Modeling of Magic Water Clusters $(\text{H}_2\text{O})_{20}$ and $(\text{H}_2\text{O})_{21}\text{H}^+$ with the PM3 Quantum-Mechanical Method

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The PM3 quantum-mechanical method is able to model the magic water clusters $(\text{H}_2\text{O})_{20}$ and $(\text{H}_2\text{O})_{21}\text{H}^+$. Results indicate that the H_3O^+ ion is tightly bound within the $(\text{H}_2\text{O})_{20}$ cluster by multiple hydrogen bonds, causing deformation to the symmetric $(\text{H}_2\text{O})_{20}$ pentagonal dodecahedron structure. The structures, energetics, and hydrogen bond patterns of six local minima $(\text{H}_2\text{O})_{21}\text{H}^+$ clusters are presented. © 1993 by John Wiley & Sons, Inc.

INTRODUCTION

The $(\text{H}_2\text{O})_{21}\text{H}^+$ cluster ion is a prominent "magic number entity" as detected with numerous experimental conditions.¹⁻³ Kassner and Hagen used molecular cluster theory to predict the enhanced stability of the 21 water cluster (21 mer) based on a clathrate structure.⁴ The proposed clathrate structure is a pentagonal dodecahedron with a single water molecule or hydronium ion in the center. A computer simulation by Holland and Castleman supported their suggestion that $(\text{H}_2\text{O})_{21}\text{H}^+$ has a neutral water molecule trapped in the center of the cage-like structure, with a mobile proton on the surface of the pentagonal dodecahedron.⁵ Monte Carlo simulations by Nagashima et al. suggested that the stable structure for $(\text{H}_2\text{O})_{21}\text{H}^+$ has an H_3O^+ ion trapped inside a deformed pentagonal dodecahedral cage.² This cluster is expected to be especially stable as a consequence of the strong Coulombic interaction between the encaged H_3O^+ ion and the surrounding 20 water molecules. These scientists also observed from the mass spectral peak for $\text{NH}_3(\text{H}_2\text{O})_{20}\text{H}^+$ that the NH_4^+ ion can replace the H_3O^+ ion in the center of 20 waters.²

Yang and Castleman have shown that the 21 mer is thermodynamically stable because the ion survived more than 10^5 collisions with He during a 20-ms trip through their reactor.³ Definitive experimental evidence of the pentagonal dodecahedron structure was provided by Wei et al., who used trimethylamine (TMA) molecules as tags to identify dangling hydrogens on water clusters.⁶ They made mixed neutral clusters by expanding vapor containing water and TMA through a pulsed nozzle, ionizing the clusters by multiphoton ionization, and separating the

product ions by time-of-flight mass spectrometry. The results of this experiment revealed that the $(\text{H}_2\text{O})_{21}(\text{TMA})_m\text{H}^+$ ion distribution was a maximum when $m = 10$ with an abrupt drop in intensity when $m = 11$. This experiment proved that the $(\text{H}_2\text{O})_{21}\text{H}^+$ ion has a total number of 10 hydrogen bonding sites available for TMA to bind. The deformed pentagonal dodecahedron is the only possible structure for the $(\text{H}_2\text{O})_{21}\text{H}^+$ ion that provides a total of 10 dangling hydrogen atoms.² Thus, it is experimentally known that the $(\text{H}_2\text{O})_{21}\text{H}^+$ structure must be a deformed pentagonal dodecahedron, although the exact geometry is not known.

The semiempirical quantum-mechanical methods developed by Dewar and coworkers⁷⁻¹⁰ have been successful at reproducing molecular energies, replicating molecular structures, and interpreting chemical reactions. However, only the most recent of these methods, the PM3 method,¹⁰ has successfully described intermolecular hydrogen bonding of neutral molecules.¹⁰⁻¹⁴ PM3 correctly models the hydrogen bonding of small water clusters ($n = 2-5$),¹⁰⁻¹² whereas the AM1 method is not able to correctly model the geometries of either the water dimer or small water clusters.¹¹⁻²⁰

The ability of the PM3 Hamiltonian to model intermolecular hydrogen bonding between neutral molecules has been attributed to the reduction of two-center repulsive forces brought about by the parameterization of the Gaussian core-core interactions.¹² We have undertaken a PM3 study of the $(\text{H}_2\text{O})_{21}\text{H}^+$ system to provide structural and thermodynamic information about this magic water cluster.

METHOD

The $(\text{H}_2\text{O})_{20}$ pentagonal dodecahedron was built using Chem 3D Plus software (Cambridge Scientific

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Computing, Inc., Cambridge, MA) on a Macintosh II computer (Apple Computer, Inc., Cupertino, CA). The 20 mer was designed with hydrogen bond lengths of 1.7 Å and with the lone pairs of each oxygen oriented toward the hydrogens of the neighboring donor molecules. The 20 mer was fully geometry optimized with the PM3 method¹⁰ using MOPAC 5.0 software.²¹ The keyword PRECISE was used to increase the criterion for terminating all optimizations 100-fold over normal MOPAC limits and the keyword XYZ was used to run these calculations in Cartesian coordinates. The output 20 mer structure was then used as input for six 21 mer calculations, with an H_3O^+ ion placed in different regions inside the 20 mer clathrate shell. All PM3-calculated structures were characterized as stationary points and true minima using the keyword FORCE.

In addition to the optimization calculations, single self-consistent field (ISCF) calculations were performed to determine the contribution of hydrogen bond energy for the H_3O^+ ion. In the ISCF calculations, the H_3O^+ and $(\text{H}_2\text{O})_{20}$ subunits of the $(\text{H}_2\text{O})_{21}\text{H}^+$ ion are "frozen" to determine the heats of formation for these species in the deformed pentagonal dodecahedron 21 mer. This is done by isolating the H_3O^+ and $(\text{H}_2\text{O})_{20}$ subunits in the exact conformation of the $(\text{H}_2\text{O})_{21}\text{H}^+$ ion, followed by a single self-consistent-field (ISCF) calculation to determine the heats of formation of each subunit. In this way, the heats of formation of each subunit are determined when "frozen" in the conformation of the $(\text{H}_2\text{O})_{21}\text{H}^+$ ion. A thermodynamic cycle was used to determine the contribution to hydrogen bonding in the various structures as calculated by the PM3 method.

RESULTS AND DISCUSSION

The PM3 geometric results are displayed in Figures 1–3 for the global minima of $(\text{H}_2\text{O})_{20}$ and six local minima $(\text{H}_2\text{O})_{21}\text{H}^+$ -calculated structures. Figure 1a displays the oxygen atoms of the $(\text{H}_2\text{O})_{20}$ cluster arranged in the predicted pentagonal dodecahedron along with the hydrogen bond distances and oxygen–oxygen separation distances for every hydrogen-bonded water molecule. Figure 1b presents another view of Figure 1a with all atoms displayed. Hydrogen bond distances range from 1.753 to 1.847 Å and hydrogen bond angles range from 155 to 179° for the $(\text{H}_2\text{O})_{20}$ magic water cluster. Oxygen–oxygen separation distances range from 2.705 to 2.769 Å. An AM1 calculation of the pentagonal dodecahedron completely disrupts this symmetric structure, forming small groups of bifurcated clusters. This AM1 calculation agrees with previous AM1 results on water clusters^{11–20} where bifurcation of water molecules occurs.

The PM3 heat of formation for one optimized water molecule is $-53.43 \text{ kcal mol}^{-1}$ and the heat

Figure 1. (a). PM3-optimized structure for $(\text{H}_2\text{O})_{20}$ illustrating the oxygen atoms and the pentagonal dodecahedron symmetry. Oxygen–oxygen separation distances and hydrogen bond lengths are listed for all nearest neighbor oxygens. (b). $(\text{H}_2\text{O})_{20}$ structure showing every atom. Broken lines illustrate the hydrogen bonds. In this view, the foremost pentagonal ring in (a) has been rotated down and to the right. The hydrogen bond lengths for the foremost pentagonal ring in (a) are listed.

of formation of the 20 mer is $-1185.41 \text{ kcal mol}^{-1}$, hence yielding an association energy of $-116.88 \text{ kcal mol}^{-1}$ when 20 water molecules, separated by infinite distances, form the $(\text{H}_2\text{O})_{20}$ cluster. The 20 mer has 30 hydrogen bonds, yielding an average hydrogen bond energy of $-3.90 \text{ kcal mol}^{-1}$, in good agreement with the experimental value of $-3.59 \text{ kcal mol}^{-1}$ for water hydrogen bonds obtained by thermal conductivity measurements.²²

Figure 2 displays the oxygen atoms for the six lowest-energy $(\text{H}_2\text{O})_{21}\text{H}^+$ ion structures, with hydrogen bond distances and oxygen–oxygen separation

Figure 2. PM3-optimized $(\text{H}_2\text{O})_{21}\text{H}^+$ ion structures for six local minima (I-VI) illustrating the oxygen atoms and the deformation of pentagonal dodecahedron symmetry. Oxygen-oxygen separation distances and hydrogen bond lengths are listed for all nearest neighbor oxygens. The H_3O^+ ion in the middle of the 20 water shell deforms the pentagonal dodecahedron by virtue of multiple hydrogen bonds. The oxygens that are hydrogen bond acceptors for H_3O^+ are solid.

Figure 3. Detailed hydrogen bonding patterns that the H_3O^+ ion makes that deform the pentagonal dodecahedron $(\text{H}_2\text{O})_{20}$ structure in clusters I-VI. The solid oxygen hydrogen bond acceptors can be compared with Figure 2, showing the overall orientation of the water acceptors within the $(\text{H}_2\text{O})_{20}$ structure.

distances labeled. In the figure, the atoms that are hydrogen bond acceptors for the H_3O^+ ion are solid. Figure 3 shows the hydrogen bonding patterns that the H_3O^+ ion makes with the 20 mer cluster for structures I–VI.

The lowest-energy $(\text{H}_2\text{O})_{21}\text{H}^+$ cluster, **I**, has hydrogen bond distances varying from 1.748 to 1.838 Å and hydrogen bond angles varying from 140 to 178° for the clathrate shell. The oxygen–oxygen separation distances range from 2.487 to 2.763 Å. The H_3O^+ ion makes five hydrogen bonds to the clathrate shell, with bond angles between the hydronium ion and the shell ranging from 96.7 to 163.8°. The *solid* oxygen atoms in Figure 2 are the hydrogen bond acceptors for the three hydrogen atoms of the hydronium ion. The two oxygen atoms separated by 2.487 Å are adjacent atoms in the same pentagonal face. Figure 3, **I**, displays the details of the hydrogen bonding interactions. Using the nomenclature of Jeffrey and Saenger,²³ there are three three-center and one two-center hydrogen bonds. The first three-center hydrogen bond, with hydrogen bond lengths of 1.697 and 1.812 Å, is known as a bifurcated donor because one hydrogen donates to two acceptors. The two water molecules involved as acceptors in the bifurcated-donor hydrogen bond also form a two-center hydrogen bond between each other. Because these two waters are hydrogen bonded to each other and to the same hydrogen on the hydronium ion, their geometry is most distorted from the normal pentagonal face. For instance, the hydrogen bond length of 1.838 Å and oxygen–oxygen separation distance of 2.487 Å are the maximum and minimum for structure **I**. The hydrogen bond angle for these two waters is 122.2°. The second three-center hydrogen bond has hydrogen bond lengths of 1.788 and 1.751 Å, and is also a bifurcated-donor hydrogen bond. The water that is common to the two three-center bifurcated-donor hydrogen bonds forms a three-center bifurcated-acceptor hydrogen bond, serving as the acceptor to two hydrogens of the hydronium ion (1.812, 1.788 Å). This bifurcated-acceptor hydrogen bond system does not appear to be a strong interaction. The two hydrogen bond angles are sharply bent, forming O—H—O angles of 96.7° (1.812 Å) and 98.5° (1.788 Å) for the bifurcated-acceptor system. Thus, it appears that the bifurcated acceptor is an accident of this particular geometric arrangement, forced by the two three-center bifurcated-donor hydrogen bonds and the two-center hydrogen bond formed between the two waters in the same pentagon of the clathrate structure. The three-center bifurcated-acceptor hydrogen bond is rarely observed in the crystalline state and is not found in any of the ice structures.²³ When the bifurcated-acceptor hydrogen bond is found, as in some nucleoside crystal structures, it is always in conjunction with three-center bonds.²³

The second lowest-energy $(\text{H}_2\text{O})_{21}\text{H}^+$ cluster, **II**,

has hydrogen bond distances varying from 1.751 to 1.822 Å and hydrogen bond angles ranging from 141 to 179°. The oxygen–oxygen separation distances span 2.591–2.766 Å. The H_3O^+ ion makes four hydrogen bonds to the $(\text{H}_2\text{O})_{20}$ cluster with less distortion of the pentagonal dodecahedron framework than for **I**. The hydrogen bond angles formed by the interactions of the hydronium ion with the clathrate shell range from 125 to 177°. As shown in Figure 2, the hydronium ion in structure **II** does not interact with two waters that are adjacent on one pentagonal face as it does in structure **I**. Figure 3 reveals that in **II** the H_3O^+ ion forms one three-center bifurcated-donor and two two-center hydrogen bonds.

The deformed pentagonal dodecahedron **III** has hydrogen bond distances and angles ranging from 1.713 to 1.821 Å and 136 to 180°. Oxygen–oxygen separation distances range from 2.592 to 2.767 Å, with the exception of one 2.175-Å separation distance. The H_3O^+ ion makes four hydrogen bonds to the clathrate shell, deforming the pentagonal dodecahedron, as can be seen by comparing Figures 1a and 2(**III**). The short O—O separation distance of 2.175 Å results from one hydrogen atom on H_3O^+ , which forms hydrogen bonds with both oxygens. These two oxygens now have an O—H—O bond angle of 99.8°, as the hydrogen is displaced as the two oxygens are pulled together by the H_3O^+ ion. Thus, this $(\text{H}_2\text{O})_{21}\text{H}^+$ ion is assembled with a total of 33 hydrogen bonds.

Structure **IV** (Fig. 2) is the most deformed pentagonal dodecahedron, with significant out-of-plane bending as the hydronium ion interacts with five different water molecules. The hydrogen bond pattern of the H_3O^+ ion shown in Figure 3 reveals that there are two three-center bifurcated-donor hydrogen bonds and one two-center hydrogen bond.

Structure **V** has a unique hydrogen bond pattern, with one two-center hydrogen bond, two three-center bifurcated-donor hydrogen bonds, and one three-center bifurcated-acceptor hydrogen bond. As seen in Figure 3, the bifurcated-acceptor hydrogen bonds of 1.784 and 1.852 Å are also part of the two bifurcated-donor hydrogen bond systems.

Figure 2 reveals that the H_3O^+ ion in structure **VI** interacts with four water molecules on the same pentagonal face and one water below that plane. Figure 3 shows the hydrogen bond framework of the pentagonal face (1.780, 1.812, and 1.796 Å) and reveals that there is one two-center and two three-center bifurcated-donor hydrogen bonds.

A thermodynamic cycle has been used to examine the hydrogen-bonded energetics of the 21 mers. Scheme 1 illustrates the cycle where the overall reaction of 20 waters and a hydronium ion reacting to make the 21 mer can be calculated in two steps. Step 1 is the conversion of the 20 water molecules and the hydronium ion into the $(\text{H}_2\text{O})_{20}$ cluster and the H_3O^+ ion “frozen” in the conformation of the final

Scheme 1.

21 mer structure. Step 2 is the formation of the 21 mer from these two frozen structures. The heats of formation of the frozen structures were calculated by ISCF calculations on the geometries of the separated species from the optimized 21 mer. In this procedure, a single SCF calculation is done on the H_3O^+ ion in the conformation of the $(\text{H}_2\text{O})_{21}\text{H}^+$ cluster of interest to determine the heat of formation for the H_3O^+ ion frozen in the conformation of the $(\text{H}_2\text{O})_{21}\text{H}^+$ cluster. A similar calculation is done for the $(\text{H}_2\text{O})_{20}$ cluster. The sum of these two heats of formation yields the ISCF frozen energies in Scheme 1. Table I contains the energetic information for structures I–VI. In the table, the calculated heats of formation for the six deformed pentagonal dodecahedron $(\text{H}_2\text{O})_{21}\text{H}^+$ clusters are given, along with the heats of formation for the ISCF calculations. Also shown are the ΔH s for each step in Scheme 1 and the hydrogen bond types of the H_3O^+ ion.

For I, Table I reveals that the heat of formation for this cluster is $-1117.29 \text{ kcal mol}^{-1}$. The heat of formation for the $(\text{H}_2\text{O})_{20}$ cluster frozen in the conformation of I is $-1157.70 \text{ kcal mol}^{-1}$ and for H_3O^+ $160.045 \text{ kcal mol}^{-1}$. The enthalpy of formation of 20 waters and the hydronium ion, all separated by infinite distance, is $-909.44 \text{ kcal mol}^{-1}$, as each fully optimized water has a heat of formation of -53.426

kcal mol^{-1} and the fully optimized hydronium ion is $159.077 \text{ kcal mol}^{-1}$. The enthalpy of reaction for step 1 (ΔH_1) is the sum of the ISCF frozen heats (-997.66) minus the sum of the 20 waters and hydronium ion heats (-909.45), or $\Delta H_1 = -88.21 \text{ kcal mol}^{-1}$. The enthalpy of reaction for step 2 (ΔH_2) is found from the ISCF heats and the $(\text{H}_2\text{O})_{21}\text{H}^+$ heat of formation. This allows the assignment of $2.94 \text{ kcal mol}^{-1}$ per hydrogen bond of the 20 mer within the 21 mer ($\Delta H_1/30$) and a hydrogen bond energy of $23.9 \text{ kcal mol}^{-1}$ per hydrogen bond for the hydronium ion ($\Delta H_2/5$). These numbers are averages as the strength of each of these slightly different hydrogen bonds cannot be individually determined. It could be argued based on the hydrogen bond angles described previously for I that the hydronium ion forms three strong hydrogen bonds with three of the waters and two weak hydrogen bonds with the fourth water. In this case, the estimate for the hydrogen bond energy for the hydronium ion would be closer to $39.9 \text{ kcal mol}^{-1}$ ($\Delta H_2/3$). The least complicated systems to assess are structures II and III, where only four hydrogen bonds form between the hydronium ion and the clathrate shell. For II, the average hydrogen bond energy attributed to the hydronium ion is $28.5 \text{ kcal mol}^{-1}$ ($\Delta H_2/4$). For III, the average hydrogen bond energy is $29.2 \text{ kcal mol}^{-1}$ for the H_3O^+ ion.

Formation of the $(\text{H}_2\text{O})_{20}$ cluster from 20 separated waters releases $116.88 \text{ kcal mol}^{-1}$. Thus, in the 21 mer I the deformed pentagonal dodecahedron gains $27.71 \text{ kcal mol}^{-1}$ upon deformation of the 20 mer shell, and $0.96 \text{ kcal mol}^{-1}$ by straining the hydronium ion, but releases $119.63 \text{ kcal mol}^{-1}$ from the interactions of the H_3O^+ ion with the water cage. The overall ΔH for the formation of the 21 mer I from 20 waters and the H_3O^+ ion is $-207.84 \text{ kcal mol}^{-1}$.

Comparison of the energetics of structures I–VI outlined in Table I with the geometries displayed in

Table I. Energetics for six $(\text{H}_2\text{O})_{21}\text{H}^+$ structures calculated with the PM3 method.

Structure	ΔH_f ($\text{H}_2\text{O})_{21}\text{H}^+$	ΔH_f ISCF Frozen ($\text{H}_2\text{O})_{20}$	ΔH_f ISCF Frozen H_3O^+	ΔH_1	ΔH_2	ΔH	Types of H Bonds
I	-1117.29	-1157.70	160.04	-88.21	-119.63	-207.84	2 three-center bifurcated donor 1 three-center bifurcated acceptor 1 two-center
II	-1117.03	-1163.09	160.04	-93.60	-113.99	-207.58	1 three-center bifurcated donor 2 two-center
III	-1116.31	-1159.55	160.22	-89.87	-116.99	-206.86	1 three-center bifurcated donor 2 two-center
IV	-1115.76	-1159.64	160.39	-89.80	-116.52	-206.31	2 three-center bifurcated donor 1 two-center
V	-1113.89	-1159.73	159.86	-90.41	-114.02	-204.43	2 three-center bifurcated donor 1 three-center bifurcated acceptor 1 two-center
VI	-1112.84	-1151.16	160.58	-81.13	-122.26	-203.39	2 three-center bifurcated donor 1 two-center

Enthalpies of formation for the six $(\text{H}_2\text{O})_{21}\text{H}^+$ clusters, ISCF enthalpies of formation for the $(\text{H}_2\text{O})_{20}$ and H_3O^+ subunits, enthalpies of reaction for the steps depicted in Scheme 1, and the types of hydrogen bonds formed by the interaction of the hydronium ion with the clathrate shell.

Figures 2 and 3 reveals that while the H_3O^+ ion is tightly bound within the $(\text{H}_2\text{O})_{20}$ cluster many conformations are possible. The six clusters have heats of formation within 5 kcal mol^{-1} of each other. The contrast between these six minima is the interplay between the strain energy required to deform the $(\text{H}_2\text{O})_{20}$ pentagonal dodecahedron and the energy returned by tight binding of the H_3O^+ ion within the deformed pentagonal dodecahedron. The ΔH_1 for structure II has the greatest magnitude, implying that the structure of the $(\text{H}_2\text{O})_{20}$ subunit within the 21 mer is the most energetically favorable of all six minima. In contrast, VI has the lowest energy for the $(\text{H}_2\text{O})_{20}$ subunit. The magnitude of ΔH_2 shows how much energy is released when the H_3O^+ ion bonds to the already-deformed 20 mer. The most energy is released when forming VI, the structure with the least stable $(\text{H}_2\text{O})_{20}$ cage. Based on these thermodynamic arguments, structure I is the lowest-energy minima because of the optimum balance between strain energy of the $(\text{H}_2\text{O})_{20}$ cage and energy returned by optimal formation of hydrogen bonds between the hydronium ion and the $(\text{H}_2\text{O})_{20}$ cage.

CONCLUSIONS

The PM3 quantum-mechanical method is able to model the geometry of the magic water cluster $(\text{H}_2\text{O})_{20}$, and predict hydrogen bond energies within $0.5 \text{ kcal mol}^{-1}$ of experimental values for water hydrogen bonds.²² PM3 results on the magic water ion cluster $(\text{H}_2\text{O})_{21}\text{H}^+$ indicate that the H_3O^+ ion is tightly bound within the $(\text{H}_2\text{O})_{20}$ cluster, with multiple strong hydrogen bonds formed by the three hydrogen atoms of the hydronium ion. The six reported minima indicate that many conformations are energetically possible within the deformed pentagonal dodecahedron framework. The strong hydrogen bonding interactions between H_3O^+ and $(\text{H}_2\text{O})_{20}$ are responsible for the deformation of the pentagonal dodecahedron. Six unique hydrogen bond patterns have been calculated for the interaction of the H_3O^+ ion with the $(\text{H}_2\text{O})_{20}$ cluster. The lowest-energy structure has the optimum balance between strain energy required to deform the $(\text{H}_2\text{O})_{20}$ cage and energy returned by the formation of a strong hydrogen bond pattern between the hydronium ion and the $(\text{H}_2\text{O})_{20}$ cage.

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