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Global Search for Minimum Energy $(H_2O)_n$ Clusters, $n = 3-5$

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The Gaussian-3 (G3) model chemistry method has been used to calculate the relative $\Delta G°$ values for all possible conformers of neutral clusters of water, $(H_2O)_n$, where $n = 3-5$. A complete 12-fold conformational search around each hydrogen bond produced 144, 1728, and 20 736 initial starting structures of the water trimer, tetramer, and pentamer. These structures were optimized with PM3, followed by HF/6-31G* optimization, and then with the G3 model chemistry. Only two trimers are present on the G3 potential energy hypersurface. We identified 5 tetramers and 10 pentamers on the potential energy and free-energy hypersurfaces at 298 K. None of these 17 structures were linear; all linear starting models folded into cyclic or three-dimensional structures. The cyclic pentamer is the most stable isomer at 298 K. On the basis of this and previous studies, we expect the cyclic tetramers and pentamers to be the most significant cyclic water clusters in the atmosphere.

Introduction

Numerous experimental and theoretical studies have focused on understanding the structure of small water clusters, $(H_2O)_n$, with $n = 3-5$.[1−47] We have recently predicted that besides the water dimer, the cyclic trimer, cyclic tetramer, and cyclic pentamer are also present in the earth's lower atmosphere under humid conditions.[48,49] A recent study of the atmosphere in the near-infrared has revealed that the water dimer is present at a temperature of 292.4 K.[50] This study suggests that the water dimer concentration is approximately 6×10^{14} molecules/cm^3 for saturated air at 292.4 K. We have recently used model chemistry methods[51−55] to predict the concentration of the water dimer and other cyclic water clusters where $n = 2-6$.[48] At a temperature of 292.4 K, the water pressure of saturated air is 0.02228 atm, and the partial pressure of the dimer is 1.67×10^{-15} atm, which is equivalent to a concentration of 4×10^{14} water dimers/cm^3. This number is quite close to the value of 6×10^{14} water dimers/cm^3 estimated from the recent experiment.[50] On the basis of the good agreement between the calculated and experimental numbers, we predicted that the quantities of cyclic water trimers, tetramers, and pentamers are only 2−4 orders of magnitude less concentrated than the water dimer in saturated air. In the previous work, we assumed that the cyclic form of the trimers, tetramers, and pentamers were the lowest energy structures. In this work, we test that hypothesis by examining the thermochemistry for formation of all conformers of the $(H_2O)_n$ water clusters, with $n = 3-5$, using model chemistry methods. We combine an extensive search of the potential energy hypersurfaces for the water trimer, tetramer, and pentamer, with G3 calculations on each conformer. This allows for the determination of all minima on the G3 hypersurfaces. We discuss the atmospheric implications of these results.

Methods

The Gaussian-n[51,52] and complete basis set[53−55] model chemistries were developed for the accurate calculation of structure and thermochemistry for gas-phase reactions. Water clusters have been extensively studied by experimental and high-level ab initio methods, and we have used the published results of these studies to evaluate the effectiveness of the Gaussian-n and complete basis set model chemistries in modeling the structures, enthalpies, and free energies of cluster formation, without correction for basis set superposition error (BSSE).[48,49,56,57]

The initial water cluster structures were built with SPARTAN[58] as linear chains, and a complete conformational search was performed in SPARTAN by rotating each hydrogen bond by 12 steps of 30 degree increments to produce 12^2 initial trimers, 12^3 initial tetramers, and 12^4 initial pentamers. Each starting structure was geometry optimized using the PM3 method,[59] followed by a Hartree−Fock self-consistent field optimization using the 6-31G* basis set to produce starting structures for the model chemistry method.[60] In addition, we constructed models of structures reported in the literature. We used the G3[52] method available within Gaussian 03, version B.02,[61] to determine the free energy of each cluster. We used version C.02 for anharmonic calculations.[62] In the G3 method, vibrational zero-point energy is obtained though geometry optimization at the HF/6-31G* level followed by scaling the frequencies by 0.8929. MP2(full)/6-31G* geometries are then used for the evaluation of the G3 energies. We calculated the G3 internal energies at 0 K and the internal, enthalpic, and free energies at 298.15 K. The electronic energy was obtained by subtracting the zero-point energy from the G3 internal energy at 0 K. The conformational populations for the water clusters were determined using the Boltzmann distribution equation, using the relative energies of each conformer.

Results

The structures of the clusters studied in this work are displayed in Figures 1 and 2. One trimer and four tetramers were located through the conformational search. In addition, a second trimer and a fifth tetramer were optimized on the basis of previous structures in the literature. The conformational search of the trimer failed to find the uuu cyclic structure with

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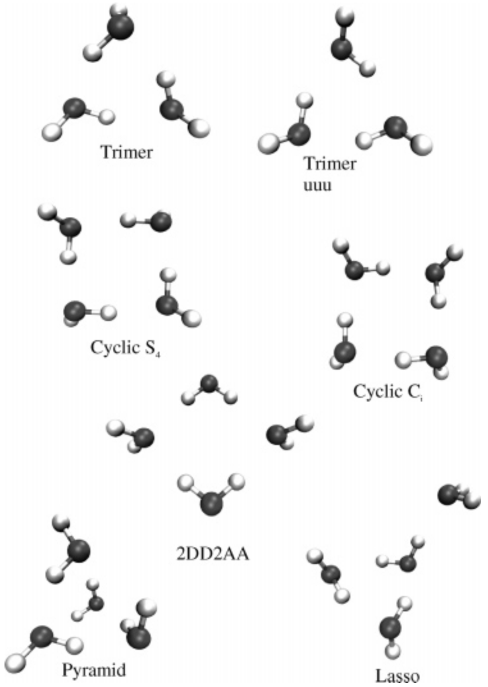

Figure 1. MP2(full)/6-31G* geometries of two water cluster trimers and five water cluster tetramers obtained with the G3 model chemistry.

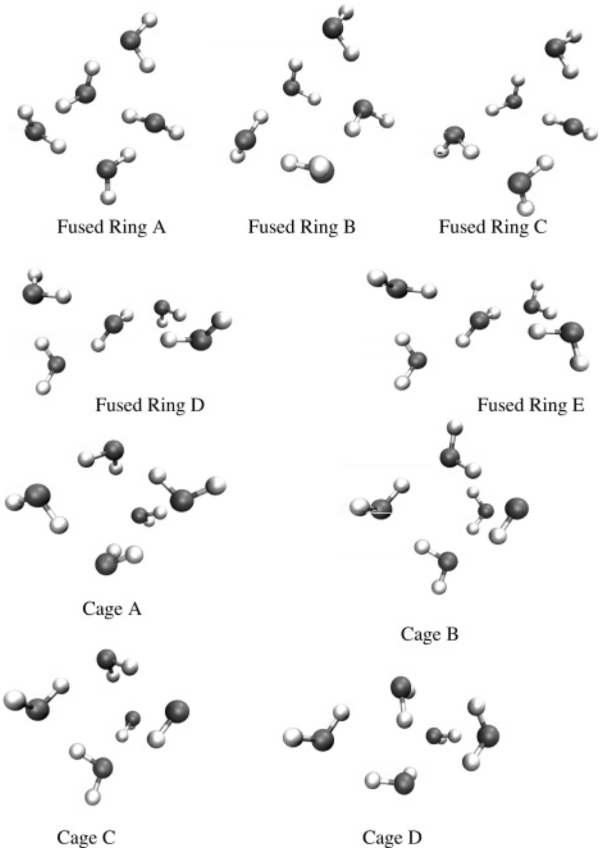

Figure 2. MP2(full)/6-31G* geometries of nine water cluster pentamers obtained with the G3 model chemistry.

all dangling hydrogens on the same side of the cyclic plane. This structure has an electronic energy 0.08 kcal/mol higher than the minimum that has one hydrogen on the opposite side of the cyclic plane relative to the other two hydrogens. As shown in Figure 1, the four tetramers include two cyclic structures that have been described before using empirical potentials and ab initio chemistry, with S_4[4,5,23,27,28,31,32,36,63,64] and C_i[27] symmetry, and two additional structures described as a pyramid[27,31] and a lasso.[5,32] An additional structure that we did not find through our conformational search was the 2DD2AA structure, displayed in Figure 1. We located 10 pentamers, the cyclic structure that has been reported previously,[3,5,19,20,23,28,31,32,34−36,64] and the 9 additional structures displayed in Figure 2. Five of these consist of fused rings, and the other four are cagelike structures. Fused rings and cage structures have been reported previously.[3,5,20,27,36] Table 1 contains a comparison of harmonic and anharmonic frequencies for the water dimer. Table 2 contains relative electronic energies at 0 K, ΔE_{el}, relative energies including zero-point energy at 0 K, ΔE_0, relative energies at 298.15 K, $\Delta E_{298}{}^0$, relative enthalpies, $\Delta H_{298}{}^0$, and relative free energies, $\Delta G_{298}{}^0$. Table 2 also contains the Boltzmann distributions of the tetramers at 298.15 K. Table 3 contains the same information for the 10 pentamers. Coordinates of all 16 structures calculated at the MP2/6-31G(d) level, as well as absolute energies, enthalpies, and free energies of each structure, are provided as Supporting Information.

Discussion

G3 Methodology. An important point that needs to be addressed is the adequacy of the G3 method for this study. While the G3 method has seen widespread success, hydrogen-bonded systems require careful attention. For instance, to obtain the most accurate hydrogen-bonded structures requires MP2 calculations with large basis sets; the G3 method only uses a 6-31G* basis in geometry optimization (although all electrons are correlated, not just the valence electrons). In addition, an accurate calculation of entropies is critical to obtain accurate free energies, and the entropy calculation is dependent on obtaining accurate frequencies. The lowest energy modes of hydrogen-bonded systems are generally quite anharmonic, and the G3 method uses HF/6-31G* harmonic frequencies that are scaled by 0.8929. A body of work has shown that development of the partition function from a density of rotational/vibrational energy states should be done within the anharmonic approximation, as the harmonic approximation quite clearly leads to an underestimation of this density.[46,65,66] We will address these two issues.

The geometries of cyclic water clusters have been well-studied at the MP2 level with aug-cc-pVnZ basis sets,[67] with n = D, T, Q, and 5 for the water dimer and trimer.[38] The geometries converge at the aug-cc-pVTZ level. Single-point energies using the same basis sets on geometries of the cyclic trimer, tetramer, and pentamer obtained at the MP2/aug-cc-pVTZ level were used for estimation of the MP2 complete basis set limit.[38] We have used the G3 method to study the structures and energetics of formation of cyclic water clusters.[48,49,57] Although somewhat surprising, we have found that the MP2(full)/6-31G* geometries agree well with both available experimental structures and with MP2 calculations using larger basis sets. For instance, as outlined below, the MP2(full)/6-31G* O−O distance for the S_4 symmetry water cluster tetramer is closer to the vibrationally averaged O−O distance determined from high-resolution gas-phase spectroscopy than the MP2/aug-cc-pVQZ structure. The MP2(full)/6-31G* cyclic water trimer, tetramer, pentamer, and hexamer structures, along with the cage hexamer and the prism hexamer, are in excellent agreement with experiment and with MP2 methods that use more extended basis sets.[49]

Extensive computational work[68−75] has been completed toward replicating and understanding the experimental anharmonic vibrational frequencies of the water dimer.[25,74,76−85] In

TABLE 1: HF/6-31G* Harmonic, Anharmonic, Scaled Harmonic, MP2 Anharmonic, and Experimental Anharmonic Frequencies for $(H_2O)_2$

frequency classification	harm HF/6-31G*	anharm HF/6-31G*	scaled harm HF/6-31G*	scaled+ anharm HF/6-31G*	MP2 anharm D95++(2d,2p)[a]	MP2 anharm aug-cc-pvTZ[b]	experiment
acceptor ν_3	4179	3997	3732	3732	3779	3753	3745[c,d]
donor ν_3	4162	3992	3717	3717	3772	3745	3735[c,d]
acceptor ν_1	4065	3909	3630	3630	3666	3648	3660 ± 5[e]
donor ν_1	4028	3893	3597	3597	3599	3583	3601[c]
donor ν_2	1853	1798	1654	1654	1618	1595	1616[f]
acceptor ν_2	1824	1775	1628	1628	1608	1585	1599[f]
out-of-plane bend (OPB)	619	521	553	521	525	502	523[f]
in-plane bend (IPB)	383	308	342	308	323	310	311[f]
intermolecular stretch (S)	181	135	162	135	150	138	143[g]
acceptor twist (AT)	142	84	127	84	120	114	108[h]
acceptor wag (AW)	135	82	121	82	122	113	103[h]
donor torsion (DT)	115	80	103	80	78	60	88[h]
std. deviation (all)	265	169	23.8	20.1	17.0	14.9	
std. deviation (low modes)	61.2	15.2	25.0	15.2	12.6	16.6	

[a] Reference 74. [b] Reference 75. [c] Reference 25, gas phase. [d] Reference 80, gas phase. [e] Reference 25, extrapolated from matrix data. [f] Reference 74, neon matrix, 5 K. [g] Reference 85, gas phase. [h] Reference 84, gas phase.

TABLE 2: Relative Energies in kcal/mol and Boltzmann Distribution Percentages (298.15 K) for Five $(H_2O)_4$ Structures

structure	ΔE_e	ΔE_0	$\Delta E_{298}°$	$\Delta H_{298}°$	$\Delta G_{298}°$	distribution (%)
cyclic S_4	0	0	0	0	0	51.5
cyclic C_i	0.99	0.73	0.87	0.87	0.26	33.0
pyramid	4.08	3.06	3.74	3.74	0.71	15.5
lasso	6.98	6.03	6.73	6.73	3.80	0.1
2DD2AA	11.14	8.55	10.27	10.27	4.51	0.0

TABLE 3: Relative Energies in kcal/mol and Boltzmann Distribution Percentages (298.15 K) for 10 $(H_2O)_5$ Structures

structure	ΔE_e	ΔE_0	$\Delta E_{298}°$	$\Delta H_{298}°$	$\Delta G_{298}°$	distribution (%)
cyclic	0	0	0	0	0	95.3
fused ring A	2.83	2.3	2.16	2.16	2.43	1.6
cage A	1.43	1.75	1.59	1.59	2.56	1.3
fused ring B	1.25	1.65	1.44	1.44	2.76	0.9
cage B	2.22	2.45	2.34	2.34	2.97	0.6
cage C	1.25	1.93	1.53	1.53	3.84	0.1
fused ring C	3.55	3.58	3.62	3.62	3.89	0.1
fused ring D	5.04	5.41	5.33	5.33	5.71	0.0
fused ring E	5.43	5.59	5.62	5.62	5.75	0.0
cage D	6.47	6.48	6.54	6.54	7.11	0.0

Table 1, we present our HF/6-31G* calculated harmonic, scaled harmonic, and anharmonic frequencies of the water dimer, the MP2/aug-cc-pVTZ anharmonic frequencies from Jordan and coworkers,[75] the MP2/D95++(2d,2p) anharmonic frequencies of Bouteiller and Perchard,[74] and the most reliable experimental anharmonic frequencies for the water dimer.[25,74,80,81,84,85] All of the anharmonic frequencies in Table 1 were computed using Barone's second-order perturbative approach.[62] The first column of the table classifies each mode, and the last column of the table contains the most accurate experimental values as selected by the Buck, Huisken, Saykally, and Perchard groups.[25,74,81,84,85] The interpretation of the high-resolution spectroscopy experiments is difficult, and the literature attests to the constant efforts to make sure of the correct assignment of each peak in the water dimer spectrum.[85] In addition, while matrix experiments are easier to interpret, it is clear that the effect of the matrix perturbs the frequencies from their gas-phase values, by as much as 20% for the anharmonic modes.[74] This makes comparison of experiment and theory difficult; we believe we have assembled the currently accepted most accurate values for the gas-phase water dimer.

The standard deviations for the different methods against the experimental numbers in column eight show that the standard deviation for the HF/6-31G* method drops from 265 cm^{-1} for harmonic frequencies to 169 cm^{-1} for anharmonic frequencies. Using the MP2/aug-cc-pVTZ method,[75] the standard deviation drops to 15 cm^{-1} while for the DP95++(2d,2p) basis set the MP2 standard deviation is 17 cm^{-1}. The DP95++(2d,2p) basis set is best for the anharmonic modes, while Dunning's augmented correlation consistent triple-ζ basis set is best overall. Of most interest for the present discussion is that scaling the HF/6-31G* harmonic frequencies by 0.8929, the procedure followed in the G3 model chemistry, results in a standard deviation of 24 cm^{-1}. The five low-mode intermolecular frequencies, which are the most important for the entropy determination, have a standard deviation of 25 cm^{-1}. The lowest five anharmonic HF/6-31G* frequencies agree about as well with experiment as the MP2 anharmonic frequencies, suggesting a strategy of using scaled HF/6-31G* frequencies above 1000 cm^{-1} and using anharmonic HF/6-31G* frequencies below 1000 cm^{-1} to improve the G3 method for systems with anharmonicity. The overall standard deviation for this combined scaled/anharmonic method is 20 cm^{-1}.

Because the scaled HF/6-31G* frequencies for the water dimer are quite reasonable relative to the experimental values, it stands to reason that the G3 method, which has been optimized for accurate thermochemical calculations, should yield good results for water clusters. The comparison of the energies for formation of a water dimer from two water molecules reveals excellent agreement with both experiment and MP2/CBS limit calculations. The value for the electronic energy, ΔE_{el}, at the MP2/CBS limit is estimated to be -4.98 ± 0.2 kcal/mol,[37] while the G3 value is -5.14 kcal/mol.[48] The experimental value for the standard enthalpy of dimerization has been determined by thermal conductivity measurements to be -3.59 ± 0.5 kcal/mol at 373 K.[86] The G3 calculated value for $\Delta H°$ at 373 K is -3.2 kcal/mol.[48] At this same temperature, the experimental free energy of dimerization is 3.34 ± 0.5 kcal/mol,[86] while the G3 calculated value is 3.29 kcal/mol.[48] Similar results are found for other clusters. For instance, the MP2/CBS limit reveals that the D_{2d} water octamer is 0.05 kcal/mol lower in electronic energy than the S_4 octamer.[87] The G3 method predicts the same electronic energy difference and predicts that the D_{2d} octamer is 0.35 kcal/mol lower in free energy at 298 K.[57] Thus, compared to experiment and to MP2/CBS limit benchmark calculations, the G3 method does an excellent job at calculating structures and energetics of water clusters. The use of scaled frequencies at the HF/6-31G* level appears to be adequate within the range of uncertainty of experimental values.

Structures. The structure of the water trimer minimum is identical to previous electronic structure results.[2,5,7,9,16−18,21,23,29,30,32,34,36,40−42,47,49,63,64] While the cyclic trimer is clearly the experimental global minimum at low temperatures,[16,42] other calculated trimer structures have been reported. Empirical force fields lead to more minima than just the cyclic structure,[2,5,14,31] as do quantum chemical calculations at lower levels of theory.[19,23,27] Wang and Gunn have used a semiempirical valence bond approach to locate four equilibrium structures of water trimers.[23] Besides the cyclic minima, they found two linear structures and a different cyclic structure than we located. The first linear structure is oriented like our starting linear structures, with each water acting as a hydrogen bond donor to the next water. The second linear structure has the middle water donating two hydrogen bonds to the other two waters. The alternate cyclic structure has one water serving as a double hydrogen bond donor and a second water in the role of a double hydrogen bond acceptor. In addition, empirical force field calculations[14] and HF/3-21G optimizations[19] predicted a cyclic trimer with all the dangling hydrogens pointing in the same direction relative to the cyclic plane, or uuu. We have optimized these starting structures and find that only the uuu cyclic trimer with dangling hydrogens all on the same side of the cyclic plane is a true minimum at the HF and MP2 levels. All linear structures, as well as the alternate cyclic structure that has one water as a double hydrogen bond donor and a second water as a double hydrogen bond acceptor, reverted to the canonical cyclic trimer. Our search protocol, which consisted of setting up 144 initial geometries by rotating 30 degrees around each hydrogen bond in a linear water trimer and then using the PM3 method for initial optimization, failed to locate the uuu cyclic trimer. The PM3 optimizations resulted in 67 structures, which all converged to the electronic cyclic minimum upon optimization with HF/6-31G*. The strengths and weaknesses of the PM3 method for studying hydrogen bonding are well-known,[88] and in this case the alternate structure was not found in our search protocol. In this instance, the search procedure must not have formed any structures close to the uuu minima, as a PM3 optimization from the HF/6-31G* uuu configuration did result in a PM3 uuu structure.

The cyclic S_4 tetramer and cyclic pentamer are very similar to previous results.[3,6,17,26,34,38,49] The earliest experimental work using molecular beam deflection studies are consistent with a linear dimer and a cyclic trimer, tetramer, and pentamer structure.[1] Xantheas has shown that the cooperativity of the hydrogen-bonding network in water clusters is critical for understanding the stability of different arrangements of waters.[89] He found that homodromic hydrogen-bonding networks, those that have sequential donor−acceptor arrangements between all water molecules, are the most stable. This phenomena explains why the most stable trimers, tetramers, and pentamers are homodromic rings.[89]

The highly symmetric, homodromic, S_4 cyclic tetramer has the free hydrogens alternating up and down around the ring. The experimental gas-phase structure is practically planar, and the vibrationally averaged O−O distance is 2.79 Å.[26] The MP2/aug-cc-pVDZ structure has O−O distances of 2.743 Å, the MP2/aug-cc-pVTZ structure has O−O distances of 2.732 Å, and the MP2/aug-cc-pVQZ geometry has O−O distances of 2.731 Å.[38] The corresponding O−O distance for the G3 MP2(full)/6-31G(d) structure is 2.748 Å. The pyramid has five or six apparent hydrogen bonds, but only four have appropriate bond distances and bond angles. The apparent hydrogen bond distances in the bottom of the pyramid are 1.794, 1.902, and 2.361 Å, while the apparent hydrogen bonds connecting the top water to the pyramid are 1.867, 1.965, and 2.440 Å. The relevant bond angles are 156.5, 148.8, and 122.6 degrees on the bottom of the pyramid and 147.4, 150.4, and 118.6 degrees connecting the top water to the pyramid. Thus, the pyramid structure has four true hydrogen bonds.

On the basis of the interplay between enthalpic and entropic effects, Ludwig has predicted that besides the cyclic, pyramid, and lasso structures, a star structure and a linear chain should also exist.[32] We tried numerous linear chains which all folded during HF/6-31G(d) optimization in Gaussian 03. We optimized a starting star structure, and it folded to the pyramid. An additional structure, suggested by Benson and Siebert, is a cyclic structure consisting of one double donor water directly across from a double acceptor.[4] This structure optimizes to the C_i isomer. Wang and Gunn located a bifurcated structure, with a hydrogen bond from one water bisecting the two hydrogens on the acceptor water.[23] This hydrogen-bonding arrangement is similar to that obtained from the known deficiencies in the AM1 method.[88]

The chiral homodromic cyclic pentamer consists of five waters that donate hydrogen bonds in a cooperative fashion, with the free hydrogens arranged pointing up, down, up, down, and down, and with an average experimental O−O distance of 2.76 Å.[26] The experimental O−O−O angles are about 108 degrees and the hydrogen bond angles are nearly linear. The MP2(full)/6-31G(d) O−O distances average 2.740 Å. The MP2(full)/6-31G(d) O−O−O bond angles average 108.0 degrees, and the corresponding hydrogen bond angles average 176.3 degrees. Clearly, MP2(full) geometries used in the G3 model chemistry are in excellent agreement with experiment.

Thermochemistry. There are two stable cyclic trimers. These are the chiral, homodromic cyclic trimer[26,49] and the uuu cyclic isomer with all of its dangling hydrogens pointing in one direction. The uuu isomer is less stable at all levels, with a ΔE_0 of 0.50, $\Delta E_{298}{}^0$ of 0.73, $\Delta H_{298}{}^0$ of 0.73, and $\Delta G_{298}{}^0$ of 0.004 kcal/mol relative to the canonical homodromic trimer. It is possible that correction for anharmonicity in the frequency calculations would change the entropies and the $\Delta G_{298}{}^0$ difference, and we are currently testing the effect of anharmonic frequencies on calculated free energies for hydrogen-bonded structures.

As shown in Table 2, the G3 model predicts two predominant cyclic tetramer structures and a pyramid structure at 298 K. The cyclic C_i geometry has a center of inversion and is 0.99 kcal/mol higher than the S_4 cluster on the $(H_2O)_4$ potential energy hypersurface. The pyramid structure, which has been located previously with empirical potentials[30] and ab initio calculations,[27] is 4.1 kcal/mol higher than the cyclic S_4 structure. The lasso structure, identified with empirical potentials[5] and ab initio calculations,[36] is 6.98 kcal/mol higher than the S_4 isomer on the potential energy hypersurface. Examining the enthalpic effect, the two cyclic structures both have four hydrogen bonds and the arrangement of dangling hydrogens in the S_4 structure has the least H−H repulsion, resulting in approximately 0.9 kcal/mol more enthalpy release upon formation of the S_4 structure. The pyramid releases 3.7 kcal/mol less heat relative to the S_4 isomer. The lasso consists of a trimer attached to the fourth water molecule, and as the hydrogen bonds in the trimer are weaker than those in the cyclic tetramer structure,[48] the enthalpy gain converting from the lasso to the S_4 structure is 6.7 kcal/mol. The entropic effect favors the pyramid and lasso relative to the cyclic structures. The 2DD2AA structure is 10−11 kcal/mol higher in electronic energy relative to the other two cyclic structures. Adding zero-point energy reduces this penalty by two kcal/mol, and adding entropic effects reduces the difference to 4.25−4.5 kcal/mol. Xantheas has attributed the enhanced stability of homodromic cyclic structures to the cooperativity of hydrogen bonding that structures such as S_4 and C_i display. An additional way to rationalize this effect is that the 2DD2AA structure has very unfavorable dipole−dipole interactions, as the dipole moments of the two individual DD waters are pointing in opposite directions from each other. The dipole moments of the two AA waters are pointing directly at each other. The cyclic structures that display cooperativity have their individual water dipoles with components that build upon each other in the plane of the cycle. Examining electrostatic charges derived from the molecular electrostatic potential, at the HF/6-31G* level, the donor (D) oxygens in the 2DD2AA structure have a charge of −0.90 while the acceptor (A) oxygens have a charge of −0.82. All hydrogens in the 2DD2AA structure have a charge of 0.43. For the S_4 structure, all four oxygens have the same electrostatic charge, −0.93. The hydrogens involved in hydrogen bonding have a charge of 0.48 while the dangling hydrogens have charges of 0.45. This charge analysis supports the idea of increased polarization in the S_4 structure, a polarization that is impossible for the 2DD2AA cluster. We have seen this effect for clusters of eight waters as well.[57]

Table 3 reveals that even though there are 10 pentamers on the G3 potential energy hypersurface, only the cyclic structure is present in any significant quantity at 298.15 K. The cyclic structure has the lowest electronic energy, the lowest internal energy, the lowest enthalpy, the greatest amount of entropy, and the lowest free energy relative to the other nine pentamers.

Implications for Atmospheric Chemistry. Our previous work assumed that only small cyclic water clusters were present in the atmosphere, and on the basis of this assumption and accurate free-energy calculations, we predicted that the number of trimers, tetramers, and pentamers present in the lower troposphere on a humid day would be about 10^{12}, 10^{11}, and 10^{10} clusters/cm^3, respectively. The complete analysis presented here of all possible $(H_2O)_n$ water clusters, with $n = 2-5$, does not change the original conclusion. Examining the forcing effect of water clusters is of great interest.[90] Since every polyatomic molecular species has 3N-6 vibrational modes, the bigger the water cluster, the more effective it is as a greenhouse gas. Besides having more IR active modes, each water cluster absorbs a different range of IR radiation, effectively increasing the ability of the atmosphere to retain heat. Water clusters can form complexes with many different species in the atmosphere, which could substantially alter the effective gas-phase concentration of reacting molecules.[50] Small shifts in absorption spectra of hydrates and complexes of molecules with hydrates could have a significant contribution to climate effects.[91] Pfeilsticker et al. have noted that the HO_2 molecule is photochemically linked directly to the most important oxidative molecule, OH, and therefore an addition or ligand-exchange reaction could change the oxidative capacity of the atmosphere.[50] Similarly, chemical reactions that can be catalyzed by water[92−96] can potentially be catalyzed by one, two, three, four, or five water molecules, with the cyclic trimers, tetramers, and pentamers being the predominate water clusters. These clusters are also available to bind to neutral organic molecules, which could be an important route for atmospheric aerosol formation.[97]

Conclusion

We have performed a comprehensive search of water clusters containing three, four, and five water molecules, combined with calculations of previously reported structures in the literature. We find that there are no stable linear or branched chain water structures predicted by PM3, HF/6-31G*, or MP2(Full)/6-31G* computational models. We found two cyclic trimers, three cyclic tetramers, and one cyclic pentamer. In addition, we found two additional tetramers that consist of a trimer with an additional water in the same plane (lasso) or above the plane (pyramid). We found five fused-ring and four cagelike pentamers, in addition to the cyclic cluster. The cyclic structures dominate the potential energy hypersurface from 0 to 300 K. A comparison of the most reliable compilation of experimental frequencies for the water dimer with MP2 anharmonic and HF scaled harmonic frequencies reveals that the scaled frequencies used in the G3 method are reliable for the calculation of entropy. Thus, the G3 method is an accurate predictor of both structure and energetics for water clusters.

These results support the suggestion that gas-phase reaction chemistry will be catalyzed by water clusters[91−96] and that small shifts in absorption spectra of hydrates and complexes of molecules with hydrates could have a significant contribution to climate effects.[48,91]

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Supporting Information Available: Coordinates of all 17 structures calculated at the MP2/6-31G(d) level as well as absolute energies, enthalpies, and free energies of each structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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