Cooperativity and hydrogen bonding network in water clusters

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Abstract

Clusters of water molecules are held together by hydrogen bonding networks. These networks are differentiated by the participation of the individual water molecules in the hydrogen bonds either as proton donors (d), proton acceptors (a) or their combinations. It has long been assumed that the stability of clusters is determined by the dominant two-body interactions between the water molecules. We have found that homodromic hydrogen bonding networks, i.e. those exhibiting donor–acceptor (da) arrangements between all water molecules, are associated with the largest non-additivities among other networks present in low lying minima of small water clusters. This finding offers a novel explanation for the stability of homodromic rings that are the global minima for the clusters trimer through pentamer. Among the non-additive terms, three-body terms are mainly responsible for determining the relative stabilities between the various trimer through pentamer isomers. This suggests that purely two-body pairwise additive potentials will result in errors exceeding 20% for clusters larger than the pentamer. Among all higher order components, the three-body term was found to be the most important. © 2000 Published by Elsevier Science B.V. All rights reserved.

Since Pindar, the Greek philosopher who used to refer to it as “Ἀρίστον μέν ύδωρ” (significant indeed water), water has received much attention because of its abundance in nature and its role in many biological and chemical processes [1,2]. A molecular level understanding of the structure of water has been sought for almost half a century, yet there exists no comprehensive model that can sufficiently describe a wide range of both its microscopic and macroscopic properties [3].

Small clusters of water molecules can be considered as prototypes for understanding the fundamental interactions that govern hydrogen bonding. A renewed interest in these systems and their relevance in probing the structure of liquid water has been recently fueled by the vibration–rotation–tunneling (VRT) microwave experiments of Saykally and co-workers [4–13]. These measurements have provided the first experimental data on the low frequency anharmonic tunneling motions. The VRT experiments have confirmed earlier first principles theoretical predictions [15–20] suggesting that the global minima of the trimer through pentamer clusters have “ring” structures consisting of homodromic configurations with one hydrogen bond per molecule in which all members act as both proton donors and acceptors (da) to
nearest neighbors. For the water hexamer, the experimentally obtained rotational constants for the global minimum were best fit by a cage rather than a ring structure [13,14].

An apparent manifestation of the cooperative effects in the first few water clusters has been associated with a systematic contraction of the nearest-neighbor O–O separation [20] and a red shift of the hydrogen-bonded OH stretch frequency with increasing cluster size [20,21]. For the ring water tetramer and pentamer the band positions for these frequencies are at 3416 and 3360 cm\(^{-1}\) respectively [21], compared to 3415 \(\pm\) 5 cm\(^{-1}\) for liquid water [22]. The corresponding (vibrationally averaged) O–O separations obtained from the experimentally fitted rotational constants are 2.78 [8–10] and 2.76 Å [11,12] as compared to 2.84 Å for liquid water at 4°C [23] and 2.74 Å for normal ice at 223 K [24]. These results are rather unexpected considering the different environments experienced by each water molecule in the cluster when compared to liquid water. Although the cyclic structure of the water trimer could be rationalized in terms of maximizing hydrogen bonding between three water molecules, there is no obvious “physically intuitive” argument justifying the energetically preferential ring arrangements of the water tetramer and pentamer with respect to other possible structures that have a larger number of hydrogen bonds. The fact that the ring minima up to the pentamer have only one hydrogen bond per water molecule suggests that they sample part of the configuration space not likely probed by configurations in bulk water in which every water molecule participates on the average in two hydrogen bonds. Two questions therefore arise: (i) what is the underlying physical effect resulting in the ring structures of the first few water clusters, if not the maximization of the number of hydrogen bonds and (ii) are the modeling requirements quantitatively different for these structures than for bulk water?

A quantitative account of the cooperative effects can be achieved by decomposing the interaction energy \(\Delta E_n\) of a system of \(n\)-bodies (water molecules) see, e.g. [25]

\[
\Delta E_n = E(1,2,3,4,\ldots,n) - nE_w
\]

\[
\equiv \sum_{i=1}^{n} E(i) - nE_w \quad \text{Relaxation}
\]

\[
+ \sum_{i=1}^{n-1} \sum_{j>i} \Delta^2 E(ij) \quad \text{two-body}
\]

\[
+ \sum_{i=1}^{n-2} \sum_{j>i} \sum_{k>j} \Delta^3 E(ijk) \quad \text{three-body}
\]

\[
+ \sum_{i=1}^{n-3} \sum_{j>i} \sum_{k>j} \sum_{l>k} \Delta^4 E(ijkl) \quad \text{four-body}
\]

\[+ \cdots + \Delta^m E(1,2,3,4,\ldots,n) \quad \text{n-body}, \quad (1)
\]

where \(E(i), E(ij), E(ijk), \ldots\) are the energies of the various monomers, dimers, trimers, etc. in the cluster and \(E_w\) is the energy of the isolated water molecule. The relaxation or deformation component represents the energy penalty for distorting the individual fragments in the equilibrium cluster geometries with respect to those in isolation. The pairwise-additive two-body interactions and the higher three- through \(n\)-body non-additive components are defined as

\[
\Delta^2 E(ij) = E(ij) - \{E(i) + E(j)\}, \quad (2)
\]

\[
\Delta^3 E(ijk) = E(ijk) - \{E(i) + E(j) + E(k)\} - \{\Delta^2 E(ij) + \Delta^2 E(ik) + \Delta^2 E(jk)\}, \quad (3)
\]

\[
\Delta^4 E(ijkl) = E(ijkl) - \{E(i) + E(j) + E(k) + E(l)\} - \{\Delta^2 E(ij) + \Delta^2 E(ik) + \Delta^2 E( jl) + \Delta^2 E(kl)\} - \{\Delta^3 E(ijk) + \Delta^3 E(il) + \Delta^3 E(ikl) + \Delta^3 E( jkl)\}. \quad (4)
\]

Since it is of interest to investigate the effect of the local hydrogen bonding network on the cooperativity, we performed this analysis for the global and various low-lying networks of the \((H_2O)_n\) clusters \((n = 3–6)\) that exhibit different hydrogen bonding environments. The latter are differentiated by the bonding arrangement of the individual
water molecules participating in neighboring hydrogen bonds either as proton donors (d), proton acceptors (a) and their combinations (dd,da,aa), as defined in Fig. 1. The energy decomposition is performed at the minimum energy geometries optimized at the second order perturbation (MP2) level of theory [26] using Dunning’s aug-cc-pVDZ basis set [27,28]. During the MP2 calculations all electrons were correlated for consistency with our earlier calculations for the minima [20]; this as opposed of “freezing” the O(1s) electrons has practically no effect in the computed structures and relative energy terms. The individual energy terms include corrections for basis set superposition error (BSSE) estimated by the function counterpoise method [29] as outlined elsewhere [30]. The calculations are performed with the GAUSSIAN-94 [31] and MOLPRO-94 [32] suites of programs. It should be noted that the basis set used here is far from being able to yield converged absolute binding energies for the clusters. However it reproduces both the order and relative energies of, for instance, the closely spaced various hexamer isomers to within 0.1 kcal mol$^{-1}$ or better when compared to results with the aug-cc-pV5Z set and/or the estimates of the MP2 complete basis set limit [33]. The energy separation for the trimer through pentamer networks considered here is much larger than the corresponding one for the hexamers, a fact that clearly justifies the use of the aug-cc-pVDZ set for the purpose of the present study.

The various water trimer, tetramer, pentamer and hexamer networks considered in this study are shown in Fig. 2. Their binding energies relative to the isolated fragments and the magnitude of the three-body term (in parentheses) are also indicated in kcal mol$^{-1}$. A breakdown of the total energy difference of the various networks from the most stable isomer for each cluster in terms of differences in the relaxation, two-, three- and higher order contributions is listed in Table 1.

The global minimum of the water trimer is a cyclic structure in which all water molecules act as both proton donors and acceptors (da) to neighbors [4–7,17,19]. The two “open” local minima exhibiting (a,dd,a) and (d,aa,d) arrangements are almost isoenergetic with each other, lying 6.1 kcal mol$^{-1}$ higher in energy [34]. Besides small differences in the relaxation energies of the fragments due to the strain associated with the formation of the ring (0.3 kcal mol$^{-1}$ in favor of the “open” isomers), the energy separation between them and the cyclic minimum can be almost equally attributed to differences in the two- and three-body terms (cf. Table 1). The differences in the two-body terms (3.4 and 3.6 kcal mol$^{-1}$, respectively) are due to the fact that the “open” structures have slightly repulsive two-body components (0.5 and 0.7 kcal mol$^{-1}$) between the end fragments. Of comparable significance are the differences of the three-body term (3.0 and 2.8 kcal mol$^{-1}$) between the cyclic and the open minima. The latter arise from the fact that the three-body term is large and attractive ($-2.5$ kcal mol$^{-1}$) for the cyclic but smaller and repulsive (0.3 and 0.5 kcal mol$^{-1}$) for the “open” minima, as shown in Fig. 2.

The water tetramer global minimum is also a cyclic structure of $S_4$ symmetry having a (da,da,da,da) arrangement [8–10,20]. A cage structure in which three water molecules act as (da) and the
fourth as a double donor and a single acceptor (dda) lies 4.8 kcal mol\(^{-1}\) higher. Even higher in energy (10.5 kcal mol\(^{-1}\)) lies a (dd,aa,dd,aa) ring minimum of D\(_{2h}\) symmetry. The energy separation between these structures can be mainly attributed to the differences in the three-body terms which contribute twice as much as the differences in the corresponding two-body terms. For example, the contribution in the energy separation between the global and cage minima is 3.0 kcal mol\(^{-1}\) for the three-body terms and 1.6 kcal mol\(^{-1}\) for the two-body terms as can be seen from Table 1. The same is true for the energy difference between the global and the D\(_{2h}\) minima: almost 2/3 comes from differences in the three-body terms with the remaining 1/3 due to differences in the corresponding two-body terms. The four-body term is negligible (−0.5, +0.1 and −0.1 kcal mol\(^{-1}\)) for all three networks found in the tetramer minima considered here.
The cyclic (da,da,da,da,da) arrangement is also the global minimum for the water pentamer \[11,12\]. A cage structure having six hydrogen bonds and a (da,daa,da,aad,da) network lies 1.7 kcal mol\(^{-1}\) higher in energy. The sum of two-body interactions for the cage structure is 1.3 kcal mol\(^{-1}\) more attractive than for the global minimum. Here the relative energies are determined solely by the three-body term, which is 2.1 kcal mol\(^{-1}\) more attractive for the ring than the cage structure, therefore compensating for the less attractive two-body term. The four-body term also contributes 0.8 kcal mol\(^{-1}\) in favor of the ring structure whereas the five-body term is negligible (<0.03 kcal mol\(^{-1}\) for both arrangements).

For the water hexamer the number of isomers that are close (within 1 kcal mol\(^{-1}\)) in energy is larger [35–37] as previously reported by Jordan and co-workers and recently by others [38–40]. These previous studies were mainly concerned with the relative stability of the various isomers while the many-body energy decomposition was performed for the ring \(S_6\) structure [37]. Interest in this cluster stems from the observation that it represents the “transition” from ring to a more compact, cage-like structures as regards the global minimum. When considering minimum energy differences alone the minimum energy configuration is that of the “prism” isomer (cf. Fig. 2) with at least three other isomers within 1 kcal mol\(^{-1}\) higher in energy. However, in agreement with previous results [13,14,35–40], inclusion of zero-point energy corrections results in the configuration with the two capping water molecules (“cage” isomer) being the global minimum. The ring (da) homodromic network of \(S_6\) symmetry lies 0.9 kcal mol\(^{-1}\) above the “prism” minimum (cf. Table 1), a separation mainly arising from the difference in the two-body term (5.0 kcal mol\(^{-1}\)) in favor of the “prism” besides a significant contribution of the higher order (three- through five-body) terms in favor of the ring network. This is due to the fact that, in accordance with the observation for the smaller clusters, the ring \(S_6\) minimum exhibits the largest non-additive (three- through five-body) components of the binding energy among all other hexamer minima.

We, therefore, propose that the underlying physical effect behind the formation of small rings of the trimer through pentamer clusters exhibiting homodromic hydrogen bonding networks is the result of the maximization of the non-additive components of their binding energies. Homodromic networks were found to be associated with the largest non-additive components among other networks that are present in low-lying minima of the clusters examined. These non-additive components and, in particular, the three-body term

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Network</th>
<th>(\Delta(\Delta E)_{\text{Total}}) (kcal mol(^{-1}))</th>
<th>(\Delta(\Delta E)_{\text{Relax}}) (kcal mol(^{-1}))</th>
<th>(\Delta(\Delta E)_{2-B}) (kcal mol(^{-1}))</th>
<th>(\Delta(\Delta E)_{3-B}) (kcal mol(^{-1}))</th>
<th>(\Delta(\Delta E)_{4-B}) (kcal mol(^{-1}))</th>
<th>(\Delta(\Delta E)_{5-B}) (kcal mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimer</td>
<td>(a,dd,a)</td>
<td>6.1</td>
<td>-0.3</td>
<td>3.4</td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(d,aa,d)</td>
<td>6.1</td>
<td>-0.3</td>
<td>3.6</td>
<td>2.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetramer</td>
<td>(da,da,da,dda)</td>
<td>4.8</td>
<td>-0.4</td>
<td>1.6</td>
<td>3.0</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(dd,aa,dd,aa)</td>
<td>10.5</td>
<td>-0.9</td>
<td>3.5</td>
<td>7.5</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Pentamer</td>
<td>(da,daa,-da,aad,da)</td>
<td>1.7</td>
<td>-0.0</td>
<td>-1.3</td>
<td>2.1</td>
<td>0.8</td>
<td>0.1</td>
</tr>
<tr>
<td>Hexamer</td>
<td>Cage</td>
<td>0.1</td>
<td>-0.1</td>
<td>0.3</td>
<td>0.1</td>
<td>-0.1</td>
<td>-0.1</td>
</tr>
<tr>
<td></td>
<td>Book</td>
<td>0.2</td>
<td>-0.1</td>
<td>2.1</td>
<td>-1.3</td>
<td>-0.4</td>
<td>-0.1</td>
</tr>
<tr>
<td></td>
<td>(S_6)</td>
<td>0.9</td>
<td>-0.2</td>
<td>5.0</td>
<td>-2.5</td>
<td>-1.1</td>
<td>-0.3</td>
</tr>
</tbody>
</table>

The water hexamer energy differences are computed with respect to the more stable “prism” isomer (note that the “cage” minimum becomes more stable among all hexamer isomers upon inclusion of zero-point energy corrections). Positive/negative numbers indicate contributions against/in favor of the network with respect to the global minimum.
determine the stability of the ring structures relative to other isomers for the water tetramer and pentamer. The water hexamer is the “turning point” where the magnitude of the total two-body additive component “takes over” in determining the most stable structure. Even for this cluster, however, the homodromic network in the ring S6 minimum has the largest three- and four-body components among all networks in the other local minima. This finding suggests that asymmetric and locally inhomogeneous cluster environments may require more burdensome theoretical treatment than the on-the-average homogeneous environment found in liquid water. Purely two-body pairwise-additive interaction potentials, such as the ones derived from the water dimer potential energy surface, will result in errors exceeding 20% for clusters larger than the pentamer (cf. Table 2). Although effective two-body pairwise-additive potentials like TIP4P which can be considered as incorporating non-additive effects implicitly can be quite successful in reproducing the binding energies in a limited range of cluster sizes [41] when compared to more accurate many-body potentials [41–43], these models are not transferable across different environments (clusters, liquid water, ice phases) that exhibit different relative magnitudes of non-additivities [44,45]. Transferable models should include accurate estimates of many-body components and especially the three-body term and its dependence upon the local hydrogen bonding network environment. Interaction potentials with explicit consideration of the three-body interaction terms have been, for instance, previously used to model the structure and properties of various ice phases [46–48]. An alternative way of incorporating parts of higher-order many-body interactions is via the induction scheme (see Refs. [44,45,49]) whereas every water molecule is represented by a dipole and/or higher [50] moments that are determined iteratively. A recent study [51] has suggested that the three-body potential in the water trimer is dominated by mainly the second-order and induction non-additivity. Furthermore, it suggested that if induction effects are to be included by iteration of the induced dipole moments and the corresponding electric fields, then one should proceed with this iteration beyond the first step.

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