Minimum structures and dynamics of small water clusters

S. C. Farantos, S. Kapetanakis, and A. Vegiri
Department of Chemistry, University of Crete, and
Institute of Electronic Structure and Laser,
Research Center of Crete, FORTH, Iraklion, Crete 711 10, Greece

Abstract

Water clusters, $(H_2O)_n$, with $n = 7-18$ monomers, are studied with molecular dynamics methods and an empirical potential function which includes many body polarization interactions. Minimum energy geometries are obtained with the quenching technique and random initial conditions. It is shown that several minima have cubic type arrangements of the oxygen atoms. These geometries may be considered as formed by the fusion of the cubic structures of the octamer and square tetramers and correspond either to stable minima or to minima with a cubic core surrounded by the extra molecules of the cluster. The dodecamer shows a special stability, and this and larger clusters guarantee an average hydrogen bond per water molecule close to the experimentally found value of 1.7 for liquid water. The power spectra of all cubic conformations show the low frequency band observed in the millimeter region. A possible association of the stability of these multicubic clusters with the peculiar properties of liquid water is discussed.

1 Introduction

Considerable research has been carried out on atomic and molecular clusters in the last years. One of the motivations for this type of research is to develop an understanding of the physical and chemical properties of bulk matter through finite aggregates of the building up units.[1]

Extensive work has been done for van der Waals systems[2] and metallic clusters.[3] Hydrogen bonded systems, such as water, are less studied from the cluster point of view, although numerous simulations of liquid water have been performed.[4–11]

Furthermore, a number of phenomenological models based on the cluster formation have been published which describe some of the peculiar behavior of liquid water.[12] One such model has been recently proposed by Benson and Siebert.[13] These investigators assume that in liquid the equilibrium

$$(\mathrm{H_2O})_8 \rightleftharpoons 2\,(\mathrm{H_2O})_4, \tag{1}$$

is taking place, and compute the heat capacity of water. They argue, that the cyclic square of the tetramer and the cubic structures of the octamer guarantee large entropic changes, although, they were unable to give arguments about the dynamical stability of these particular clusters. By adopting an empirical approach in estimating the thermodynamic quantities of the octamer and tetramer, the authors achieved a reasonable agreement between calculated and observed heat capacities of liquid water for the temperature range of 0-100 ^{0}C.

In a recent paper (hereafter referred as paper I), Vegiri and Farantos[14] have studied by molecular dynamics techniques the n-mer clusters of water with $n = 3-6$, and 8. The potential function used was that of Cieplak, Kollman, and Lybrand.[8] Both, the pairwise additive part of the potential without and with the polarization many body interaction terms were examined. The latter was calculated by an iterative procedure using the permanent and induced dipole moments of water molecules.

Static and dynamic properties of water clusters revealed that the tetramer with a square geometry for the oxygen atoms and the free hydrogens in *trans* position, and the octamer with the oxygen and hydrogen atoms forming cubes of S_4 or D_{2d} symmetry, are the most stable structures. The stability of theses clusters was confirmed by the energy per hydrogen bond plots, the energy at which a phase transition was observed in the caloric curve and root mean square (r.m.s.) fluctuations of the oxygen-oxygen bonds, as well as from the power spectra and Maximal Lyapunov Exponents (MLE).

If we could characterize the above results as results obtained from first principles, the macroscopic model of Benson and Siebert[13] receives a substantial support. This is the first time in the literature of liquid water for which cubic clusters are proposed for understanding the peculiar properties of water.

In spite of the success of Benson and Siebert model in reproducing the specific heat, some obvious shortcomings of the model exist. The octamer provides a hydrogen bond per water molecule which is equal to 1.5, and this is less than the estimated 1.7 for liquid water. Furthermore, the cubes of the octamers give a volume which is too small compared to the observed molar volume of liquid water, 18 cm^3/mol H_2O. These imply that in liquid phase there should exist assemblies of larger clusters. Benson and Siebert circumvent this problem with the hypothesis of the existence of hydrogen bonded oligomers of octamers and reject the possibility of having larger clusters by the fusion of octamers and tetramers.

The problem of identifying the formation of particular clusters in liquid water remains a challenge for both experimentalists and theoreticians. Thus, it will be useful if information about the structures and the properties of water aggregates is accumulated. In this paper, we expand our previous work and explore the minimum energy geometries and dynamics of $(H_2O)_n$ clusters, with $n = 7 - 18$. We do find that stable cubic like water aggregates can be formed either by the fusion of smaller cubic constructions with a square tetramer, or by forming a cubic core surrounded by the extra water molecules.

The paper is organized as follows. In section II, we present the methodology for locating stationary points on a multidimensional potential energy surface and the basic cluster dynamic techniques. In section III, the results are described, and in section IV, a discussion is developed for a possible association of our results with the problem of the macroscopic behavior of liquid water. However, we emphasize that the conclusions of this work are pertinent to water clusters and they should be considered as providing some assistance in analyzing the results of proper simulations of liquid water.

2 Methods of cluster dynamics

The classical dynamics of the clusters are studied by solving the Newton-Euler equations of motion for rigid bodies.[15] To avoid singularities inherent into the Euler angle representation of the reorientations of the rigid bodies we use quaternions.[16,17] Thus, for each molecule we integrate thirteen equations of motion which are related to the three cartesian coordinates of the center of mass of the molecule and their conjugate momenta, the four quaternions, and the three principal angular velocities.

According to our previous practice for a systematic investigation of the structure of phase space, and thus the dynamics of the system, the location of the stationary geometrical objects are required. These are stationary points, periodic orbits, or even tori and reduced dimension tori.[18] In paper I it was shown, that the dynamics of the hydrogen bonded systems are mainly chaotic, but some adiabatic separability of groups of particular motions results into the separation of the frequency bands observed in the power spectrum. For large clusters the location of the stationary points and particularly of the minima is a difficult task, and this is what we try first in order to understand the dynamical behavior of the system.

In the present work we use two methods for the location of the minima of the potential energy surface,

i) the quenching technique, which makes a trajectory to drop in the underlying minimum, and

ii) the Newton-Raphson algorithm to obtain the zeros of the forces.

The latter method is more suitable for the location of a general stationary point (minimum, saddle, or maximum), and is very efficient when it is combined with the quenching method which secures good initial conditions.

For a general system of N degrees of freedom and with hamiltonian H the stationary points are found by solving the nonlinear algebraic equations,[18]

$$\frac{d}{dt}\vec{x}(t) = J\frac{\partial H(\vec{x})}{\partial \vec{x}} = J\nabla H(\vec{x}) = 0, \tag{2}$$

where, $\vec{x}$ is the vector of coordinates and their conjugate momenta, and

$$J = \begin{pmatrix} 0_N & I_N \\ -I_N & 0_N \end{pmatrix}. \tag{3}$$

0_N and I_N are the zero and unit $N \times N$ matrices respectively. $J\nabla H(\vec{x})$ is a vector field, and J satisfies the relations,

$$J^{-1} = -J \quad \text{and} \quad J^2 = -I_{2N}. \tag{4}$$

The Newton-Raphson method is adopted by solving iteratively the equations,

$$\vec{x}_{k+1} = \vec{x}_k + \delta\vec{x}, \tag{5}$$

where $\delta\vec{x}$ are computed by solving the linear system of equations,

$$A\delta\vec{x} = -\nabla H(\vec{x}_k). \tag{6}$$

A is the matrix which contains the second derivatives of the hamiltonian,

$$a_{ij} = \frac{\partial^2 H}{\partial x_i \partial x_j}, \tag{7}$$

evaluated at the point $\vec{x}_k$. Of course, for a hamiltonian system with a quadratic dependence on the momenta the above scheme is reduced in searching for the zeros of the forces.

The first derivatives of the potential are calculated analytically, but the second derivatives are obtained numerically. Special care is needed solving eqs (6), because of the redundant variables in the definition of the quaternions. Provided that we have made a good initial guess the convergence of the Newton-Raphson method is between linear and quadratic.

The classical trajectories are integrated for 437 ps using the algorithm of Shampine and Gordon.[19] This is a variable time step and variable order predictor-corrector algorithm, and conserves the total energy with seven significant digits. The first 125 ps of the trajectory are used for equilibrating the system, whereas average quantities are obtained for 312 ps. The trajectories run correspond to zero total linear and angular momenta, and energy was pumped to the cluster by scaling the velocities, such as the energy increments were 0.5 kcal/mol at a time.

The stability and dynamics of the clusters are determined by calculating the following quantities. i) The caloric curve, i.e., the change of the mean kinetic energy, E_k, or the temperature with the total energy, E_T. ii) The root mean square oxygen-oxygen bond length fluctuations,

$$\delta(E) = \frac{2}{n(n-1)} \sum_{i<j}^{n} \frac{[< r_{ij}^2 > - < r_{ij} >^2]^{1/2}}{< r_{ij} >}, \tag{8}$$

where $<>$ means time average, and r_{ij} is the distance between the atoms i and j. The summation is over all molecules, n.

We have also calculated the oxygen atom velocity autocorrelation function, $C(t)$, at specific energies and the related power spectra, $I(\omega)$;

$$C(t) = \sum_i^n \frac{< \vec{v}_i(t) \cdot \vec{v}_i(0) >}{< \vec{v}_i(0) \cdot \vec{v}_i(0) >}, \tag{9}$$

$$I(\omega) = \int_{-\infty}^{\infty} C(t) \exp(i\omega t) dt. \tag{10}$$

An efficient method for exploring the topology of the potential function is the quenching of the system to the underlying minima when we integrate along a particular trajectory. With this method we can trace the regions of phase space which are visited during the time evolution of the system.

The potential function is that of Cieplak et al.[8] and has been described before. This model has charges placed on the two hydrogen atoms and on the bisector of the HOH angle and assumes rigidity of the individual water monomers. The additive part of the potential is a sum of the electrostatic interactions, oxygen-oxygen repulsions, Morse-type attractions of hydrogens with oxygens, and dispersion interactions. Many body interactions are introduced through a polarization term which models the main part of the second order induction energy.

In our previous study of water clusters we examined the importance of the polarization forces for the minimum energy geometries and dynamics. We found a contribution of about 14% in the total energy, and no significant influence in the dynamical trends of the cluster. However, we do find that for some clusters the polarization energy changes the order of some closely lying relative minima as in the case of hexamer and octamer.

In order to save computer time all dynamical calculations are carried out with the additive potential function of CKL. However, the geometries of a few minima are also tested with the full potential function applying the Newton-Raphson technique. Furthermore, additional calculations have been performed with other potential functions as we discuss it in Section 4.

Finally, we expect that the assumption of rigid molecules to be satisfactory for low intramolecular excitations, because of the large differences in the frequencies among the intra and intermolecular vibrations.

3 Results

3.1 $(H_2O)_n$, n = 8, 12, 16, 18

One of the major outcomes of paper I was the finding of the stability of the square tetramer and cubic octamer. The absolute minimum of the tetramer is a square formed by the oxygen atoms, and with the hydrogens, which do not participate in the hydrogen bonds, in *trans* position. The first relative minimum is a rectangle with the free hydrogens in *cis* position and lying 0.56 kcal/mol above the ground state. The longer side of the rectangle is between the oxygen atoms that carry the *cis* free hydrogens.

For the octamer two cubic structures with almost the same energy were found and with S_4 and D_{2d} symmetry respectively. The octamer may be considered as formed by the fusion of two tetramers with the hydrogen bonds sequentially bonded along the same direction for the S_4 symmetry species, and in opposite directions in the D_{2d} species. The tetramers are bonded by their *trans* free hydrogens. Different bonding combination schemes of the tetramers yield different cubic structures of the octamer. We found in the range of up to 1.5 kcal/mol eight different cubes. The above geometries are in agreement with the predictions of other investigators who used different potential functions.[20,21]

What will happen if we consider the fusion of an octamer with a tetramer to produce a dodecamer cluster? Shall we make a stable rectangular arrangement, and even more, could we construct larger clusters by further adding tetramers? These questions have led us to examine minimum energy geometries for the $(H_2O)_n$ clusters with $n = 12, 16$, and 18.

In Figure 1 we present potential minima with cubic type geometries found for the above clusters. For completeness we also show the B_0 and D_{2d} minima of the tetramer and octamer respectively, described in paper I. The criterion for connecting two oxygen atoms with a straight line is the bond length to be less than 5.8 a_o.

We have searched for minima by starting from high energy configurations and randomly orienting the hydrogen atoms for more than one hundred trials. Therefore, it is certain that minima with energies between those we have located or even lower are missing. However, this random search for minima reveals those types of conformations which are more abundant in configuration space. The cubic type minima seem to be of this kind, and more importantly correspond to an average hydrogen bond per water molecule which increases from 1 in the tetramer to 1.8 in the 18-mer: 1 ($n = 4$), 1.5 ($n = 8$), 1.67 ($n = 12$), 1.75 ($n = 16$), and 1.78 ($n = 18$).

The dodecamer shown in Figure 1 is two S_4 octamers sharing one face. One can construct other cubic geometries by using D_{2d} symmetry octamers or combinations of S_4 and D_{2d} symmetry octamers. A few of the quenched geometries of the 12-mer are shown in Figure 2. We label them by an increasing integer which corresponds to the increasing energy of the conformation. The energies of the quenched structures, estimated with the pairwise potential, are stored in Table I with the same order. Notice in Figure 2 a minimum (12-3) with pentagonal sides as well as a cubic type conformation at higher energy (12-4 at -93.3 kcal/mol).

The caloric and r.m.s. curves of the dodecamer shown in Figure 3 reveal that this cluster is quite stable. From these curves we estimate the melting temperature to be $T_m = 170$ K, which is close to that of octamer,[14] and significantly lower from the value given by Buffey at. al[22] (205 K).

A minimization graph is shown in Figure 4 produced from a trajectory at the energy of -7 kcal/mol and per water molecule. This energy is lower than the necessary energy for large amplitude motions. Nevertheless, we find a few transitions to occur, mainly to higher energy minima. The system spends most of its time in the area of the 12-2 minimum shown in Figure 2, from where it started. Apparently, the energy of 1.3 kcal/mol available to each water molecule is not enough for the trajectory to overcome the barriers that are required in order to reach the lower energy cubic geometries. The trapping of the trajectory after the time of 270 ps indicates phenomena of coexistence.[23,24]

The search for minimum energy geometries in the 16-mer gave the structure 16-0 (Figure 1) as the lowest energy minimum, and several relative minima with irregular geometries or highly deformed cubes. Characteristically, the conformation 16-1 (-133.3 kcal/mol) is a cube surrounded by water molecules which form pentagons. It is worth mentioning that the number of conformations with pentagonal sides increases for clusters larger than the dodecamer.

Relative minima of the 18-mer are shown in Figure 5. Note, that the lowest minimum, which we have found, has a non cubic geometry, whereas the higher energy minima correspond to deformed cubic structures. Although, we have made several minimization searches, still it is difficult to argue that there are not lower minima or other between those we have located.

The energies tabulated in Table I for the 18-mer are more uniformly distributed than those of the 12-mer. Therefore, we expect these clusters to be less stable. Figure 6 shows the caloric and the r.m.s. fluctuations of the O-O bond lengths for the 18-mer. From these curves the melting temperature is estimated at $T_m = 140$ K.

Quenching by running a trajectory at -7.1 kcal/mol and per H_2O molecule, the energy at which the first peak in the r.m.s. curve appears, reveals that the trajectory visits several minima (Figure 7). The characteristic trapping of the trajectory between two states for several ps is seen in this figure. Furthermore, we can see that the cluster spends most of its time exploring the high energy parts of the potential, indicating the existence of an increased number of relative minima for this large cluster.

The frequency bands found by calculating the power spectrum of a trajectory at -120 kcal/mol are similar with those of smaller clusters. Since, the power spectrum is obtained from the autocorrelation function of the oxygen velocities only two bands are observed (Figure 8). One between 10 and 80 cm^{-1}, and one in the range of 100-300 cm^{-1}. The band of the low frequencies is about seven times more intense than the intensities of the higher frequencies, which are associated mainly with the stretching modes of the hydrogen bonds. Of course, there are bands of even larger frequency ranges that are related to motions which lead to the breaking of the hydrogen bonds, and the harmonic frequency analysis in the next section yields frequencies up to 900 cm^{-1}. Similar graphs of the power spectra are produced for all clusters with $n \geq 4$. This leads to the conclusion that the frequency bands are characteristics of the local properties of water clusters.

The structural stability of the minimum energy geometries has further examined by Newton-Raphson minimization calculations and with the polarization terms included in the potential. Starting with the geometry obtained with the pairwise potential the convergence to a geometry slightly deformed from the initial one was a confirmation of the structural stability of cubic clusters. The contribution of the polarization energy to the total energy of the cluster is about 14%.

3.2 $(H_2O)_n$, n = 7, 9, 13, 17

In Figure 9 the lowest energy minima found for 7-, 9-, 13-, and 17-mer are shown. The heptamer is the cluster with just one molecule deficit to form the cube and was not studied in paper I. The lowest minimum, 7-0, has a geometry which consists of two tetramers with one common water molecule. This conformation is not reported by Kim et.al[25] who have used the Matsuoka, Clementi, and Yoshimine potential (MCY) plus three- and four-body corrections. However, we have found the relative minima which they present in their article. As is expected, heptamer has a high density of minima and a lower than the octamer phase transition temperature (112 K). In Figure 10 the caloric and r.m.s. curves are presented, and the values of a few of the relative minima are tabulated in Table I.

It can be seen in Figure 9 that clusters larger than the octamer which do not satisfy the rule of $n = 4m$ for the number of monomers, show minima with a cubic type core and with the extra molecule on the surface. This is more apparent for the enneamer which has been thoroughly studied.

Figure 11 shows the r.m.s. fluctuations of the O-O bond lengths, and Figure 12 presents geometries of some relative minima. The plethora of minima found for the 9-mer could be anticipated since now the different cubic structures of the octamer are combined with the ninth molecule placed on different sides of the cube. The lowest energy minimum, 9-0 (Figure 9), may be viewed as originated from the octamer of S_4 symmetry, the lowest with the pairwise potential,[14] and the ninth molecule bridging two corners of the cube. Minimum 9-7 shown in Figure 12 is formed from a higher energy cube of the octamer.

Despite of all these relative regular structures the caloric curve shows an early phase transition at about 1.2 kcal/mol per water molecule (T_m = 105 K). This is in accord to our conclusion that the cluster is less stable when the density of the minimum energy geometries increases.

In Figure 13, we show the quenching plot by running a trajectory at -55.8 kcal/mol. The trajectory starts with initial conditions from the area of the minimum 9-5 (Figure 12). It contains one four-hydrogen bonded molecule, and for about 50 ps the trajectory oscillates between this minimum and the minimum 9-6 (Figure 12). The geometry of the latter differs only in the arrangements of some of their free hydrogens.

Apparently, these type of motions, between the two isomers, do not break a hydrogen bond and thus, the energy is trapped for a long time. The next most frequently visited structure is a deformed cube, 9-4. The trajectory is trapped in the area of this minimum but some excursions to higher energy minima are observed. In contrast, the more regular geometry 9-7 traps the trajectory for about 65 ps without showing any visit to other minima.

In Figure 9 the minimum energy geometries of 13-mer and 17-mer are shown. Minima based on the cubic structures of the previous cluster (12- and 16-mer) and with the extra molecule on different sides of the core are expected as in the case of the 9-mer, which we indeed find. We have not computed caloric and minimization curves for these clusters, but we anticipate similar behavior with that of the enneamer.

3.3 Harmonic frequencies and thermodynamic functions

Once we have located the minima on the potential function it is easy to carry out a harmonic frequency analysis by diagonalizing the Hessian matrix of the potential. We have found for the *trans* tetramer the harmonic frequencies to vary between 32 and 730 cm^{-1}, for the D_{2d} octamer the frequencies are between 42-914 cm^{-1}, and for the dodecamer in the range of 40-914 cm^{-1}. These values are obtained with the complete potential, pairwise plus polarization, and are higher than the frequencies extracted from the power spectra.

Thermodynamic functions of temperature have been calculated for the tetramer, octamer and dodecamer for the structures shown in Figure 1, at the harmonic, rigid rotor approximation, and treating the clusters as ideal gas systems.[26] In Tables II to IV we store some geometrical and energy characteristics of the clusters computed with the pairwise potential plus polarization terms. The values of the enthalpy, entropy and specific heat are also shown. In the next section we discuss the thermodynamic predictions of our calculations with respect to the model of Benson and Siebert.[13] Here, we only note that the harmonic approximation and ideal gas treatment of the clusters give a specific heat close to that of ice (at 298 K, C_v = 9.58 cal/(mol K)), a value which is half of the specific heat of liquid water.

Monte Carlo type simulations of liquid water by Cieplak et. al.[8] and with the same potential function gave a heat capacity at room temperature very close to the experimental one.

From the enthalpies and entropies the equilibrium constants are calculated for the isomerization reaction described by eq 1. The results are tabulated in Table V. Our calculations point out that the dodecamer has also a stable cubic arrangement, and therefore, the reaction

$$(H_2O)_{12} \rightleftharpoons (H_2O)_8 + (H_2O)_4, \tag{11}$$

is a candidate for taking place in liquid phase. Table VI tabulates thermodynamic quantities for this reaction. These values are indicative of the cluster but some differences are expected for different equilibrium geometries.

4 Discussion and Conclusions

The results of the previous section reveal that the fusion of the cubic structures of water octamer and the square tetramer does occur, and produces clusters with cubic conformations, although some of them are not as regular as the cubic geometries of the octamer. We have also demonstrated, that water clusters may have minima which correspond to a cubic core surrounded by the extra molecules. These results are valid for the pairwise as well as the full potential with the polarization terms included.

Quenching calculations have shown that the trajectory may stay localized in the area of some cubic structured minima for a considerable time, thus, revealing the existence of high potential barriers separating regular from irregular conformations.

Another significant result is the oscillations of the cluster between two structures which differ in the arrangements of the free hydrogens, i.e., the hydrogens which do not participate in hydrogen bonds. Such type of motion should be characterized by low energy barriers and low frequency oscillations, and therefore, some adiabatic decoupling of these degrees of freedom from the hydrogen bonding ones is expected. If this dynamical behavior persists in bulk systems, then clusters of cubic geometries as well as of other type geometries are anticipated to play a significant role in elucidating the properties of liquid water.

The first question we should ask before trying to speculate about the macroscopic behavior, is whether the minima of the studied clusters are the results of the particular potential function we use. In paper I, we gave an extended comparison of the minimum energy structures of small clusters with those predicted by other potentials.

During the revision of the present article the works of Tsai and Jordan[21] and Wales and Ohmine[27,28] were published on $(H_2O)_n$ clusters with $n = 8, 12, 16$ and 20. Both groups of investigators have used the TIP4P potential function[29] which is also based on Coulombic interactions of point charges but it uses Lennard-Jones potentials to describe the oxygen-oxygen attractions. It is quite pleasing to see that most of their conclusions are in agreement with the results of this article. Tsai and Jordan[21] have studied more systematically the structures of the water clusters and have confirmed the stability of the cubic geometries of the dodecamer by Hartree-Fock and MP2 calculations. They have found that stable cubic structures can be formed by lining up cubes of S_4 or D_{2d} symmetry sharing a common face. Wales and Ohmine[27,28] have carried out molecular dynamics calculations for the octamer and icosamer. We underline the agreement in the melting temperatures of our calculations with theirs for the octamer.

In our work, we have shown the existence of cubic type minima by stacking a second layer of cubes like in the 16-mer and 18-mer. The production of the cubic type conformations of small water clusters from two functionally different potentials is definitely significant in the investigation of the neutral water clusters for which experimental knowledge is still lacking.

We wanted to further examine the dependence of the cubic structures on the potential function, and therefore, we have tested the widely used potential of Matsuoka, Clementi, and Yoshimine (MCY).[30] We do find, that the cubic minimum geometries of the CKL potential are reproduced by the MCY potential. Starting with an initial geometry as that predicted by the CKL function the Newton-Raphson procedure converges to an equivalent minimum for the MCY potential. In Figure 14 we show the geometry obtained for the dodecamer, and in Figure 15 a power spectrum for this cluster.

Furthermore, we tested the pairwise part of the potential of Niesar, Corongiu and Clementi (NCC),[10] which has been highly successful in simulations of bulk water. The cubic geometries of the 12-mer, 16-mer, and 18-mer are reproduced.

The requirements for a successful model of liquid water are really high. It must explain the thermodynamic anomalies such as the high specific heat, the peaks of the radial distribution functions as come out from X-ray scattering experiments, and finally spectroscopic and relaxation properties. Although our computations on small clusters do not allow extrapolation of the results to the bulk state, nevertheless, here we attempt to speculate about possible consequencies of the formation of cubic clusters in liquid water. This becomes more interesting after the publication of the Benson-Siebert model.

The existence of larger cubic aggregates than the octamer, like that of the dodecamer, seems to heal some of the shortcomings of the Benson and Siebert phenomenological model.[13] First, the average hydrogen bond per water molecule increases to 1.7 for the dodecamer and even up to 1.8 for the 18-mer, values which are in proximity with the observed value of liquid water. Furthermore, if we assume the equilibrium of dodecamers (eq 11), then we achieve larger molar volumes as well.

In Tables V and VI we have tabulated the values of the change of enthalpy and entropy per water molecule for the reactions 1 and 11 computed from the thermodynamic quantities stored in Tables II-IV. The equilibrium constants are then obtained from the formula,

$$-RTlnK = \Delta G^0 = \Delta H' - T\Delta S'. \tag{12}$$

We note, that $\Delta H'$ and $\Delta S'$ change slightly in the range of the temperatures we examine.

We have applied the model of Benson and Siebert[13] to compute the specific heat of liquid water from our theoretical values. For room temperature we extract the value C_p = 12.9 cal/(mol K). This value is less than the experimental one as well as the value which Benson and Siebert have obtained by 5 cal/(mol K). This deficit is mainly attributed to the harmonic vibrational treatment of the clusters, and the necessary corrections in the changes of enthalpy and entropy which are required because of the liquidation. Of course, if we adopt the empirical values for the thermodynamic functions of Benson and Siebert their results are reproduced.

We emphasize, that our zero order approximation give the 70% of the observed heat capacity, and improvements are expected by adding higher order corrections in the thermodynamic functions. This conclusion is supported from the Monte Carlo simulation of Cieplak, Kollman, and Lybrand[8] who computed a value for the specific heat equal to 17.3 cal/(mol K) at 25 ^{0}C.

The approximations introduced by Benson and Siebert are reasonable and the good general agreement with the experimental results support the hypothesis of the equilibrium between octamer and tetramer. However, the change of the heat capacity with temperature is not satisfactory, which suggests, that further improvements are needed. It is really difficult to believe that octamers and tetramers are the only clusters in liquid water. It is more plausible that a large number of equilibrium reactions are taking place in the liquid among which reactions 1 and 11 are probably playing a leading role.

The model of Grunwald[31] is based on the assumption, that a state of water molecule in liquid phase is determined by the time average network environment. He assumes two states, the tetrahedrally and the five coordinated water molecules, and the latter guarantees a less polarized environment than the tetrahedral one. Although, Grunwald rejects the existence of distinct clusters, his assumption satisfies another requirement for a model of liquid water, that is, the average coordination number should be about 4.5. From Figure 1 we can see that the 16-mer, and 18-mer have minima which include water molecules with five hydrogen bonds, two are donated and three are accepted, and that agrees with one of the proposed structures of Grunwald.[31] The lack of this property in the octamers led Benson and Siebert to assume oligomers of octamers.

Furthermore, a model based on cubic clusters in liquid water would give the second peak in the radial distribution of the O-O bond distances. Experimentally, a peak have been found[32] at 8.5 a_o after the first high intensity peak, revealing a second neighbor shell. This property is satisfied by the octamer and larger clusters. In Tables III and IV we store O-O distances, where we can see that some of the bonds are in this range.

Cieplak, Kollman, and Lybrand in their Monte Carlo calculations[8] computed the O-O radial distribution function and they were unable to produce this second peak, in spite of the good agreement that achieved for the first peak. If the cubic clusters remain in a large aggregate of water molecules, as those used in simulations of liquid water, has to be proved. It is however, quite plausible that the cubic conformations are not picked up in the Monte Carlo simulation, but they can show up in dynamical calculations because of the relative stability of these structures. Tsai and Jordan have reached to a similar conclusion when they tried to obtain cubic minimum energy geometries for the $(H_2O)_{16}$ and $(H_2O)_{20}$ by a Monte Carlo simulated annealing method.[21]

Another important experimental fact worth discussing is the observed broad shoulder, at about 30 cm^{-1}, in the power absorption coefficient of water.[33] Previous calculations in order to reproduce these low frequencies in the power spectra of the trajectories had to assume large water clusters with 60 molecules.[34] As we have discussed it in paper I the low range of frequencies is first observed in the square tetramer and remains for larger clusters. This is the result of the torsional motion of two neighboring planes formed by four oxygen atoms, ($O_1O_2O_3$, and $O_1O_4O_3$). The low frequency band may be extended up to zero with the appropriate excitation in energy.

The above analysis leads to the conclusion, that the adoption of the cubic clusters for modeling the properties of liquid water seems to have a significant number of benefits, and supports the *two-state* model of Benson and Siebert.[13] To the best of our knowledge, this is the first time equilibrium reactions such as 1 and 11 are proposed to model the liquid phase. Our computations have shown that cubic arrangements are predicted from different type potential functions and for medium size clusters.

Acknowledgements

We thank Prof. Papagiannakopoulos for bringing to our attention the work of Benson and Siebert, and Prof. Benson for communicating to us his work on liquid water. We are glad to acknowledge research support from the European Community SCIENCE program (Grant No SC1*0331-C).

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TABLE I: Energies in kcal/mol of a few quenched structures of water clusters obtained with the pairwise additive potential.

$(H_2O)_7$	$-49.61, -49.53, -49.11, -49.99, -49.97$
	$-48.71, -48.70, -48.69, -48.66, -48.59$
$(H_2O)_9$	$-68.71, -68.60, -68.36 - 68.21, -68.04$
	$-68.00, -67.80, -67.30, -67.11, -67.09$
$(H_2O)_{12}$	$-99.26, -98.73, -94.48, -94.21, -93.31,$
	$-92.70, -92.30 - 91.88, -91.66, -91.55$
$(H_2O)_{13}$	$-105.55, -105.03, -102.93, -101.94, -101.82$
	$-101.25, -100.87, -100.39, -100.20, -100.16$
$(H_2O)_{16}$	$-134.30, -133.31, -130.63, -129.92$
$(H_2O)_{17}$	$-144.40, -143.93, -143.82, -143.25, -142.96$
	$-142.55, -142.44, -142.27, -141.66, -141.43$
$(H_2O)_{18}$	$-154.88, -154.29, -153.56, -153.14, -152.25,$
	$-152.00, -151.41, -149.28$

TABLE II: The lowest energy minimum (E_{min}), O-O distances (R_{OO}), the range of harmonic frequencies (ω), the zero point energy, principal moments of inertia (I), enthalpies (H'_t), entropies (S'_t) and specific heats (C_{pt}) per water molecule of *trans* - $(H_2O)_4$. The energy is measured with respect to isolated water molecules and using polarization interaction terms. The entropy and specific heat are measured in cal/(mol K), and mass in electron masses, m_e. H_t is the internal energy measured from the *z.p.e.* of the species.

$$
\begin{aligned}
E_{min} &= -25664 \text{ cal/(mol)} \\
R_{OO} &= 5.5, 7.8\, a_o \\
\omega &= 32 - 730 \text{ cm}^{-1} \\
z.p.e. &= 9679 \text{ cal/(mol)} \\
I &= 1023150.42\ 1023150.42\ 2011434.08\ m_e.a_0^2
\end{aligned}
$$

T/K	H_t	H'_t	S'_t	C_{pt}
250	6094	-2473	22.34	8.80
300	7916	-2017	23.86	9.39
350	9841	-1536	25.23	9.83
400	11843	-1035	26.46	10.17

TABLE III: The lowest energy minimum (E_{min}), O-O distances (R_{OO}), the range of harmonic frequencies (ω), the zero point energy, principal moments of inertia (I), enthalpies (H'_o), entropies (S'_o) and specific heats (C_{po}) per water molecule of $(H_2O)_8$ (D_{2d}). The energy is measured with respect to isolated water molecules and using polarization interaction terms. The entropy and specific heat are measured in cal/(mol K), and mass in electron masses, m_e. H_o is the internal energy measured from the $z.p.e.$ of the species.

E_{min}	=	-70383 cal/(mol)
R_{OO}	=	$5.4, 5.6, 7.6, 8.3, 9.5\, a_o$
ω	=	$42 - 914$ cm^{-1}
$z.p.e.$	=	24260 cal/(mol)
I	=	4006167.57 4006167.57 4146401.12 $m_e.a_0^2$

T/K	H_o	H'_o	S'_o	C_{po}
250	10256	-4483	16.12	8.08
300	13641	-4060	17.59	8.81
350	17282	-3605	18.93	9.37
400	21122	-3125	20.16	9.81

TABLE IV: The lowest energy minimum (E_{min}), O-O distances (R_{OO}), the range of harmonic frequencies (ω), the zero point energy, principal moments of inertia (I), enthalpies (H'_d), entropies (S'_d) and specific heats (C_{pd}) per water molecule of $(H_2O)_{12}$. The energy is measured with respect to isolated water molecules and using polarization interaction terms. The entropy and specific heat are measured in cal/(mol K), and mass in electron masses, m_e. H_d is the internal energy measured from the $z.p.e.$ of the species.

E_{min}	=	-115021 cal/(mol)
R_{OO}	=	$5.4, 5.6, 7.2, 8.2, 9.5, 11.1, 12.3, 13.6\, a_o$
ω	=	$40 - 914$ cm^{-1}
$z.p.e.$	=	38953 cal/(mol)
I	=	5973679.28 11267777.61 11267777.61 $m_e.a_0^2$

T/K	H_d	H'_d	S'_d	C_{pd}
250	14294	-5148	13.55	7.82
300	19233	-4736	15.01	8.61
350	24586	-4290	16.34	9.21
400	30261	-3817	17.57	9.68

TABLE V: Equilibrium constants of the reaction $(H_2O)_8 \rightleftharpoons 2\,(H_2O)_4$. Enthalpy is in units of cal/mol and per water molecule, and entropy in cal/(mol K) and per water molecule.

T/K	$\Delta H'^{a}$	$\Delta S'$	K_1
250	2010	6.22	0.148
300	2043	6.27	0.763
350	2069	6.30	1.214
400	2090	6.30	1.712

$^{a}\Delta H' = \Delta H/8 = H'_t - H'_o$

TABLE VI: Equilibrium constants of the reaction $(H_2O)_{12} \rightleftharpoons (H_2O)_8 + (H_2O)_4$. Enthalpy is in units of cal/mol and per water molecule, and entropy in cal/(mol K) and per water molecule.

T/K	$\Delta H'^{a}$	$\Delta S'$	K_{11}
250	1335	4.64	0.705
300	1357	4.67	1.076
350	1375	4.69	1.463
400	1389	4.69	1.838

$^{a}\Delta H' = \Delta H/12 = 2H'_o/3 + H'_t/3 - H'_d$

Figure Legends

1. Minimum energy geometries of $(H_2O)_n$ clusters with cubic arrangements of oxygen atoms. The energies of the tetramer and octamer are -22.31 and -61.14 kcal/mol respectively. Other energies are given in Table I in the same order as indicates the second integer in the label of the cluster, and with zero denoting the lowest energy. These values are obtained with the pairwise part of the CKL potential.

2. As Figure 1 but for other minimum energy geometries of the dodecamer.

3. The root mean square fluctuation of the O-O bond lengths, $\delta(E)$, (a), and the caloric curve (b) of the dodecamer. The calculations have been performed with the pairwise potential and with zero total angular momentum. Energies are in kcal/mol, and E_T, and E_k denote the total energy and the average kinetic energy respectively.

4. A quenching plot of the dodecamer from a trajectory at -84 kcal/mol. V_{min} denotes the energies of the quenched geometries.

5. Minimum energy geometries of the 18-mer. Energies are stored in Table I.

6. The r.m.s. fluctuation curve (a), and caloric curve (b) of the decaoctamer. Energies in kcal/mol.

7. The energies of the relative minima, V_{min}, of the 18-mer found by the quenching technique for a trajectory at -124 kcal/mol. The quenching is performed every 1 ps. Energies in kcal/mol. Note the locking of the trajectory between two relative close minima.

8. The power spectrum of 18-mer obtained by calculating first the correlation function (eq 7) from a trajectory at -120.3 kcal/mol.

9. As Figure 1 but for the 7-, 9-, 13-, and 17-mer water clusters.

10. The r.m.s. (a), and caloric (b) curves of the heptamer. The calculations have been performed with the pairwise potential and with zero total angular momentum. Energies in kcal/mol.

11. The r.m.s. (a), and caloric (b) curves of the enneamer. The calculations have been performed with the pairwise potential and with zero total angular momentum. Energies in kcal/mol.

12. Minimum energy geometries of the enneamer associated with the minima visited by the trajectory shown in Figure 13.

13. A quenching plot of the enneamer with a trajectory at -55.8 kcal/mol.

14. The $(S_4)_2$ minimum of the dodecamer given by the MCY[30] potential function. $E = -106.64$ kcal/mol.

15. A power spectrum obtained with the MCY potential from a trajectory at -102.1 kcal/mol and starting with the equilibrium geometry of the dodecamer shown in Figure 14.