Hydrogen-Bond Networks in Water Clusters (H₂O)₂₀: An Exhaustive Quantum-Chemical Analysis

Andrei M. Tokmachev,*[a] Andrei L. Tchougréeff,[a,b] and Richard Dronskowski[a]

Water aggregates allow for numerous configurations due to different distributions of hydrogen bonds. The total number of possible hydrogen-bond networks is very large even for medium-sized systems. We demonstrate that the targeted ultra-fast methods of quantum chemistry make an exhaustive analysis of all configurations possible. The cage of $(H_2O)_{20}$ in the form of the pentagonal dodecahedron is a common motif in water structures. We calculated the spatial and electronic structure of all hydrogen-bond configurations for three systems: idealized cage $(H_2O)_{20}$ and defect cages with one or two hydrogen bonds broken. More than 3 million configurations studied provide unique data on the structure and properties of water clusters. We performed a thorough analysis of the results with the emphasis on the cooperativity in water systems and the structure-property relations.

Introduction

Most of anomalous properties of water are attributed to the cooperative behaviour of strong hydrogen bonds (H-bonds) between water molecules. Extended H-bond networks first appear in water clusters. Many of water clusters are important components of the atmospheric chemistry,[1] cloud and ice formation, thereby linked to the earth's radiation balance and precipitation patterns. Sometimes even liquid water is thought of in terms of flickering water clusters[2] although this hypothesis is debatable.

Not all water clusters are equally stable and important, however. Protonated clusters $H^+(H_2O)_n$ exhibit exceptional stabilities for some "magic numbers" n. The smallest of such numbers is n=21, and the enhanced stability of this cluster was confirmed by numerous experiments based on different experimental conditions and techniques.[3] It was suggested[4] that $H^+(H_2O)_{21}$ is a pentagonal dodecahedron with the H_3O^+ ion trapped inside the cage.

Titration of dangling hydrogen atoms with trimethylamine (TMA) confirms this hypothesis: the cluster $H^+(H_2O)_{20}$ forms a complex with 11 molecules of TMA, while the cluster $H^+(H_2O)_{21}$ can coordinate only 10 molecules of TMA.[5] It is also consistent with the XPS spectrum of O 1s core level not exhibiting any internal structure[6] and spectroscopic (IR) results,[7] pointing to a highly symmetric structure formed by three-coordinated water oxygen atoms. The pentagonal dodecahedra are probably highly stable, being major structural elements for all three common types of gas clathrate structures: sI, sII, and sH hydrates.[8]

The hypothetical character of the above structural predictions calls for theoretical studies. If one considers clusters of a fixed size n, different forms (morphologies) of the oxygen-atom framework are possible. In the case of $(H_2O)_{20}$, four major structural classes were proposed[9] (see Figure 1). Their relative stabilities are determined by a fine balance between hydrogen

bonding and strains in the rings, and each of the classes was predicted as an energy minimum.[10] The dodecahedral structure can be stabilized due to a larger number of dangling O-H bonds interacting with other molecules.
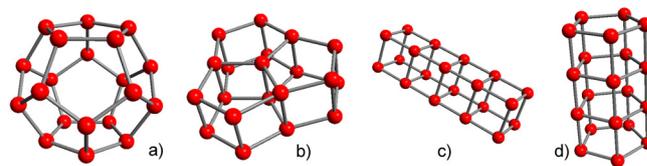

Figure 1. Major classes of water clusters $(H_2O)_{20}$: a) dodecahedron; b) edge-sharing pentagonal prisms; c) fused cubes; d) face-sharing pentagonal prisms.

When the morphology of the cluster is defined, there is still a lot of freedom for placing H atoms. Normally, the "ice rules"[11] (basically requiring that water molecules are not ionized) are imposed on the positions of dangling O-H bonds and directions of H-bonds. The number of isomers is usually large even for medium-sized water systems and each of them corresponds to some local extremum on the potential energy surface: for

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example, there are 30,026 symmetry-independent H-bond arrangements in the case of the dodecahedral cluster $(H_2O)_{20}$. A variety of methods (force fields,[12] DFT,[13] semiempirical[14] and *ab initio* methods[15]) has been used to find and characterize the H-bond networks with the lowest energy (or a few of them) for the dodecahedral cluster. At the same time the energy difference between the H-bond networks is relatively small and many of them can be thermally populated, thus affecting the physical properties of the cluster. Therefore, it is desirable to study a large number of H-bond configurations, preferably all of them. The only reported study of the whole set of H-bond isomers for this cluster[16] is made by the OSS2 empirical force field.

A full quantum-chemical analysis of all possible configurations aimed to extract statistical data would be a great step forward in understanding the H-bond networks. The development of highly efficient linear-scaling methods[17] brings new possibilities to large-scale calculations. Here we report the first exhaustive quantum-chemical study of all symmetry-distinct H-bond configurations of the dodecahedral cluster $(H_2O)_{20}$ as well as more complex systems with the same morphology. Of course, the interaction of the cage with the chemical environment, which is normally the case, may significantly affect the stability of the H-bond configurations or even bring a partial order to the positions of H atoms but we believe that the regularities found and the insights gained from the present analysis of the unperturbed cluster are quite general.

Results and Discussion

Before starting to present the results of the calculations it is necessary to discuss their potential accuracy. Although the specialized ultra-fast method used in the present work well reproduces the properties of small water systems (see the "Computational Methods" section) there is an obvious question about the reliability of the results. Cluster of 20 water molecules is a very complex system. Reputable methods of computational chemistry predict different most favourable morphologies, different most stable H-bond networks, and different binding energies.

Taking into account that the energy differences between H-bond configurations are often very small, the reliability of the predictions of their energetic order by any available computational method is at least doubtful. At the same time one can expect that the general properties of the total energy distribution as well as structure/property relations determined by an analysis of a vast set of data are less contingent on the computational method. This is the area where the results are significantly more reliable and thus our ability to perform an exhaustive analysis of H-bond networks is a great advantage.

Nevertheless, an analysis of optimal H-bond configurations produced by different methods can be insightful. Figure 2 shows the optimized configurations with the highest and the lowest energies. The optimal H-bond configuration differs from those reported in Refs. [9, 18-20] but they are close in energy and actually similar: they all have the same configuration of dangling O-H bonds. There are 28 different configurations with this property, and 5 of them are reported as global minima in different studies certifying that this structure of dangling O-H bonds is the most preferable among 1,648 symmetry-independent ones. Similarly, the least stable isomer differs from that reported in Ref. [21] only by the directions of H-bonds. The difference between our result and preceding ones is that we now find the minimum-energy structure by comparing the energies of *all* H-bond isomers.
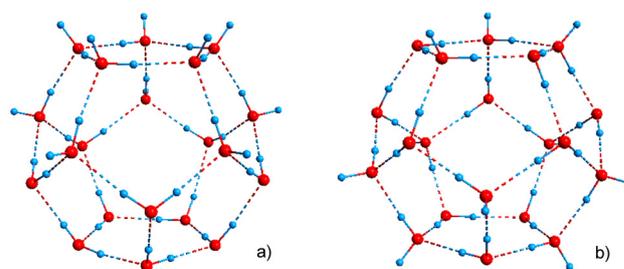

Figure 2. Characteristic configurations of water clusters $(H_2O)_{20}$: a) the highest-energy configuration; b) the lowest-energy configuration.

Turning to energies, their values can be characterized by the asymmetric cumulative distribution function (CDF) given by Figure 3 (the average value is -1395.92 kcal/mol and the standard deviation is 4.36 kcal/mol). The energy difference between the least and the most stable isomers is 35.44 kcal/mol, which is somewhat smaller than the value (*ca.* 40 kcal/mol) obtained by the OSS2 force field.[16] The energy distribution is far from being normal (as seen for example from its asymmetry parameter 0.493 and the excess kurtosis 0.514) and the best fit is given by the Burr distribution CDF.[22] The binding energy for the most stable isomer is -190.58 kcal/mol, which is smaller by absolute value than those obtained by different force fields (between -197 and -202 kcal/mol).[18] A more important characteristic of a cluster is its cooperative energy. It can be defined as the difference between the binding energy and the energy of the H-bond in the water dimer multiplied by the number of H-bonds. The cooperative energy is negative for all H-bond isomers, and it ranges between -39.56 and -4.12 kcal/mol.
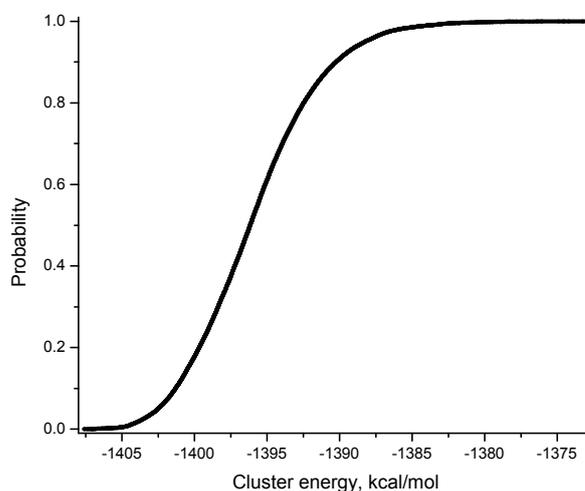

Figure 3. Cumulative distribution function (CDF) for the energy.

The pentagonal dodecahedron formed by the oxygen atoms of $(H_2O)_{20}$ has 30 edges, and each of them can be an H-bond. We consider also distorted structures with less than 30 H-bonds. The first structure has 29 of them (we denote it as Hb29; the original cluster is thus Hb30) and 11 O-H bonds directed outwards. The number of allowed H-bond networks grows dramatically and there are 443,112 symmetry-independent defect

configurations. The other structure is Hb28 with 28 H-bonds and 12 dangling O-H bonds allowing for 2,772,313 H-bond configurations. The exhaustive analysis is still feasible by our method, so that the spatial and electronic structures of all the configurations have been fully optimized. The energetically most favourable configurations for both Hb29 and Hb28 are given in Figure 4. One can notice that in both configurations the missing H-bonds between the water molecules with dangling O-H bonds, and the two missing H-bonds in the most stable isomer of Hb28 are the edges of the same face of the dodecahedron.
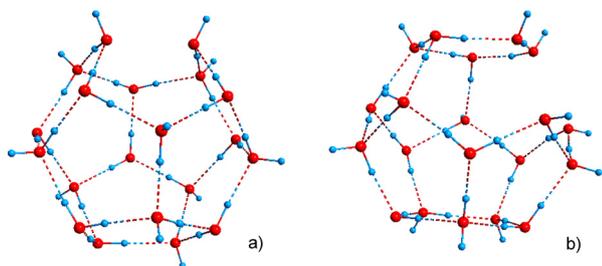

Figure 4. The lowest energy configurations of water clusters $(H_2O)_{20}$ with broken H-bonds: a) Hb29 structure; b) Hb28 structure.

The energy distributions for Hb29 and Hb28 (see Supporting information) are visibly asymmetric (like that for Hb30). They have the average values -1387.69 and -1379.48 kcal/mol with the standard deviations of 4.91 and 4.98 kcal/mol, respectively. The cooperative energy can be of either sign with the largest destabilization energies being 2.44 kcal/mol for Hb29 and 5.39 kcal/mol for Hb28. The absolute value of the cooperative energy per H-bond for Hb30 isomers varies between 0.14 and 1.32 kcal/mol with the average of 0.93 kcal/mol. When one H-bond is broken the (absolute) cooperative energy for these three characteristic points decreases by 1.89, 6.55, and 3.19 kcal/mol, respectively. The next broken bond decreases it further by 1.54, 2.95, and 3.18 kcal/mol, respectively. Thus, the cooperativity follows *different* patterns for these points of the energy distribution and the data do not fit to a simple model of the cooperative energy as dependent on the number of H-bonds.
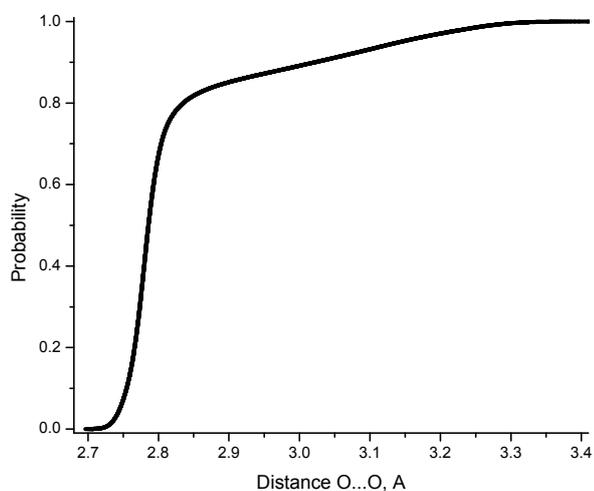

Figure 5. Cumulative distribution functions (CDF) for hydrogen bond lengths.

Figure 5 shows the distribution of bond lengths for all 900,780 H-bonds in Hb30 clusters. There are no H-bonds shorter than 2.69 Å, *i.e.*, we do not observe anomalously short H-bonds, which were claimed to be responsible for the self-dissociation of the clusters;[21] instead, some bonds are relatively long. Nevertheless, about 80% of the bonds are between 2.7 Å and 2.8 Å, with the density maximum at about 2.77 Å, to be compared with the averaged experimental O···O separations of 2.78 Å for the tetramer[23] and 2.76 Å for the pentamer,[24] as well as with the characteristic values 2.84 Å for liquid water and 2.74 Å for normal ice. The average radius of the cavity is 3.96 Å, to be compared with the radius of dodecahedral cavities in the clathrate hydrate sI, which equals 3.95 Å.[25] The angular distortion (non-linearity) of the H-bonds (see Supporting information) is significant.

The CDF for the H-bond lengths (Figure 5) looks like a combination of several CDFs. The same is true for other H-bond characteristics. Figure 6 exemplifies it by showing the CDF of HOMO energies for H-bonds. It has two distinct steps alluding to the presence of two types of H-bonds: strong trans- and weak cis-bonds.[26] This hypothesis is invalid, however, and a more general classification of the bonds according to their closest neighbours is necessary. There are five types of H-bonds;[20, 27] three of them are cis-bonds (c2, c0, and c1a with 2, 0, and 1 dangling O-H bonds at the oxygen atoms, respectively) and two types are trans-bonds (t1d and t1a with the dangling bond at the donor or acceptor O atom, respectively). Figure 6 also demonstrates the decomposition of the total CDF of HOMO energies into the sum of narrower S-shape CDFs for the above five types of H-bond. The CDFs for t1a and c1a bond types are close for all the bond characteristics and thus can be united (these types are responsible for large bond lengths O···O, see Figure 5).
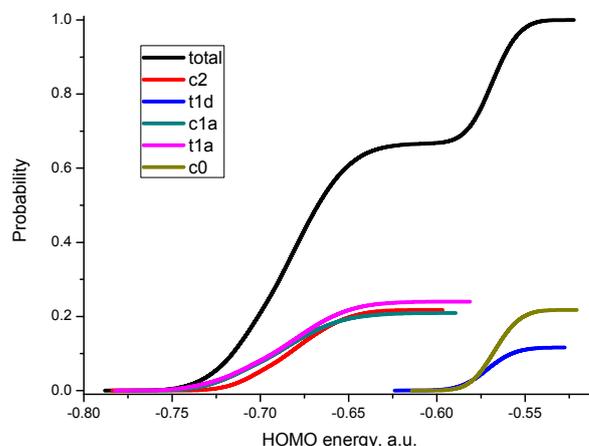

Figure 6. Cumulative distribution function (CDF) of the highest occupied molecular orbital (HOMO) energies for H-bonds and its decomposition over 5 types of bonds.

The correlations between the energy and the cluster radius, the average H-bond length, and angular distortions are rather poor. On the other hand, different suggestions about the correlation of the cooperative energy and the electronic structure have been proposed.[28] One of them is that the cooperativity manifests itself by an increasing s-character of the lone pair. In our calculations this parameter occurs naturally but there is no significant correlation. Another suggestion[28] is that the

cooperativity is associated with the increased positive charge on the hydrogen donor atom, and this one seems to be true. There is a remarkably good linear dependence ($R^2=0.976$) between the average atomic charge on the H donor atoms in the cluster and its energy (see Figure 7). The linear dependence is even better if we neglect the relaxation of the cluster's spatial structure. Thus, the relative stability of the cluster is determined by the *polarization* of H-bonds.
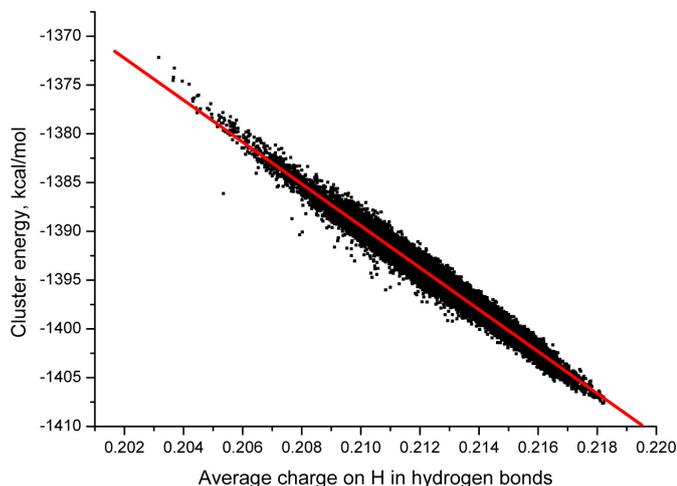

Figure 7. Approximately linear correlation between the cluster energy and the average charge of H atoms in hydrogen bonds.

Both the energy and the atomic charges are ultimately determined by the H-bond network topology, and it is desirable to work out a predictive model. Figure 2 suggests that the low-energy isomers correspond to a small number of neighbouring pairs of dangling O-H bonds. There is indeed some correlation between this characteristic and the energy (see Supporting information) but, for example, there are isomers with nine neighbouring O-H pairs with smaller energy than some isomers with only five such pairs. Moreover, our analysis (see Supporting information) shows that the energy difference between the least and the most stable isomers for a given configuration of O-H bonds can be up to 7 kcal/mol with the average value close to 3 kcal/mol.

Alternatively, one may consider the structure of the H-bonds. The data show that the correlation of the energy with the numbers of trans- and cis-bonds (see Supporting information) as well as with the 5 types of H-bonds described above are weak. Graph invariants[16] are a more general set of variables. To define them one introduces bond variables b_k for each H-bond k. These variables take the values ±1 depending on the direction of the H-bond in a given H-bond configuration. We considered second-order invariants defined as

$$I_{kl} = \sum_{\alpha=1}^{G} g_\alpha (b_k b_l),$$

where the sum is over all the elements of the symmetry group (I_h in the case of pentagonal dodecahedron) and g_α is the group operation acting on the product of bond variables. There are seven linearly independent second-order invariants, counting symmetry-different pairs of hydrogen bonds. The energy of the clusters can be well approximated ($R^2=0.963$) by a linear

combination of these invariants (see Figure 8) showing that the energy of the cluster can be reasonably described by taking into account only pair (effective) interactions.
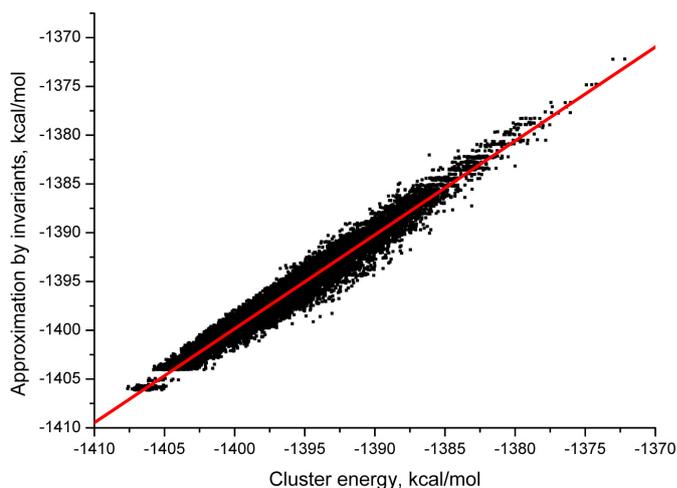

Figure 8. Approximately linear correlation between the cluster energy and a linear combination of graph invariants.

Conclusion

Water clusters are fascinating structures exhibiting some properties of the bulk water but differing from them due to the presence of dangling O-H bonds. The dodecahedral cluster $(H_2O)_{20}$ attracts a lot of attention because this highly symmetric structure constantly appears in different experimental settings. The complexity of the water cluster is due to the large number of different H-bond arrangements, which affect its properties. Here we reported the first quantum-chemical study of all symmetry-independent H-bond networks for dodecahedral neutral water clusters with 30, 29, and 28 H-bonds. The total number of configurations studied exceeds 3 millions.

The results obtained look quite reasonable. The approach used opened the possibility for a statistical analysis of the properties of these water clusters. We determined cumulative distribution functions for the energy of the clusters, their spatial and electronic structure characteristics. With these data at hand it is possible to consider the properties of the whole set of H-bond isomers. We analyzed the structure of the most stable isomers and checked different possibilities for the energy dependence on the structure of the H-bond network. We found that the dependence of the cooperativity energy on the number of H-bonds is very different for different parts of the energy distribution for the clusters. We checked a few hypotheses for the dependence of the cooperativity energy on the spatial and electronic structure parameters. It turns out that there is a linear correlation between the cluster energy and the average charge on the hydrogen donor atoms in the H-bonds. This suggests that their polarization is responsible for the cooperativity.

Computational Methods

The structures of the water clusters were computed by the specialized SLG method[29] based on the local description of the electronic structure in terms of electron groups. The high computational efficiency is a consequence of the small number of electronic-structure variables and the use of atomic multipoles for interatomic

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Coulomb interaction.[30] While the O-H bonds are described by geminals, H-bonds and lone pairs are represented by products of local molecular orbitals.

We used the PM3 parameterisation[31] of the NDDO Hamiltonian, which has been successfully applied to H-bonding in small-to-medium water clusters.[32] The only parameter to adjust is the resonance parameter for hydrogen in H-bonds, which we set to be 6.46 eV. The SLG optimized structures of the water molecule and its dimer are much better than those of the original SCF/PM3: *e.g.*, the length of the H-bond in the water dimer is 3.05 Å, to be compared with the experimental (2.98 Å) and with the SCF/PM3 (2.77 Å) values (one should also take into account that it is a floppy complex). The same applies to the energies: the binding energy of the dimer (-5.03 kcal/mol) is perfectly reproduced by SLG, while SCF/PM3 underestimates it (-3.5 kcal/mol).

In the case of larger water systems it is difficult to find reference points. We compare our SLG results with those of *ab initio* calculations. Ref. [33] compares the results of water ring calculations with an aug-cc-pV5Z basis set for MP2 and 16 DFT methods, which are widely used for H-bonded systems. In the case of the most stable isomer of water tetramer the SLG method predicts the dissociation energy to be 27.46 kcal/mol, which can be compared with the MP2 value of 27.66 kcal/mol and the DFT ones ranging from 24.43 kcal/mol to 30.51 kcal/mol (the average value is 26.90 kcal/mol). When water pentamer is considered the SLG dissociation energy is 34.67, while the MP2 value is 36.25 kcal/mol and the DFT values range from 32.42 kcal/mol to 40.41 kcal/mol with the average over 16 methods being 35.65 kcal/mol. These comparisons certify that the accuracy of the SLG method is similar to that of *ab initio* methods when applied to water aggregates.

The generation of all the possible configurations of the H-bond network is a separate problem. We implemented a backtracking (depth-first search) algorithm to find all the configurations. One needs only symmetry-independent configurations. The symmetry corresponds to the idealized core of oxygen atoms and not to the clusters. The symmetry group (I_h) has 120 operations and it allows to reduce the number of configurations significantly: 30,026 instead of 3,600,000 configurations compatible with the "ice rules".

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Entry for the Table of Contents

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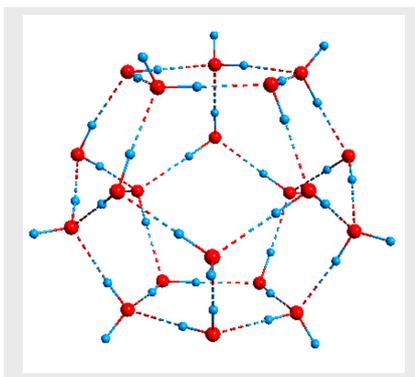
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Hydrogen-Bond Networks in Water Clusters (H$_2$O)$_{20}$: An Exhaustive Quantum-Chemical Analysis

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Supporting Information

Hydrogen-Bond Networks in Water Clusters (H_2O)$_{20}$:
An Exhaustive Quantum-Chemical Analysis

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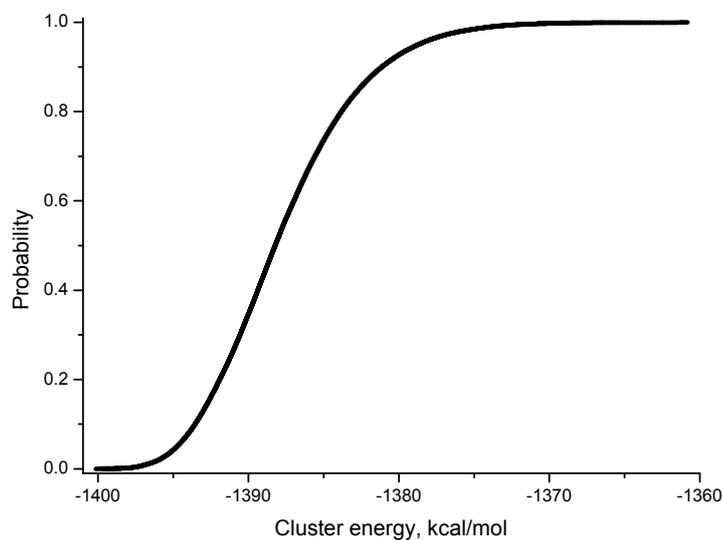
Figure S1. Cumulative distribution function for the energy of Hb29 structure.
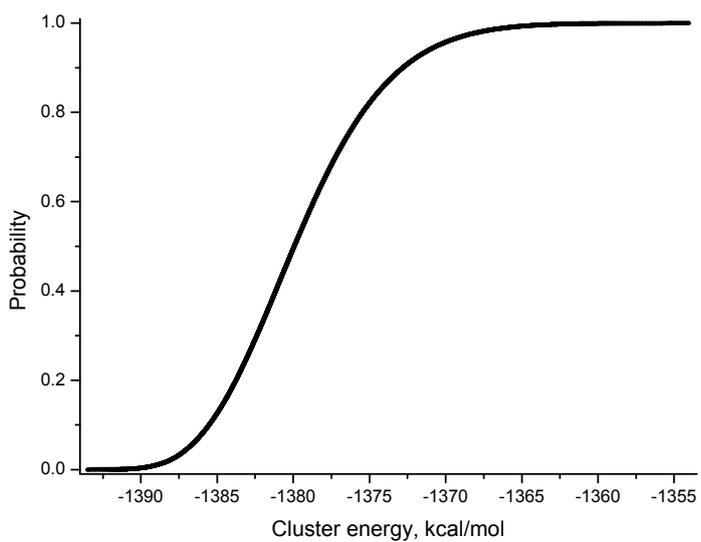
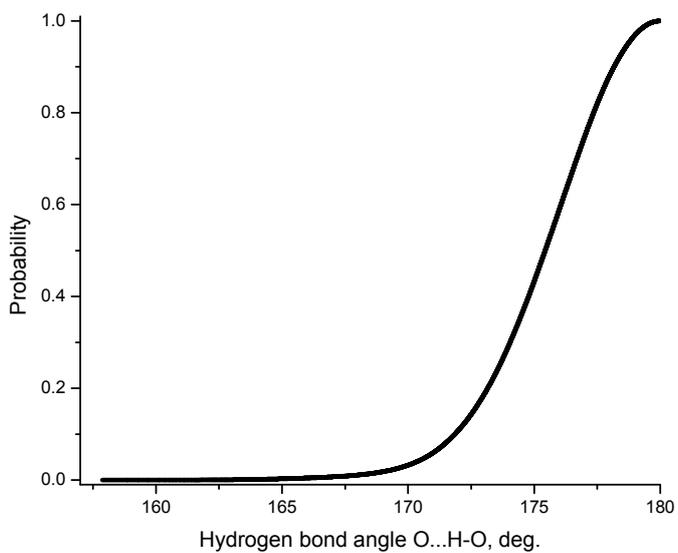Figure S2. Cumulative distribution function for the energy of Hb28 structure.

Figure S3. Cumulative distribution function for angles ∠O···H-O.
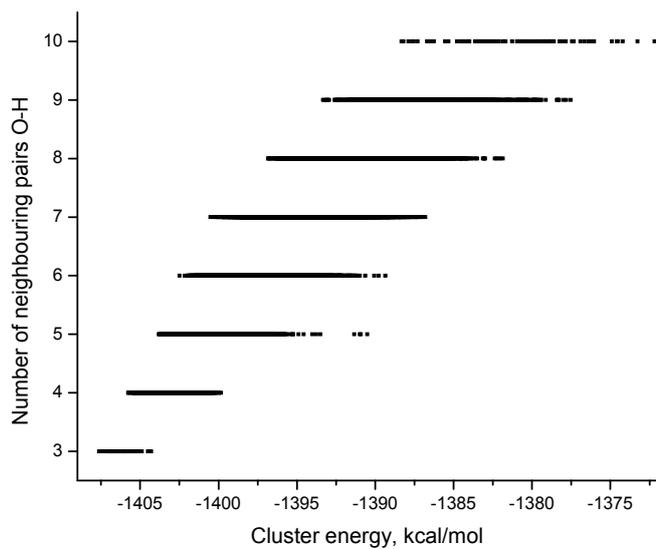
Figure S4. Correspondence between the cluster energy and the number of neighboring pairs O-H.
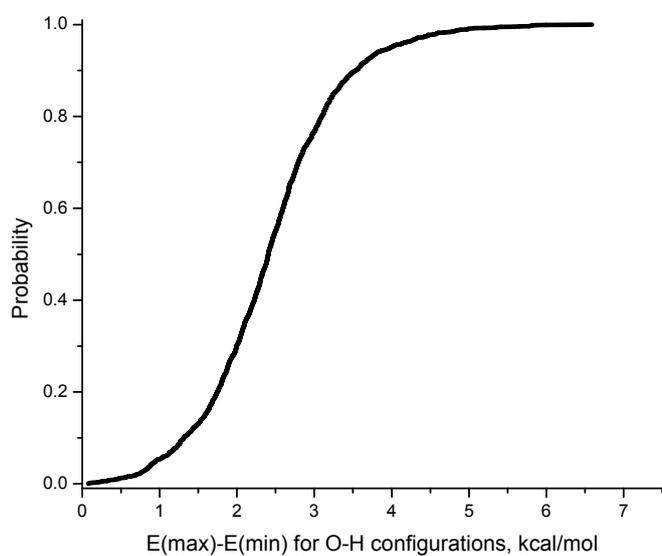

Figure S5. Distribution of maximal energy differences for clusters with the same set of dangling O-H bonds.
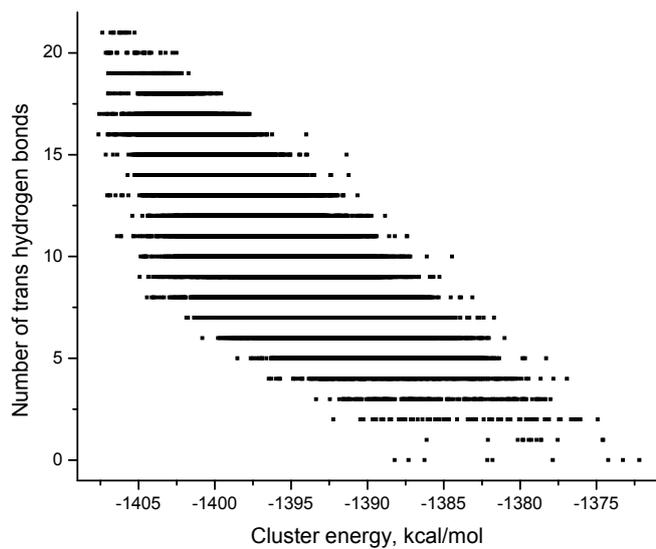
Figure S6. Correspondence between the cluster energy and the number of trans hydrogen bonds.