by classical potentials of water. These potentials were devised for computer simulations to mimic the behavior of this substance mainly in the liquid state. Our aim was to observe how different approaches perform in dilute systems.

When calculating cluster configurations and intermo-

TABLE XIII. Results for the hexamers using polarizable models [E: total intermolecular energy (kJ/mol); d_{O-O} : average oxygen-oxygen distance (Å); D_T : total dipole moment of the arrangement (D); D_i : average induced dipoles(D)].

	BSV	DC	SWM4-DP	SWM4-NDP	GCP
E	-168.033	-170.913	-180.961	-180.062	-181.945
d_{O-O} cage	2.847	2.829	2.809	2.814	2.828
D_T	1.871	1.807	1.692	1.663	1.876
D_i	0.692	0.708	0.497	0.503	0.659
E	-167.961	-171.54	-179.688	-178.825	-181.806
d_{O-O} prism	2.887	2.873	2.851	2.863	2.858
D_T	2.465	2.265	2.279	2.224	2.688
D_i	0.691	0.72	0.494	0.501	0.656
E	-169.197	-169.125	-178.268	-177.579	-180.545
d_{O-O} book	2.802	2.791	2.776	2.778	2.785
D_T	1.975	2.115	2.054	2.078	2.137
D_i	0.779	0.759	0.544	0.559	0.723
E	-167.925	-164.788	-172.637	-171.642	-177.311
d_{O-O} cyclic	2.764	2.768	2.751	2.751	2.737
D_T	0.0	0.0	0.0	0.0	0.0
D_i	0.849	0.802	0.591	0.602	0.784
E	-167.217	-167.953	-177.674	-176.624	-180.377
d_{O-O} open prism	2.851	2.843	2.82	2.826	2.827
D_T	2.206	2.522	2.754	2.666	2.299
D_i	0.712	0.716	0.506	0.51	0.67
E	-159.207	-162.236	-170.834	-170.013	-169.868
d_{O-O} V	2.869	2.886	2.851	2.857	2.895
D_T	2.341	2.334	1.17	1.159	1.345
D_i	0.647	0.677	0.402	0.403	0.538
E		-167.911	-169.229	-168.566	-172.702
d_{O-O} VI	VIII	2.797	2.84	2.843	2.846
D_T		2.528	1.461	1.432	1.465
D_i		0.736	0.493	0.501	0.668
E	-157.382	-161.01	-170.126	-169.85	-171.342
d_{O-O} VII	2.861	2.838	2.821	2.823	2.836
D_T	0.776	1.354	1.076	1.034	0.933
D_i	0.643	0.671	0.455	0.468	0.61
E	-165.165	-162.624	-170.483	-169.6	-175.075
d_{O-O} VIII	2.816	2.815	2.798	2.8	2.79
D_T	1.992	2.439	2.617	2.599	2.752
D_i	0.791	0.748	0.544	0.554	0.732

lecular energy in the literature, typically only that form is determined which belongs to the absolute energy minimum. The only exception is the hexamer because this cluster has several minima with energies very close to one another. We went beyond this picture because the set of different structures and energies can serve as a “fingerprint” of a model, provided additional quantum chemical calculations will study not only the absolute minima but the whole PES, as it was done by Mó *et al.*⁴⁰ for trimers.

While the results of quantum chemical calculation are not accepted as the absolute truth, the most recent cluster studies of Xantheas and co-workers^{36,42} have been carried out carefully using all available techniques to obtain reasonable results. Thus, our comparisons, apart from the dimer where experimental results are also available, are twofold. We compare the results of different models with the results of quantum chemistry and with the results of other models.

We studied five nonpolarizable models. We opted for the SPC/E (Ref. 11) and the TIP4P (Ref. 8) because these are

probably the most popular planar, nonpolarizable models of ambient water. The TIP4P served as a reference model because it was studied earlier.^{25,26} These models are still widely used for calculating properties even outside of the realm of bulk liquid. Since the TIP4P has two recent refinements, the TIP4P-EW (Ref. 9) and the TIP4P/2005 (Ref. 10) with improved properties, we included them in these calculations, too. To have a contrast with models of four charges we studied the TIP5P model,^{14,15} too. As one might expect, nonpolarizable models gave poor estimates of gas cluster properties.

The larger emphasis, however, was on polarizable models. There are numerous models in the literature polarizable by certain rules. We restricted ourselves to seven models of them. Three of these models use the same approach. There are fixed constant charges and a polarizable point dipole.^{16–18} An alternative of these models is the Drude oscillator model which applies a massless charge attached by a spring to the oxygen^{20,21} or a predefined site.²² Since the actual motion of

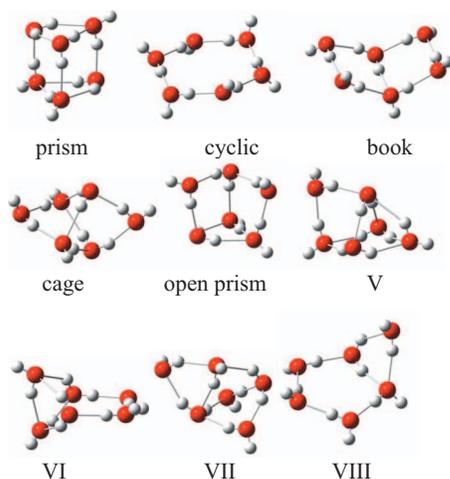


FIG. 7. Picture of the hexamer clusters.

the spring charge is very small, the model is very close to the point dipole models. To see the importance of spherical polarization we studied the SPC-FQ and the TIP4P-FQ models because these models can be polarized only in the molecular plane.²³

Taking everything into account the GCP model¹⁸ had the best performance. The BSV (Ref. 16) and the DC (Ref. 17) models were also reasonably correct in terms of the quality of their clusters. Not surprisingly, the latter two models were very similar. Their philosophy is the same, only the parameters differ a bit. Although the COS models²² use four charged sites as a charge-on-spring model, the root point of the spring and the large size of the charge (8.0 esu) made them very similar to the BSV and DC models.²²

The similarity holds also for the SWM4-DP and SWM4-NDP pair.^{20,21} The exchange of the charges between the oxygen and the spring particle did not affect their behavior considerably. Due to their smaller dipole moment in water the polarization of the SWM4 models is considerably smaller than that of the rest of the models. Still, their cluster energies are the second best after the GCP model. In terms of the oxygen-oxygen distances, which is typically underestimated by the models, the order of quality is BSV > DC > GCP > SWM4. The latter three models correctly estimated the internal energy hierarchy of hexamers (prism ~ cage < book < cyclic) contrary to the rest of the models.

The position of the negative charge seems to be a determining factor in the structure and energy of water clusters. The SPC-type models have their negative charge on the oxygen, while all the other models have their negative charge on the main axis of the molecule at certain distance from the oxygen. (This is also true for the SWM4 models because these interactions have only a dipole on the oxygen. There is also a negative charge on the main axis of the molecule.) Looking at the contour diagram of electron density for the water molecule it seems a bit odd that the negative charge should be positioned off the oxygen molecule closer to the hydrogens. However, acceptable estimates of the quadrupole moment of three charges also require that the negative charge should be quite far from the oxygen. SPC-type models provided unique structures and, in the case of SPC/E, very nega-

TABLE XIV. Results for the hexamers for group III models [E: total intermolecular energy (kJ/mol); d_{O-O} : average oxygen-oxygen distance(Å); D_T : total dipole moment of the arrangement (D); D_I : average induced dipoles (D)].

	TIP5P	TIP4P-FQ	SPC-FQ	SPCf
E	-191.011	-164.377		-211.156
d_{O-O} cage	2.746	2.863	Book	2.759
D_T	2.469	1.779		2.2
D_I	...	0.699		...
E	-193.171			
d_{O-O} prism	2.786	Book	Book	Book
D_T	2.689			
D_I	...			
E	-196.918	-167.909	-173.163	-216.106
d_{O-O} book	2.69	2.815	2.809	2.717
D_T	2.493	2.053	1.972	42.374
D_I	...	0.838	1.027	...
E	-198.763	-173.206	-184.68	-213.169
d_{O-O} cyclic	2.656	2.756	2.715	2.688
D_T	0.0	0.0	0.0	0.0
D_I	...	1.021	1.296	...
E	-193.372	-164.099		-209.849
d_{O-O} open prism	2.74	2.887	VI	2.758
D_T	2.697	2.487		3.793
D_I	...	0.758		...
E	-180.09	-152.002	-144.722	-195.856
d_{O-O} V	2.752	2.969	2.925	2.773
D_T	4.93	3.264	3.519	3.857
D_I	...	0.596	0.682	...
E	-194.14	-164.905	-167.473	
d_{O-O} VI	2.695	2.946	2.922	VIII
D_T	3.317	3.577	2.511	
D_I	...	0.789	0.986	
E				-195.919
d_{O-O} VII	Prism	VIII	VIII	2.773
D_T				1.078
D_I				...
E	-192.612	-163.763	-171.713	-209.811
d_{O-O} VIII	2.707	2.835	2.82	2.731
D_T	2.585	1.88	2.2	2.231
D_I	...	0.0844	1.071	...

tive energies. In this respect, the reported good critical behavior estimates^{1,13} of SPC/E are in question. It must be merely a fortuitous cancellation of errors.

We found that the spherical polarizability of the molecules is mandatory. Despite the ingenuity of the TIP4P-FQ and SPC-FQ models,²³ their restricted polarizability fails to reproduce even the dimer properties with acceptable accuracy. Their O-O distances are very good, but their intermolecular energies seriously overestimate the quantum chemical results. If these models are to be developed further this shortcoming must be removed.

In condensed phases there is no substantial difference in quality between the three- or four-charged models. The dominating structure of water or ice at not too high pressures is a tetrahedral coordination of the molecules. In this sense, a model which favors this tetrahedral order can be advantageous especially in the solid-liquid region. However, this seems not to be the case in gas phase. The TIP5P model

generated a large number of extra structures with reasonably deep energies not found in the configuration search of other models or quantum chemical calculations.

The impact of flexibility of the molecule, not surprisingly, is decrease in energy and shortening of the O–O distance relative to the same parametrization of the rigid host model. While we studied this effect for a classical model,²⁴ the involvement of flexibility could give contradictory improvements. For polarizable models, flexibility would deepen their energy, in such a way that their intermolecular energy estimates could get closer to quantum chemical results. On the other hand, their O–O distance might become shorter which would worsen their performance in this respect.

All in all we think that the spherically polarizable models represent a good direction of developing water models with hope of transferability. The polarizability of the model does no longer require prohibitively expensive calculations using present-day computer capabilities. Introduction of Gaussian functions by the GCP model,⁴⁸ while it slightly increased the computation demand, remained still reasonably simple and represented the best performance, taking also into account its liquid state estimates reported in Ref. 18.

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