

Thermodynamics of Forming Water Clusters at Various Temperatures and Pressures by Gaussian-2, Gaussian-3, Complete Basis Set-QB3, and Complete Basis Set-APNO Model Chemistries; Implications for Atmospheric Chemistry

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Abstract: The Gaussian-2, Gaussian-3, complete basis set- (CBS-) QB3, and CBS-APNO methods have been used to calculate ΔH° and ΔG° values for neutral clusters of water, $(\text{H}_2\text{O})_n$, where $n = 2-6$. The structures are similar to those determined from experiment and from previous high-level calculations. The thermodynamic calculations by the G2, G3, and CBS-APNO methods compare well against the estimated MP2(CBS) limit. The cyclic pentamer and hexamer structures release the most heat per hydrogen bond formed of any of the clusters. While the cage and prism forms of the hexamer are the lowest energy structures at very low temperatures, as temperature is increased the cyclic structure is favored. The free energies of cluster formation at different temperatures reveal interesting insights, the most striking being that the cyclic trimer, cyclic tetramer, and cyclic pentamer, like the dimer, should be detectable in the lower troposphere. We predict water dimer concentrations of 9×10^{14} molecules/cm³, water trimer concentrations of 2.6×10^{12} molecules/cm³, tetramer concentrations of approximately 5.8×10^{11} molecules/cm³, and pentamer concentrations of approximately 3.5×10^{10} molecules/cm³ in saturated air at 298 K. These results have important implications for understanding the gas-phase chemistry of the lower troposphere.

Introduction

Numerous experimental and theoretical studies have focused on understanding the structure of small water clusters, $(\text{H}_2\text{O})_n$, with $n = 2-8$.¹⁻²⁴ Most of the theoretical focus has been on

calculating accurate structures and predicting frequencies, so that the actual experimental structures can be discovered by IR spectroscopy.^{14,15} In addition, many of the recent theoretical papers have examined the binding energy of water clusters and the effect of including zero-point energy. In this paper we focus on the thermochemistry for formation of the $(\text{H}_2\text{O})_n$ water clusters, with $n = 2-6$, using model chemistry methods. We compare ΔE to those values determined by previous workers and predict ΔH° and ΔG° for formation of various water clusters from water monomer and water cluster precursors. Many of the spectroscopic methods produce clusters in the temperature range of 5–20 K, so we have calculated ΔG° at 5 and 20 K. The troposphere has a temperature range extending from 200 to 300 K, and we have calculated ΔG° at the lower and upper ranges of temperature in the troposphere as well.

Methods

The Gaussian- n ^{25,26} and complete basis set (CBS)²⁷⁻²⁹ model chemistries have been developed for the accurate calculation of structure and energetics for gas-phase reactions. Water clusters have been

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Table 1. ΔE_e , ΔE_0 , and ΔH_{298}° for the Incremental and Total Association Energetics of Water Clusters^a

n	ΔE_e				ΔE_0				ΔH_{298}°			
	CBS-QB3	CBS-APNO	G2	G3	CBS-QB3	CBS-APNO	G2	G3	CBS-QB3	CBS-APNO	G2	G3
(A) $(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} \rightarrow (\text{H}_2\text{O})_n$: Incremental Association Energetics												
2	-5.10	-5.07	-4.98	-5.14	-3.01	-3.12	-3.04	-3.20	-3.39	-3.43	-3.43	-3.50
3	-10.17	-10.64	-10.20	-10.62	-6.09	-7.40	-6.84	-7.26	-7.84	-8.53	-8.25	-8.49
4	-11.36	-12.08	-11.95	-12.46	-8.60	-9.37	-9.36	-9.84	-9.50	-10.08	-10.22	-10.49
5	-8.31	-8.97	-8.56	-9.04	-6.09	-7.04	-6.74	-7.23	-6.60	-7.28	-7.15	-7.42
δ_{cyclic}	-8.04	-8.81	-8.24	-8.70	-6.03	-6.66	-6.18	-6.62	-6.41	-7.03	-6.66	-6.96
δ_{cage}	-11.13	-10.01	-9.97	-10.42	-7.20	-6.70	-6.55	-7.00	-8.67	-7.81	-7.85	-8.13
δ_{prism}	-12.02	-10.41	-10.26	-10.92	-7.79	-6.77	-6.54	-7.20	-9.36	-8.05	-8.00	-8.49
(B) $n\text{H}_2\text{O} \rightarrow (\text{H}_2\text{O})_n$: Total Association Energetics												
2	-5.10	-5.07	-4.98	-5.14	-3.01	-3.12	-3.04	-3.20	-3.39	-3.43	-3.43	-3.50
3	-15.26	-15.71	-15.18	-15.76	-9.10	-10.53	-9.88	-10.46	-11.23	-11.96	-11.68	-11.99
4	-26.62	-27.79	-27.13	-28.22	-17.70	-19.90	-19.22	-20.30	-20.72	-22.04	-21.91	-22.49
5	-34.93	-36.77	-35.69	-37.26	-23.79	-26.94	-25.95	-27.53	-27.33	-29.32	-29.06	-29.91
δ_{cyclic}	-42.97	-45.57	-43.93	-45.96	-30.99	-33.60	-32.14	-34.15	-33.74	-36.35	-35.72	-36.87
δ_{cage}	-46.06	-46.78	-45.66	-47.68	-30.99	-33.64	-32.51	-34.53	-35.99	-37.13	-36.91	-38.04
δ_{prism}	-46.95	-47.18	-45.95	-48.18	-31.58	-33.71	-32.49	-34.74	-36.69	-37.38	-37.06	-38.40

^a All values are given in kilocalories per mole.

extensively studied by 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 these clusters, without correction for basis set superposition error (BSSE). In principle these model chemistries,^{25–29} which extrapolate the energies to the complete basis set limit, should provide energies that do not need to be corrected for limitations in the basis set used for the different geometries in a cluster calculation.³⁰ To better evaluate the ability of the Gaussian model chemistries^{25,26} and the complete basis set model chemistries^{27–29} to accurately model gas-phase water cluster formation, we have compared the performance of the G2, G3, CBS-QB3, and CBS-APNO methods against previously reported high-level calculations.

The initial water cluster structures were built with SPARTAN³¹ and optimized by the PM3 method,³² followed by a Hartree–Fock self-consistent field optimization with the 6-31G* basis set to produce starting structures for the model chemistry methods.³³ We used the G2,²⁵ G3,²⁶ CBS-QB3,²⁷ and CBS-APNO³⁴ methods available within Gaussian 98, version A.11.3.³⁵ In the CBS-APNO method, geometries are initially optimized at the UHF/6-311G** level and vibrational zero-point energy is obtained by use of a scale factor of 0.9251. Geometries optimized at the QCISD/6-311G* level are then used for evaluation of the CBS-APNO electronic energy. In the G2 and G3 methods, vibrational zero-point energy is obtained through geometry optimization at the UHF/6-31G* level followed by scaling the frequencies by 0.8929. MP2(Full)/6-31G* geometries are then used for the evaluation of the G2 and G3 energies. The CBS-QB3 method uses B3LYP/6-311G(2d,4,p) geometries for both the zero-point energy evaluation and the evaluation of the CBS-QB3 electronic energies. The scale factor is 0.99 for the frequency calculations. Scaling of the frequencies is of particular

importance and results in more accurate values than the harmonic oscillator model would normally provide. All calculated values are for a standard state of 1 atm.

The G2, G3, CBS-QB3, and CBS-APNO methods were developed with the goal of obtaining highly accurate values for thermochemical parameters.^{25–29,36} Accurate values for enthalpies of formation, atomization energies, ionization potentials, electron affinities, proton affinities, isodesmic reactions, cation–atom reactions, molecule–atom reactions, free energies for deprotonation reactions, and accurate pK_a values have been calculated with these methods.^{29,36–43} In this paper we compare the ability of these methods to predict structures, free energy differences, and enthalpy differences upon formation of water clusters, which we compare against previously reported high-level results and experiment. We discuss the atmospheric implications of these results.

Results

The structures of the clusters studied in this work are well-known and can be found in the Supporting Information (Figures 1S–7S). Table 1S (Supporting Information) contains the electronic energies (E_e), the sum of the electronic and zero-point energies (E_0), the enthalpies at 298.15 K (H_{298}^0), and the free energies at 298.15 K (G_{298}^0), determined with the CBS-QB3, CBS-APNO, G2, and G3 methods for the water molecule and for each cluster reported in this paper. Table 1 includes calculated values for ΔE and ΔH° for the incremental reactions of a water molecule with successive water clusters and for reactions of individual water molecules to form the seven clusters discussed in this paper. Table 2 contains the values for ΔG° at $T = 5, 20,$ and 298.15 K for these same reactions. Prepared from CBS-APNO results, Table 3 contains the values for K_p over the temperature range from 200 to 300 K, along

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Table 2. ΔG^0_5 , ΔG^0_{20} , and ΔG^0_{298} for the Incremental and Total Association Free Energies of Water Clusters at 5, 20, and 298.15 K^a

n	ΔG^0_5				ΔG^0_{20}				ΔG^0_{298}			
	CBS-QB3	CBS-APNO	G2	G3	CBS-QB3	CBS-APNO	G2	G3	CBS-QB3	CBS-APNO	G2	G3
(A) $(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} \Rightarrow (\text{H}_2\text{O})_n$: Incremental Association Energetics												
2	-3.05	-3.16	-3.18	-3.24	-2.96	-3.07	-3.08	-3.15	1.74	2.08	2.01	1.94
3	-6.14	-7.42	-7.06	-7.33	-5.91	-7.21	-6.85	-7.12	4.25	1.43	1.97	1.83
4	-8.70	-9.35	-9.52	-9.77	-8.45	-9.11	-9.28	-9.52	-0.09	-1.07	-1.29	-1.66
5	-5.88	-7.03	-6.94	-7.22	-5.63	-6.80	-6.71	-6.99	1.85	-0.28	-0.11	-0.46
δ_{cyclic}	-6.05	-6.64	-6.31	-6.60	-5.77	-6.34	-6.02	-6.31	1.92	1.92	1.98	1.77
δ_{cage}	-7.23	-6.68	-6.71	-6.98	-6.95	-6.39	-6.42	-6.69	3.57	3.94	3.85	3.66
δ_{prism}	-7.82	-6.75	-6.70	-7.18	-7.54	-6.46	-6.40	-6.89	3.49	4.54	4.50	4.07
(B) $n\text{H}_2\text{O} \Rightarrow (\text{H}_2\text{O})_n$: Total Association Energetics												
2	-3.05	-3.16	-3.18	-3.24	-2.96	-3.07	-3.08	-3.15	1.74	2.08	2.01	1.94
3	-9.18	-10.58	-10.24	-10.57	-8.87	-10.28	-9.94	-10.27	5.99	3.51	3.98	3.77
4	-17.88	-19.93	-19.76	-20.34	-17.32	-19.39	-19.21	-19.79	5.90	2.43	2.69	2.11
5	-23.76	-26.97	-26.70	-27.56	-22.95	-26.19	-25.92	-26.77	7.76	2.16	2.58	1.65
δ_{cyclic}	-29.81	-33.60	-33.01	-34.16	-28.73	-32.53	-31.94	-33.08	9.68	4.07	4.56	3.43
δ_{cage}	-30.99	-33.65	-33.41	-34.54	-29.90	-32.58	-32.34	-33.46	11.33	6.10	6.43	5.31
δ_{prism}	-31.58	-33.72	-33.40	-34.74	-30.49	-32.65	-32.32	-33.66	11.25	6.69	7.08	5.72

^a All values are given in kilocalories per mole.

Table 3. Free Energies, Equilibrium Constants, Partial Pressures of Water Monomers and Dimers, Mole Fraction of the Water Dimer, and Number of Water Monomers and Dimers per Cubic Centimeter Predicted to Be Present in the Atmosphere at 216.65, 292.4, and 298.15 K^a

T	ΔG^0	K_p	$P(\text{H}_2\text{O})$	$P(\text{H}_2\text{O})_2$	$X(\text{H}_2\text{O})_2$	$N(\text{H}_2\text{O})$	$N(\text{H}_2\text{O})_2$
216.65	0.544	0.282	3.40×10^{-5}	3.26×10^{-10}	9.59×10^{-6}	1.15×10^{15}	1×10^{10}
292.4	1.97	0.0336	0.022 28	1.67×10^{-5}	7.50×10^{-4}	5.59×10^{17}	4×10^{14}
298.15	2.08	0.0299	0.031 86	3.04×10^{-5}	9.54×10^{-4}	9.30×10^{17}	9×10^{14}

^aFree energies are given in kilocalories per mole; partial pressures are given in atmospheres. Calculated values are based on the CBS-APNO values reported in Tables 1 and 2, and the saturated water pressures were obtained from the Clausius–Clapyron equation.⁴⁴

with the partial pressure of water vapor at each temperature,⁴⁴ the partial pressure of the water dimer, the mole fraction of the dimer complex, the number of water molecules at each temperature per cubic centimeter, and the number of water dimers at each temperature per cubic centimeter. From the calculated equilibrium constant and the partial pressure of the water monomers at specified temperatures, the abundance of each complex was determined.

Discussion

Structures. The structures of the water dimer, cyclic trimer, cyclic tetramer, cyclic pentamer, and three hexamers are very similar to previous results (see Supporting Information for figures and values for bond distances and bond angles).^{4,11,12,15,20,22,24} The earliest experimental work with molecular beam deflection studies is consistent with a linear dimer and a cyclic trimer, tetramer, and pentamer structure.¹ Both experiment and theory have shown that the hexamer is the transition point from two-dimensional cyclic structures to three-dimensional structures. As the overall geometries obtained by different research groups are similar, and the main focus of this paper is on thermodynamic calculations, we will defer a discussion of the structural details to a future paper. Interested readers can view the structures, bond distances, and bond angles in the Supporting Information.

Thermochemistry. As shown in Table 1, the CBS and *Gn* model methods predict ΔE_c energies of -5 to -5.1 kcal/mol and ΔE_0 energies of -3.0 to -3.2 kcal/mol for formation of the water dimer. The values for ΔE_c are in agreement with the value calculated at the MP2/CBS limit estimate of -4.98 ± 0.2 kcal/mol.²¹ For the trimer, the incremental association

energies (reaction A, Table 1) predicted by the CBS and *Gn* model methods are -10.2 to -10.6 for ΔE_c , -6.1 to -7.4 for ΔE_0 , and -7.8 to -8.5 kcal/mol for ΔH^0_{298} . For formation of the tetramer from the trimer, even more energy is released, with ΔH^0_{298} values ranging from -9.5 to -10.5 kcal/mol for the four different methods. For formation of the pentamer from the tetramer, the enthalpy decreases, with ΔH^0_{298} values ranging from -6.6 to -7.4 kcal/mol. Clearly the CBS-QB3 results are lower than the results for the other three methods. There are many possible hexamer structures,^{45–48} and we have focused on the cyclic, cage, and prism forms in this study. Previous results have shown that the global minimum on the MP2/CBS estimated electronic energy surface is the prism, followed by the cage, then the book, and then the cyclic structure.²² This result follows the number of hydrogen bonds in each cluster, with the prism containing nine hydrogen bonds and the cage, book, and cyclic structures containing eight, seven, and six hydrogen bonds, respectively. As shown in Table 1, all model chemistry methods predict that the prism hexamer tends to be the global minimum when defined by electronic energy, in agreement with extensive MP2 calculations⁴⁶ and the CBS estimates with the MP2 method.²² All of the model chemistry methods show that the energy differences between the cage and prism isomers are very small, in agreement with previous results.^{22,46} Formation of a hexamer from the pentamer favors the prism structure over the cage by 0.3 – 0.9 kcal/mol.

Total association energies show the energy or enthalpy released when n waters form an $(\text{H}_2\text{O})_n$ cluster. The estimated CBS limits for the cluster total association energies at the MP2

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level of theory are -15.8 kcal/mol (trimer),^{12,22} -27.6 kcal/mol (tetramer), -36.3 kcal/mol (pentamer), -45.9 kcal/mol (prism hexamer), -45.8 kcal/mol (cage hexamer), and -44.8 kcal/mol (cyclic hexamer).²² Effects of higher correlation suggest that the error bars on these numbers are ± 0.2 kcal/mol.²² By this criterion the CBS-APNO method matches best for formation of the trimer, tetramer, pentamer, and cyclic hexamer, while the G2 method matches best for formation of the cage and prism hexamers. The CBS-QB3 model is the least consistent, with energies diverging from the other three model chemistry methods and the estimated CBS MP2 limit as cluster size increases.

The electronic energies favor formation of the prism structure from six individual water molecules with all four model chemistry methods. Inclusion of zero-point energies reduces the differences between the structures, with CBS-QB3 predicting that formation of the prism from six water molecules is 0.6 kcal/mol lower in energy than the isoenergetic cage and cyclic structures. CBS-APNO and G3 maintain the ordering of prism, cage, cyclic but with an energy spread of just 0.11 kcal/mol for CBS-APNO and 0.35 kcal/mol for G3. G2 has formation of the cage structure just 0.02 kcal/mol lower than formation of the prism structure, which is another 0.35 kcal/mol lower than for formation of the cyclic structure. Previous results generally show that the ZPE tends to increase with increasing number of hydrogen bonds and that either cage, book, or prism is the lowest energy structure for MP2 calculations with large basis sets (with and without correction for basis set superposition error),^{21,22,46} although one study at the MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ level predicts that the cyclic hexamer is the lowest energy conformer.²⁰ Estimates at the MP2 complete basis set limit predict that the prism structure is lowest in energy, 0.1 kcal/mol lower than the cage.²² The CBS-APNO method predicts this same energy difference, with G3 predicting a slightly bigger energy spread.

Formation of a water dimer releases between 3.4 and 3.5 kcal/mol of heat at 298 K, as predicted by the enthalpy of dimerization with the four model chemistry methods. The experimental value for the standard enthalpy of dimerization has been determined through thermal conductivity measurements to be -3.59 ± 0.5 kcal/mol at 373 K.⁴⁹ The four model chemistry enthalpies of dimerization at 373 K are all -3.2 kcal/mol, in good agreement with the experimental value. Focusing on the lower half of Table 1, formation of a trimer from three water molecules is predicted to release about 3.9 kcal/mol per hydrogen bond. Formation of the tetramer is predicted to release about 5.4 kcal/mol, and formation of the pentamer is predicted to release about 5.8 kcal/mol per hydrogen bond.

For the hexamers, enthalpies at 298 K follow the ordering of the number of hydrogen bonds, with formation of the prism structure that forms eight hydrogen bonds releasing slightly more heat than formation of the cage structure with seven hydrogen bonds, whose formation releases 1 – 2 kcal/mol more than does formation of the cyclic structure with six hydrogen bonds. Formation of the prism structure from six water molecules releases 4.6 – 4.8 kcal/mol per hydrogen bond according to the four model chemistry methods, while formation of the cage releases 5.1 – 5.4 kcal/mol per hydrogen bond. Formation of the

cyclic structure releases 5.6 – 6.1 kcal/mol per hydrogen bond. Since the cyclic structure with six hydrogen bonds has less entropy than the cage structure with seven hydrogen bonds, which has less than the prism structure with eight hydrogen bonds, we anticipate that at higher temperatures the cage will quickly become more stable than the prism, and then the cyclic structure will be more stable than both of the more constrained structures.

The structures that release the most heat per hydrogen bond are the cyclic pentamer, with an average of 5.8 kcal/mol from all four model chemistry methods, and the cyclic hexamer, with an average of 5.9 kcal/mol per hydrogen bond. Excluding the CBS-QB3 numbers, which are a couple of kilocalories per mole lower than for the other three methods for the larger clusters (Table 1), the average enthalpy per hydrogen bond is 5.9 kcal/mol for formation of the cyclic pentamer from five water molecules. This same analysis reveals that the average enthalpy per hydrogen bond is 6.0 kcal/mol for formation of the cyclic hexamer from six water molecules. The cyclic pentamer and hexamer structures have near-tetrahedral geometries that are the most icelike of all the water clusters reported in this paper. The enthalpy analysis reveals that these two structures are the best stabilized geometries on a per-hydrogen bond basis.

The experimental free energy for formation of the water dimer at 298.15 K can be approximated from the ΔH° and ΔS° of dimerization measured between 358 and 386 K by thermal conductivities.⁴⁹ Assuming that ΔH does not change too drastically with temperature, the experimental ΔH° value can be combined with the experimental ΔS° value of -18.59 ± 1.3 cal/(K mol) (both obtained at 373 K) to get a pretty good estimate of 1.95 kcal/mol at 298 K. This value compares quite well to the model chemistry methods, with values ranging from 1.74 to 2.08 kcal/mol (Table 3). By comparison, Vaida and Headrick⁵⁰ have used statistical thermodynamics along with known values from spectroscopy to calculate a ΔG° of 2.3 kcal/mol at the earth's surface. At 373 K, the experimental free energy of dimerization is 3.34 ± 0.5 kcal/mol,⁴⁹ which compares to values of 3.0 , 3.44 , 3.35 , and 3.29 kcal/mol for the CBS-QB3, CBS-APNO, G2, and G3 model chemistries. Clearly the agreement between theory and experiment is excellent for the CBS-APNO, G2, and G3 methods and increases our confidence in using these methods to evaluate larger water clusters. The CBS-QB3 value is less than the experimental value but still within the range of the estimated experimental uncertainty. The excellent agreement between the experimental and model chemistry results implies that the model chemistry scaling of the frequencies appears to be an effective method for overcoming the anharmonicity of frequency calculations.

The free energy calculations displayed in the top part of Table 2 reveal that the sequential building of larger clusters from smaller clusters is favored at 5 and 20 K. So for instance, at 5 K, the G3 calculations predict that formation of the trimer from the dimer has a ΔG° of -7.3 kcal/mol, with subsequent formation of the tetramer from the trimer having a subsequent ΔG° of -9.8 kcal/mol. Formation of the pentamer from the tetramer has a standard free energy change of -7.2 kcal/mol, and formation of any of the three hexamer structures from the pentamer yield ΔG° values between -6.6 (cyclic) and -7.2 (prism) kcal/mol. At 20 K the absolute values of ΔG° are

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slightly lower but follow the same general trends. The bottom part of the table reveals that formation of each cluster, $(\text{H}_2\text{O})_n$, from n H_2O molecules at 5 and 20 K are spontaneous reactions. The bigger the cluster, the more free energy is produced. Formation of the prism hexamer produces slightly more free energy than the cage hexamer, at both temperatures, by the CBS-APNO and G3 methods. G2 predicts that formation of both structures is isoenergetic, with ΔG° values of -33.4 kcal/mol at 5 K and -32.3 kcal/mol at 20 K. CBS-QB3 predicts that the cage hexamer is preferred at 5 K and the prism hexamer is preferred at 20 K.

Comparing these predictions with previous results, Losada and Leutwyler,²⁰ using MP2/aug-cc-pVDZ geometries and frequencies, have estimated the hexamer gas-phase interconversion equilibria by calculating the temperature dependence of the partition functions of five hexamer isomers. They predict that the cyclic hexamer is the most abundant isomer below 8 K, the cage is the most abundant between 8 and 26 K, and the book is the most abundant isomer above 26 K.²⁰ They rationalize that the failure of the cyclic structure to be observed by gas-phase spectroscopy might be because the book or cage is formed first in the supersonic expansion and that the barrier for conversion from cage to cyclic must be too high for the cyclic structure to form from the cage. Kim and Kim⁴⁶ have calculated ΔG° values using larger basis sets than Losada and Leutwyler, with and without correction for BSSE, and they predict that, without inclusion of BSSE, cage is the most abundant species at 6 K, followed by book, then prism, then cyclic. With the BSSE correction, cage and book are both predicted to produce 32.0 kcal/mol upon formation of their structures from six water molecules, followed by prism (29.0 kcal/mol) and then cyclic (28.9 kcal/mol). Pedulla and Jordan⁵¹ have noted that MP2 calculations using large flexible basis sets predict the cage hexamer to be more stable than the prism, even without inclusions of zero-point energies, so it seems clear that MP2 predicts the cage hexamer to be the global minimum, consistent with its experimental observation at very low temperatures. Our results suggest that at the very lowest temperatures formation of the prism structure is slightly preferred, followed by the cage and then the cyclic structure. We do not in fact know the actual temperature of the supersonic beam expansion, but we can see that as the temperature increases the preference switches in accordance with the number of hydrogen bonds of the water cluster structures. According to our results the coldest beam should form the prism structure (nine hydrogen bonds), and as the temperature is raised the next structure formed should be the cage (eight hydrogen bonds), then the book (seven hydrogen bonds), and then the cyclic (six hydrogen bonds). The model chemistry methods predict that around 270 K the lowest entropy cyclic structure will form from six water monomers, while the cage and prism are no longer predicted to form spontaneously from water monomers. In terms of mechanism of formation, as noted above, all of the hexamers are predicted to form from the cyclic pentamer at 5 and 20 K by the CBS and G3 methods (Table 2A). The prism isomer is favored over the cage, which is favored over the cyclic, according to the CBS and G3 results. The G2 model favors the cage just slightly over the prism, but all methods agree that the cyclic structure is least favored. It is

easy to imagine a mechanism whereby the cyclic pentamer incorporates one additional water to form the cyclic hexamer, as this structure allows very facile torsional motion and tunneling,¹⁵ so the argument that the barrier for conversion from cage to cyclic is the reason that the cyclic structure is not seen below 8 K does not seem to be correct.²⁰ In other words, Table 2 shows that the cyclic hexamers can be formed either by formation from smaller clusters (like reaction A), by formation from six individual waters directly (reaction B), or by interconversion of the hexamer structures. Our results suggest that thermodynamics rules the formation of these clusters, and at temperatures around 8 K the structures with the most hydrogen bonds are the most stable. Of course a definitive answer to the ease and mechanism of the interconversion of these clusters can only be established by examining the kinetics for these reactions, which would require locating the transition-state structures that connect various pathways for rearrangement of these clusters. Only if the barriers are low would we have theoretical evidence that our suggestion is correct.

The so-called melting points for water clusters have been predicted by some groups and presumably occur when ΔG° is zero. Rodriguez et al.⁵² have used classical molecular dynamics with the TIP4P and MCY pseudopotentials, and they predict that T_m is around 50 K for the transition from the cage structure to a liquidlike structure. The melting point is a bit of a misnomer, however, as this temperature actually represents the transition point in an equilibrium process where the concentration of water monomers raised to the n th power is equal to the concentration of water clusters made from n waters. At the melting point, $K = 1$, and at higher temperatures $K < 1$. As the temperature rises we expect changes in the equilibrium ratio of clusters, which we should characterize as structural changes. Using the CBS-APNO numbers, we find that $K = 1$ at 189 K for the water dimer, 231 K for the water trimer, 268–269 K for the tetramer and the cyclic hexamer, and 275–276 K for the pentamer. These temperatures are all much higher, and in disagreement, with the classical results. Quantum chemistry can be used to predict that these small-sized clusters will rearrange on the potential energy hypersurface, to form various different combinations of clusters. However, it is difficult to imagine that a small cluster of 2–6 waters can ever be described as liquidlike, as a gas-phase cluster composed of 2–6 waters would not be subject to the same intermolecular forces as a group of 2–6 waters that are embedded within liquid water. Since the temperature of the troposphere ranges roughly from 200 to 300 K, it is clear that significant numbers of water clusters will be found in the lower troposphere. We will consider the implications of the formation and presence of these water clusters in the next section of this paper.

Implications for Atmospheric Chemistry. 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.⁵³ Their study suggests that the water dimer concentration is approximately 6×10^{14} molecules/cm³ for saturated air at 292.4 K, and they conclude that the water dimer absorbs energy in the lower troposphere, thus reducing heating of the earth's surface. They speculate that larger water clusters, with $n = 3-6$, may exist

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in numbers comparable to those of the ambient aerosol in the background troposphere, thus efficiently promoting water cluster-assisted photochemical reactions in the atmosphere. As examples they list oxidation of SO_3 to H_2SO_4 ,^{54,55} addition or ligand-exchange reactions of water clusters with molecules possessing large dipole moments or large polarizabilities, and the effective solvation of these molecules.^{50,56,57} They point out that the formation of these complexes may substantially alter the effective gas-phase concentration of reacting molecules.⁵³ 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.⁵³ We are able to address some of these speculations on the basis of the high-level ΔG° results reported in this study for water clusters.

The troposphere extends 9–12 km above the earth's surface (16–17 km in the tropics) and is the region of the atmosphere that is directly heated by the Earth's surface. The troposphere is defined in terms of temperature, from 300 K in the lower troposphere to 216.65 K in the upper troposphere.⁴⁴ The pressure of the atmosphere ranges from 0.2 to 1 atm over this altitude and temperature range. Table 3 shows the equilibrium constants calculated from ΔG° at 216.65, 292.4, and 298.15 K. Included in the table are the saturated water pressures calculated from the Clausius–Clapyron equation,⁴⁴ the partial pressure of the water dimers, the fraction of each complex present at each temperature, the number of water molecules at each temperature, and the number of water dimer complexes at each temperature. Note that the maximum in K_p occurs at the lowest temperature, which would be in the tropopause, while the maximum partial pressure for all water complexes occurs at the highest temperature, which is at ground level. As has been pointed out previously, this effect is a simple mass action effect based on the partial pressure of the water monomer, which is at its highest at ground level and drops precipitously as altitude increases.⁵⁸ Temperatures of 216.65 and 292.4 K are found at the tropopause (the ceiling of the troposphere, starting at approximately 11 km) and near ground level, respectively. At a temperature of 292.4 K, the water pressure of saturated air is 0.022 28 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/cm³. This number is quite close to the value of 6×10^{14} water dimers/cm³ estimated from the recent experiment.⁵³

The close agreement of the experimental and calculated results leads us to estimate the number of higher-order water clusters in the atmosphere. We have used the CBS-APNO free energies to calculate the number of higher-order water oligomers formed from individual water molecules following the same procedure outlined in Table 3. The number of cyclic water trimers in saturated air formed from three water molecules is 1×10^{12} clusters/cm³, the number of cyclic water tetramers formed from four water molecules is 2×10^{11} clusters/cm³, the number of cyclic water pentamers formed from five water molecules is 9.5×10^9 clusters/cm³, and the number of cyclic

water hexamers formed from six individual water molecules is only 5×10^3 clusters/cm³ at 292.4 K. At 298.15 K, the number of cyclic trimers, tetramers, pentamers, and hexamers produced from individual water molecules is 2.6×10^{12} , 5×10^{11} , 2.5×10^{10} , and 3×10^4 . The number of water trimers formed from three water molecules in the lower atmosphere is 2 orders of magnitude lower than the number of water dimers formed in the lower atmosphere. The values for ΔG° in Table 2A show that higher-order clusters will form from the lower clusters. So for instance, formation of a trimer from a water dimer and a water monomer has a CBS-APNO ΔG° of 1.43 kcal/mol at 298 K (Table 2A), which translates to a water trimer concentration of 2.5×10^{12} molecules/cm³. Formation of a tetramer from a trimer and a monomer is spontaneous at room temperature, with a ΔG° of -1.07 kcal/mol (Table 2A), which translates to a tetramer concentration of approximately 5.8×10^{11} molecules/cm³. Formation of the cyclic pentamer from the tetramer and one additional water is also spontaneous, and use of the value for ΔG° in Table 2 to calculate K_p and the number of water pentamers formed from the water tetramer and one additional water yields 3.5×10^{10} molecules/cm³. These mass action relationships based on accurate free energy calculations predict that the quantity of cyclic water trimers, tetramers, and pentamers are 2–4 orders of magnitude less than the amount of water dimer in saturated air. The concentrations of cyclic dimers, trimers, tetramers, and pentamers are on the order of 10^{14} , 10^{12} , 10^{11} , and 10^{10} clusters/cm³. Simpler theories, such as Wertheim's theory of associating systems, do not predict such a high abundance for water oligomers.⁵⁹ Our results support the speculations of Pfeilsticker et al.⁵³ that water clusters may exist in numbers comparable to the ambient atmosphere; in particular, we predict that cyclic trimers, tetramers, and pentamers should be directly observable in the lower atmosphere.

Vaida and co-workers⁶⁰ have studied the hydration of formic acid using B3LYP density functional theory with large basis sets. They note that the formic acid–water complexes containing three waters are quite stable and closely resemble the cyclic water trimer attached to a formic acid molecule. Atmospheric aerosol formation is thought to be dominated by ionic complexes, and neutral complexes are not considered important as they are generally less stable than ionic complexes. However, they make the case that, contrary to conventional wisdom, neutral molecules such as formic acid, complexed with water molecules, may be an important route for aerosol formation in the atmosphere. Our results, which show an appreciable concentration of the water trimer under the right conditions (high humidity and temperatures near 298 K, conditions that occur near ground level on a regular basis), provide a context for considering the Vaida hypothesis. Since the water trimer, tetramer, and pentamer have concentrations on the order of 10^{12} – 10^{10} molecules/cm³ in saturated air at 298 K, they are available to form complexes with small organics that have been delivered to the lower troposphere by anthropogenic means.

In a review article, Vaida et al.⁵⁸ have noted that weakly bound water complexes could play additional roles in the Earth's atmosphere. Besides the aerosol formation idea, they note that chemical reactions in the atmosphere would be altered when in the presence of water clusters and that small shifts in absorption

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spectra of hydrates and complexes of molecules with hydrates could have a significant contribution to climate effects. Indeed, Loerting and Klaus⁵⁴ have shown that larger hydrates of SO₃ with water reduce the activation energy for conversion of SO₃ to H₂SO₄. Their calculations indicate that, in our atmosphere, different reaction paths involving two and three water molecules are taken in the process of forming sulfate aerosols, which then lead to acid rain. Our results suggest that, besides the dimer and trimer, the tetramer and pentamer could also be involved in the atmospheric conversion of SO₃ to H₂SO₄. Aloisio et al.⁵⁶ have shown that the HO₂-H₂O complex is easily formed in the laboratory and they predict that up to 30% of the HO₂ in the atmosphere is hydrogen-bonded to water at altitudes between 1 and 3 km.

Global warming has been predicted to be enhanced by the presence of water dimers, and an estimate has been made for the range of total absorption from 400 to 5000 nm by the water dimer in the tropics of 1.6–3.3 W/m².⁶¹ This estimate was made on the basis of a range of water dimer concentrations from 1 × 10⁻¹⁴ to 7 × 10⁻¹³ molecules/cm³. Our results suggest that the upper limit reported in this work⁶¹ is actually a lower bound for the water dimer absorption and that the absorption for cyclic water trimers, tetramers, and pentamers will also increase the absorption of solar energy in the lower troposphere. In a global warming scenario, an increased temperature will lead to an increase in water vapor partial pressure, which leads to a nonlinear increase in the dimer, trimer, tetramer, and pentamer water cluster concentrations. These results support the suggestion that increases in temperature increases the contribution of the absorption of solar radiation by the water dimer in a positive feedback loop.⁶¹

These ideas all depend on having an appreciable presence of water clusters in the atmosphere; our highly accurate calculations on the thermodynamics of cluster formation support these hypotheses. Future experimental studies of water clusters with small molecules in the laboratory^{55,56} and in the atmosphere,⁵³ combined with high-level theoretical studies,⁵⁴ will greatly enhance our knowledge of atmospheric processes.^{50,58}

Conclusion

The CBS-APNO, G2, and G3 methods are excellent methods for determining the structures and thermodynamic values for formation of water clusters, with the results in excellent agreement with high-level complete basis set estimates at the MP2 level and with spectroscopic experiments^{4,11,12,15,20,22,24} for structures and energetics.⁴⁹ The cyclic pentamer and hexamer structures have near-tetrahedral geometries that are the most icelike of all the water clusters reported in this paper and are the best stabilized geometries on a per-hydrogen bond basis, with an average enthalpy of 5.9–6.0 kcal/mol per hydrogen

bond. The free energy calculations reveal that the sequential building of larger clusters from smaller clusters is favored at 5 and 20 K, the estimated temperature range of the spectroscopic experiments on supersonic beam expansions,¹⁵ with the cage and prism structures essentially isoenergetic, in agreement with previous results.^{3,6,11,20} Our results show that cyclic hexamers can be formed either from smaller clusters by formation from six individual waters directly, or by interconversion of the hexamer structures with increasing temperature. As the temperature is increased, the stability of hexamer structures switches from favoring the structure with the most number of hydrogen bonds to the least, in accordance with entropic considerations.

The water dimer is present in the atmosphere at a temperature of 292.4 K, with a concentration of approximately 6 × 10¹⁴ molecules/cm³ in saturated air at 292.4 K.⁵³ We predict a water dimer concentration of 4 × 10¹⁴ water dimers/cm³ at this temperature, in remarkably good agreement with the experimental estimate. We predict water dimer concentrations of 9 × 10¹⁴ molecules/cm³, water trimer concentrations of 2.6 × 10¹² molecules/cm³, tetramer concentrations of approximately 5.8 × 10¹¹ molecules/cm³, and pentamer concentrations of approximately 3.5 × 10¹⁰ molecules/cm³ in saturated air at 298 K. These results support the suggestion that water clusters with $n < 6$ exist in numbers comparable to the ambient aerosol in the background troposphere.⁵³ In addition, these results support the suggestion that gas-phase reaction chemistry will be catalyzed by water clusters^{50,54–58} and that small shifts in absorption spectra of hydrates and complexes of molecules with hydrates could have a significant contribution to climate effects.⁵⁸ Finally, these results support the suggestion that in a global warming scenario higher temperatures will lead to increased absorption of solar radiation by water clusters.⁶¹ We are continuing to investigate structure and thermochemistry of conformers of larger water clusters in our laboratory.

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Supporting Information Available: Experimental figures and table (PDF). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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