

Structural Studies of the Water Hexamer

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In this paper we report the geometries and properties of 24 structural isomers located on the MP2/6-311++g** potential energy surface of the water hexamer. At least 15 structural patterns are located within 3 kcal/mol of the most stable conformation, leading to a very complex potential energy surface, several isomers having significant contributions. A quadratic correlation between the distance from the proton to the center of the hydrogen bond with the distance between oxygen atoms for all clusters is reported. MP2/6-311++g** and CCSD(T)/aug-cc-pvdz//MP2/6-311++g** predict different stabilization orderings but are in good agreement for binding energies. Compact structures are energetically favored by electronic energies with zero point energy corrections, while noncompact cyclic structures are preferred when temperature and entropy are accounted for.

Introduction

It is difficult to overstate the significance of water. Water is arguably one of the most important substances in Nature and certainly the most studied by science.¹ Water is an essential ingredient for the existence of life as we know it: all known biochemical processes occur in aqueous environments, in many instances water acting not only as a medium but also as a catalyst. Water covers about 75% of the surface of the Earth and comprises about 70–80% by weight of all living organisms. Water is the only substance known to exist as solid, liquid, or gas under natural conditions on earth. There are at least 15 crystalline phases and several amorphous modifications of solid water.² More substances dissolve in water than in any other solvent. Despite the wealth of knowledge and the vast amount of literature dedicated to water, many unusual properties and behaviors still puzzle scientists.

Many important consequences are derived from the unusual properties of water; we cite a few: (i) Life can be sustained under extreme environments because of the ability of water to remain liquid in a wide range of temperatures and pressures. This property also allows water to be used in a variety of ways, from cooling agent in automotive radiators to solvent for many chemical reactions. This property is related to the unusually high freezing and boiling points of water compared to substances with similar molecular structures. (ii) Ice has a lower density than liquid water. If the density of ice was larger than the density of liquid water, that would cause water bodies to freeze from the bottom to the top, leaving no room for the aquatic life that thrives under ice caps in surface frozen water environments. (iii) The moderate climate of earth is in part due to the extremely high heat capacity of water, which allows the vast oceans in the planet to absorb huge amounts of solar energy without significantly increasing their temperatures or the temperatures of their surroundings. (iv) The high latent heat of evaporation allows water to store large amounts of energy in the gas phase, the energy is released upon condensation, which has given steam

a very successful history as a heating agent. (v) The extremely high surface tension allows some insects and lizards to walk on liquid water.

The water hexamer (W₆ hereforth) has been extensively studied. A number of conformations have been reported experimentally;^{3–11} however, definitive assignments to specific conformations were not always possible, due to the presence of multiple isomers.¹² Two-dimensional water sheets that contain cyclic water hexamers in boat and chair conformations around Al³⁺ have been crystallographically observed.¹³

Theoretical predictions of W₆ conformations under a wide variety of model chemistries abound; here we summarize the findings (not intended as a review) of some recent papers on the subject: Bilalbegović,² calculated NMR parameters for W₆ clusters in the prism, cage, book, bag, chain, and two cyclic (cyclohexane-like) conformations. The report states that hydrogen and oxygen chemical shifts show substantial variation upon structural changes. The geometries were taken from the work by Su, Xu, and Goddard,¹⁴ optimized with the X3LYP functional. Auer and co-workers,¹⁵ used a NEO-FMO (nuclear electronic orbital, fragment molecular orbital) combined method at the HF, B3LYP, MP2(ee,pp) levels to treat the prism geometry as a test case. All protons were treated quantum mechanically. Bates and Tschumper,¹² tackled the difficult issue of relative stability of W₆ isomers using highly correlated CCSD(T) at the CBS limit calculations; they found eight isomers, prism, cage, bag, chair, two books, and two boats, within 3 kcal/mol; the calculations predict the prism conformation to be the more stable, closely followed by the cage. The stability issue could not be resolved even at this very high level of theory. They also reported that zero point energies (ZPEs) are significant, to the point that when included, the stability order of the isomers changes; temperature has a similar energy ordering changing effect. Sediki and co-workers studied the topology and properties of three-dimensional (3D) water clusters in the chair, cage, book, and prism conformations,¹⁶ at the HF/6-31g*, B3LYP/6-31g* levels. Vibrational Raman spectroscopy of the chair, cage, and prism conformations at the MP2/aug-cc-pvdz level have been reported by Cybulski and Sadlej.¹⁷ The structures, energies, and IR of the prism, cage, book, chair, and

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boat conformations were studied by Losada and Leutwyler at the MP2/6-311++g**, MP2/aVDZ levels;¹⁸ they argue that the stability sequence of the isomers is influenced by the ZPE mainly due to the intermolecular part of ΔZPE , $\Delta ZPE_{\text{inter}}$, which is positive (destabilizing) and increases with increasing number of H bonds, disfavoring the three-dimensional isomers. Díez, Almeida, and Rincón,¹⁹ found non-negligible contributions from many body effects on the stabilities of the chair, boat, bag, book, cage, and prism conformations of W_6 at the B3LYP/6-311++g** level. A related n -body interaction energy study on the prism, cage, and cyclic conformations was reported by Pedulla, Kim, and Jordan.²⁰

The potential energy surface (PES) for W_6 is far more complicated than the few isomers reported above (prism, books, bag, cage, chain, boats, chairs) suggest. For example, for the cage isomer alone, 14 different structures were located at the MP2/DZP level,²¹ while 27 local minima were predicted at the PM3 level.²² Regarding structural issues, W_6 seems to be the transition point from planar to 3D geometrical preferences;² it is interesting to notice that for homonuclear metallic clusters, M_n , $n = 6$ is also the transition point from planar to 3D structural preferences.^{23–26}

A problematic issue in the study of molecular and atomic clusters is the generation of equilibrium structures. Recently,^{26–28} a modification of the Metropolis acceptance test in the simulated annealing optimization procedure^{29–31} was proposed as a means for generating cluster candidate structures that undergo further optimizations by traditional gradient following techniques. The method, incorporated into the ASCEC (after its Spanish acronym *Annealing Simulado Con Energía Cuántica*) program,²⁷ retains the comparative advantages and disadvantages of stochastic optimization over analytical methods,³² namely, initial guess independence, exhaustive exploration of the potential energy surface, and the ability to jump over energy barriers and to sample several energy wells on the same run without getting trapped in local minima; however, the method is still computationally intensive because of repetitive evaluation of the energy function. The method has been successfully applied to the studies of the water tetramer,²⁸ small neutral and charged lithium clusters,²⁶ the methanol tetramer,³³ and the carbonic acid dimer,³⁴ affording contributing new structures never before reported in the literature which have helped us rationalize the stabilization of small hydrogen-bonded networks.

Most of the macroscopic properties of water are thought to be a consequence of the microscopic structure. Bulk liquid water, for example, is often better described as a collection of hydrogen-bonded clusters than as an isotropic medium.³⁵ The weakness of hydrogen bonds relative to chemical bonds makes them very important,³⁶ among other factors because they can easily be made and broken at ambient temperatures, thus increasing the conformational possibilities of hydrogen-bonded networks, in both size and geometry, and giving additional support to the above-mentioned view of liquid water. However, many details of hydrogen bonding remain unclear,³⁷ probably due in part to the difficulties in accurate theoretical treatment of the complex energy decomposition schemes for these interactions.^{36,38} It seems firmly established that good accounts for electron correlation and extended basis sets are needed for the accurate treatment of small hydrogen bonding networks.²⁸ In any case, cooperative polarization and cooperative charge transfer have been postulated to be largely responsible for the formation and stabilization of small hydrogen-bonded networks.^{28,33,34,39–42} Since the conformations of the clusters determine many of their properties, and since in turn the clusters

have influence on the macroscopic structure and properties of water, a thorough knowledge of the W_6 PES is in order. In this work, we aim at an exhaustive characterization of all geometrical motifs, in an effort to help in the understanding of the structure and stability of the water hexamer.

Computational Details

We used the molecular cluster capabilities of the ASCEC program which contains an adapted version of the simulated annealing optimization procedure. The annealing algorithm was used to generate candidate structures after random walks of the PM3^{43,44} PES. The hybrid B3LYP density functional^{45–47} in conjunction with the 6-311++g** basis set was used to optimize and characterize the structures afforded by ASCEC. Further refinement and characterization of the stationary points was carried out by using second-order perturbation theory at the MP2/6-311++g** level. Analytical harmonic second derivative calculations were used to characterize all stationary points as true minima (no negative eigenvalues of the Hessian matrix) or saddle points. Highly correlated CCSD(T) energies⁴⁸ were calculated on all the MP2 located minima using the aug-cc-pvdz basis set. This choice of methodology has proven to give very good quality results in the study of small hydrogen bond networks.^{28,33,34}

Binding energies (BE) were calculated by subtracting the energy of the given hexamer from six times the energy of the water monomer, in this way, larger positive numbers correspond to larger stabilization energies. Relative binding energies (ΔBE) were calculated as the difference between the energy of the most stable hexamer and the energy of a particular structure. We used the MP2/6-311++g** ZPEs to correct the CCSD(T) electronic energies in the calculations of binding energies and relative stabilities. There are several reports that clearly reveal the failure of counterpoise correction for basis set superposition error in the study of small hydrogen-bonded clusters; specific cases are the dimers of carbonic acid (H_2CO_3)₂,⁴⁹ hydrofluoric acid (HF)₂,^{50,51} and water (H_2O)₂.⁵² Theoretical treatment of the methanol tetramer,³³ showed no significant differences by correcting for BSSE. Therefore, in this work, we restrain ourselves from applying such methodology. All optimization, frequency, and energy calculations were carried out using the Gaussian 03 suite of programs.⁵³ Isomer populations were estimated by standard Boltzmann distribution analysis.

Results and Discussion

ASCEC Conditions. We used the big bang approach to construct the initial geometries for all ASCEC runs, namely, the six water molecules were placed at the same position, allowing them to evolve under the annealing conditions. The annealing was run four times under slightly different conditions. The systems were placed inside cubes of 7 and 8 Å of length. The PM3 semiempirical Hamiltonian was used to calculate the energy of a Markovian chain of randomly generated hexamer configurations. We used geometrical quenching routes with an initial temperature of 400 K, a constant temperature decrease of 5%, and 100 total temperatures.

Cluster Structures. The W_6 equilibrium geometries were produced following the procedure outlined above. All geometry optimizations were carried out with no imposition of symmetry constraints as the structures coming from ASCEC are randomly generated and belong to the C_1 point group; however, some of the located stationary points have higher symmetries.

Geometries and Structural Issues. We found 24 different geometrical motifs on the MP2/6-311++g** PES shown in

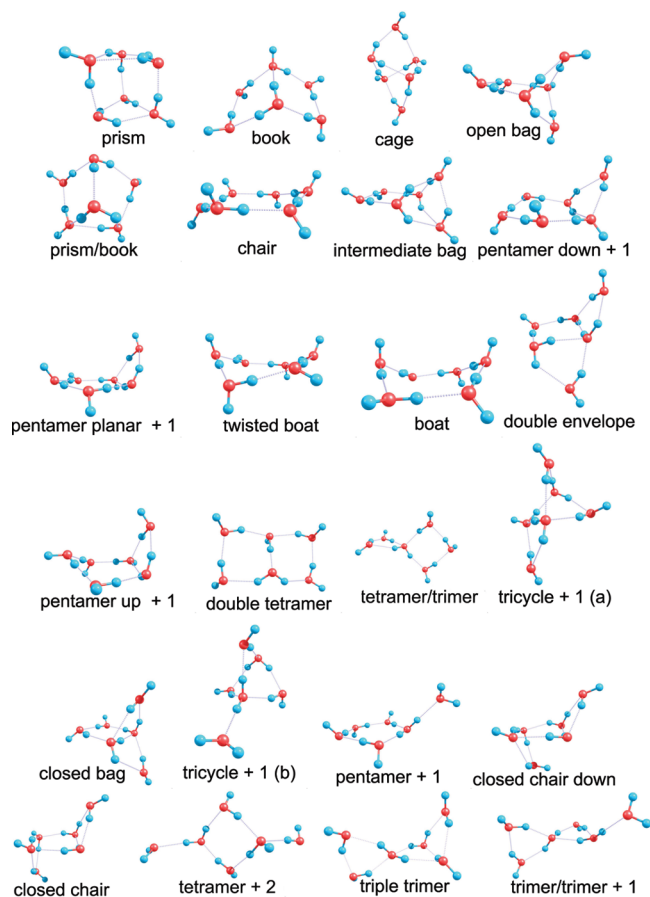


Figure 1. Structures of the water hexamer clusters at the MP2/6-311++g** level of theory.

approximate decreasing order of stability in Figure 1. An interesting observation is that despite the W_6 structures having no chiral centers, we found several enantiomer pairs due to the overall spatial arrangements of the clusters. We kept the traditional descriptive notation for those structures previously reported in the literature (prism, book, cage, etc.), and subjectively named the many new geometries found in this work. There are plenty of possibilities for each geometrical motif and surely many more structures to be found, recall for example the 14 and 27 isomers reported just for the cage alone in two different works.^{21,22} The rich PES obtained in this study is a consequence of the stochastic nature of the search of the quantum conformational space performed by the ASCEC program, which bypasses the structure-guessing step in the search for local minima.^{28,26} A similar structural complexity was observed in the study of the methanol tetramer, $(CH_3OH)_4$,³³ and carbonic acid dimer, $(H_2CO_3)_2$.³⁴

For general *linear* hydrogen bonds, the distance of the proton to the center of the hydrogen bond, q_1 , correlates quadratically with the distance between heavy atoms, q_2 ,⁵⁴ the lowest point in the parabola corresponding to an equally shared proton between the two heavy atoms, i.e., the midpoint for hydrogen transfer. Despite the hydrogen bonds not being linear in general in this work, there is a remarkable quadratic correlation between q_1 and q_2 as depicted in Figure 2. A fitting of the calculated q_1, q_2 produced the adjusted equation $q_2 = 2.1157 - 1.4432q_1 + 0.4027q_1^2$. This equation reveals that for the W_6 clusters every H atom involved in a hydrogen bond is still well attached to the water molecule that donates it: the smallest predicted q_2 is 2.62 Å, which is considerably larger than 2.12 Å, the distance required for an equally shared proton between two oxygen atoms

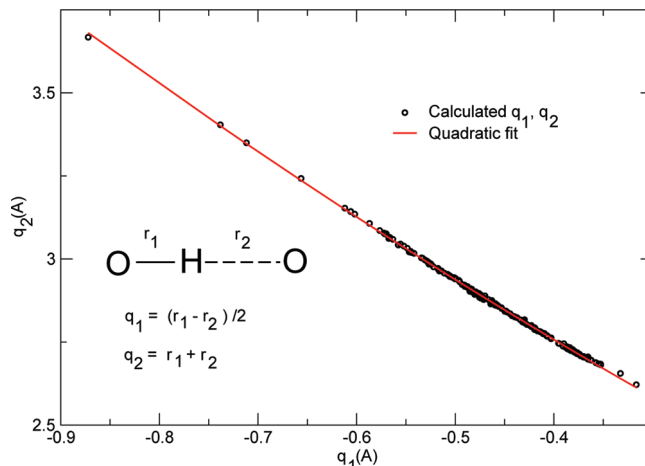


Figure 2. Correlation between q_2 , the distance between oxygen atoms and q_1 , the approximate distance of the proton to the center of the hydrogen bond for the water hexamers. Adjusted equation: $q_2 = 2.1157 - 1.4432q_1 + 0.4027q_1^2$. Most hydrogen bonds are not linear.

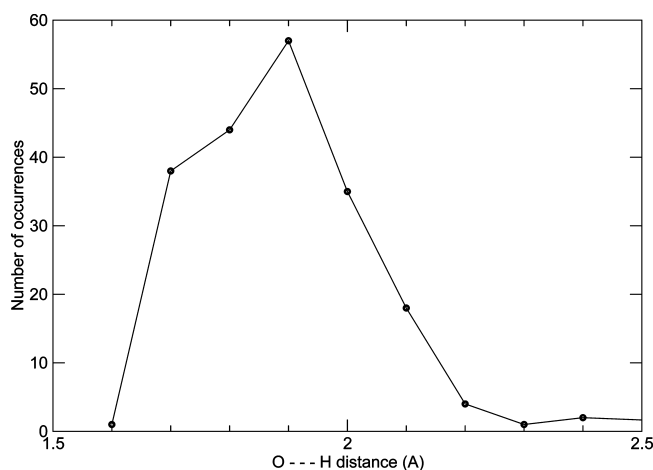


Figure 3. Distribution of the $O \cdots H$ distances for the water hexamer.

($q_1 = 0$). This observation leads us to suggest that proton transfer in the W_6 clusters is not favored. A plot resembling a Gaussian distribution, with most values falling in the 1.7–2.0 Å range for the $O \cdots H$ distances in the water hexamer, is included in Figure 3.

The interactions responsible for the stabilization of the hexamers are not enough to cause significant changes in the geometries of the water monomer. In most cases, water molecules act simultaneously as donor/acceptor of hydrogen bonds; however, in a few cases, when one molecule is dangling off a larger cyclic structure, that extra water molecule acts only as acceptor or donor of just one hydrogen bond. There are seven instances where one water molecule acts simultaneously as double donor/double acceptor of hydrogen bonds: double envelope, double tetramer, tetramer/trimer, tricycle + 1 (a), tricycle + 1 (b), triple trimer, trimer/trimer + 1. The closed bag structure has two water molecules acting simultaneously as double donor/double acceptor of hydrogen bonds.

Energies, Cluster Stabilization, and Other Properties. Table 1 classifies the structures in decreasing order of stability as predicted by MP2/6-311++g** ZPE corrected CCSD(T)/aug-cc-pvdz//MP2/6-311++g** calculations. Table 1 also shows relative energies (ΔE) and binding energies (BE) at the

TABLE 1: Energetic Analysis for the (H₂O)₆ Clusters. ΔE : Relative Energy with Respect to the Most Stable Structure at Each Level^a

structure	ΔE CCSD (T)	ΔE MP2	BE CCSD (T)	BE MP2	Δ Gibbs ^b MP2	% x_i CCSD (T)	% x_i Gibbs ^b
prism	0.0	0.8	34.1	36.2	3.0	52.8	0.3
book	0.8	0.6	33.3	36.4	1.4	13.7	4.9
cage	1.1	2.1	33.0	34.9	4.0	8.0	0.1
open bag	1.2	1.0	33.0	36.0	2.3	7.5	1.1
prism/book	1.4	1.3	32.8	35.6	2.7	5.2	0.5
chair	1.6	0.0	32.5	37.0	0.0	3.7	50.0
intermediate bag	1.9	1.8	32.2	35.2	3.2	2.1	0.2
pentamer down +1	2.0	1.3	32.1	35.7	1.8	1.8	2.5
Pentamer planar +1	2.2	1.4	31.9	35.6	1.5	1.3	3.9
twisted boat	2.5	1.0	31.6	36.0	0.4	0.8	23.7
boat	2.6	1.2	31.5	35.8	0.9	0.7	11.0
double envelope	2.7	2.8	31.4	34.2	3.0	0.6	0.3
pentamer up +1	2.8	2.2	31.4	34.8	2.2	0.5	1.2
double tetramer	3.0	3.7	31.2	33.3	4.0	0.4	0.1
tetramer/trimer	3.0	3.1	31.1	33.8	3.1	0.3	0.3
tricycle +1 (a)	3.2	4.0	30.9	32.9	4.9	0.2	≈ 0
closed bag	3.4	4.3	30.7	32.7	4.4	0.2	≈ 0
tricycle +1 (b)	4.0	4.7	30.1	32.3	4.4	0.1	≈ 0
pentamer +1	4.5	3.6	29.6	33.4	2.0	≈ 0	1.8
closed chair down	5.5	7.0	28.7	30.0	7.0	≈ 0	≈ 0
closed chair	6.1	7.3	28.1	29.7	7.2	≈ 0	≈ 0
tetramer +2	6.6	7.1	27.5	29.9	3.5	≈ 0	0.1
triple trimer	6.7	8.2	27.5	28.8	7.6	≈ 0	≈ 0
trimer/trimer +1	8.6	9.2	25.5	27.7	7.5	≈ 0	≈ 0

^a BE: Binding energy. All CCSD(T)/aug-cc-pvdz calculations using the MP2/6-311++g** optimized geometries. All relative and binding energies corrected for the unscaled MP2/6-311++g** ZPEs. All energies in kcal/mol. ^b Calculated as $G = H - TS$, $T = 298.16$ K.

CCSD(T) and MP2 levels as well as Gibbs free energies. Isomer populations estimated via Boltzmann distributions are also listed in Table 1.

Binding and relative energies calculated here are in excellent agreement with previous works for the known structures.^{12,14,55,56} Our calculations predict a very rich and complex PES: not counting the many possible isomers for each motif, there are at least 15 structural patterns within 3 kcal/mol of the most stable conformation. Our calculations also reproduce the well-known fact that for W₆, MP2 and CCSD(T) give different stabilization orderings; however there is a much better agreement for the binding energies calculated by both methods.

If only electronic energy and ZPE effects are accounted for, the general preference is for compact structures. Prism is the most stable followed by book, followed by cage, etc., at the CCSD(T)/aug-cc-pvdz//MP2/6-311++g** level. If temperature and entropy are included in the analysis, cyclic, noncompact structures are preferred as the chair, twisted boat, boat, etc., is the stability order predicted by Gibbs energies at the MP2/6-311++g** level calculated at 298.16 K. Boltzmann analysis (Table 1) predicts the existence of several contributing structures for the W₆ clusters. We point out that the energy ordering (and therefore the estimated isomer populations) reported here is subject to change as the relative stability is very sensitive to the level of theory, and therefore more sophisticated calculations could interchange the structures lying so close in energy. There is no correlation between cluster stability and the number of hydrogen bonds in the structure, for example, prism, the most stable structure, has nine hydrogen bonds, while triple trimer, the next to least stable isomer, 6.7 kcal/mol above the prism

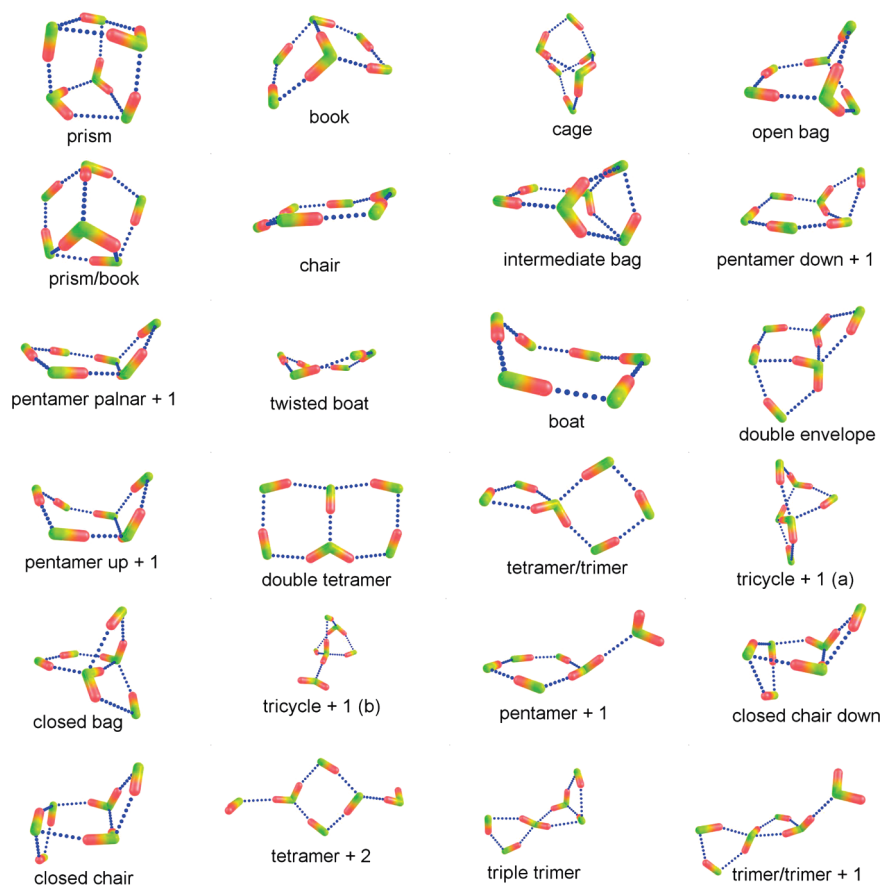


Figure 4. Stabilizing dipole-dipole interactions for the W₆ clusters. The dipole component along the O—H bond is represented by a stick, the light end (green in the colored figure) being the oxygen atom.

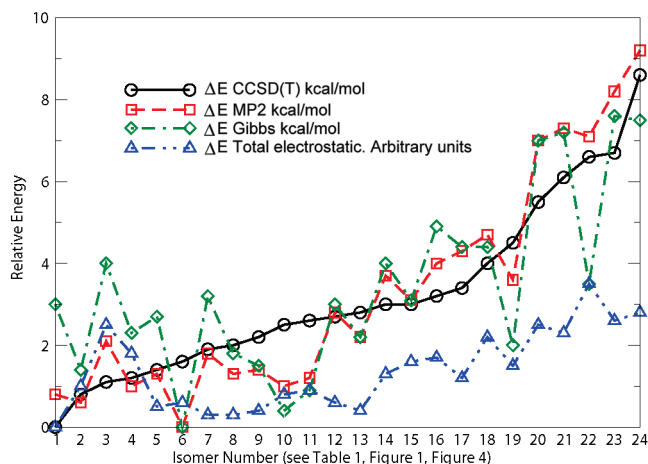


Figure 5. Relative binding energies at several levels of theory for the W_6 clusters.

exhibits eight hydrogen bonds, and chair, the sixth most stable structure, only 1.6 kcal/mol above the prism has six.

An important realization is that binding energies for $(H_2O)_6$ (34.1–24.5 kcal/mol) are larger than those for $(H_2O)_4$ (30.7–18.7 kcal/mol²⁸) at comparable levels of theory; i.e., the hexamer is more stable than the tetramer. The W_4/W_6 relative stability issue is not simply a case of a larger number of water molecules producing more hydrogen bonds: as stated above, the number of hydrogen bonds does not correlate with cluster stability.

It has been suggested that a large contribution to the stabilization of small hydrogen-bonded networks similar in nature to the ones treated here arises from dipole–dipole electrostatic interactions via cooperative polarization by virtue of the spatial arrangement of the dipole moment components along the polar bonds.^{28,33,34,39–42} The same type of stabilizations are encountered for the W_6 clusters: the individual dipole components arrange themselves to maximize the attracting electrostatic interactions in the most stable structures, while the configuration of the dipole components decreases their stabilizing power due to less favorable orientations as we advance along the least stable structures. The dipole components along O–H bonds participating in hydrogen bonding for all W_6 clusters is depicted in Figure 4. We tested this hypothesis by calculating the total electrostatic energy arising from contributions of all Mulliken predicted atom charges belonging to the stabilizing hydrogen bond network.⁵⁷ Figure 5 shows the trend of relative stabilization energies calculated for all clusters at all levels of theory reported here, the total electrostatic energy for the interactions of all point charges at the positions of the atoms belonging to dipole components along the hydrogen bonds for all the structures is also shown. We point out that an excellent trend agreement between the curves gives strong support to the dipole–dipole stabilization hypothesis for the W_6 clusters.

Conclusions and Perspectives

We report the geometries and properties of 24 structural isomers located on the MP2/6-311++g** PES of the water hexamer. The structures were found after random walks of the PM3 PES. A Boltzmann distribution analysis reveals several isomers with significant populations. There are at least 15 structural patterns within 3 kcal/mol of the most stable conformation. Overall stabilization is mainly dictated by attractive electrostatic interactions via cooperative polarization by virtue of the spatial arrangement of the dipole moment components along the polar bonds. We are confident that the

stochastic search of the conformational space has produced all possible geometrical motifs for the W_6 clusters; however, the results in this study are by no means conclusive for a complete characterization of the PES as there are more structures to be located due to the many possibilities within each structural motif. We found a quadratic correlation between the distance from the proton to the center of the hydrogen bond with the distance between oxygen atoms for all clusters. MP2/6-311++g** and CCSD(T)/aug-cc-pvdz//MP2/6-311++g** model chemistries predict different stabilization orderings but are in good agreement for binding energy calculations. Compact structures are energetically favored by electronic energies with ZPE corrections; however, noncompact cyclic structures are preferred when temperature and entropy are accounted for.

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Supporting Information Available: Cartesian coordinates for all optimized geometries. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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