Atmospheric Implications for Formation of Clusters of Ammonium and 1−10 Water Molecules

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Received: December 3, 2009; Revised Manuscript Received: February 16, 2010

A mixed molecular dynamics/quantum mechanics model has been applied to the ammonium/water clustering system. The use of the high level MP2 calculation method and correlated basis sets, such as aug-cc-pVDZ and aug-cc-pVTZ, lends confidence in the accuracy of the extrapolated energies. These calculations provide electronic and free energies for the formation of clusters of ammonium and 1−10 water molecules at two different temperatures. Structures and thermodynamic values are in good agreement with previous experimental and theoretical results. The estimated concentration of these clusters in the troposphere was calculated using atmospheric amounts of ammonium and water. Results show the favorability of forming these clusters and implications for ion-induced nucleation in the atmosphere.

Introduction

Aerosols are one of the least understood aspects of the global climate system, and these particles play a crucial role in temperature and weather. While aerosols are defined as a suspension of a solid or liquid particle in a gas, in atmospheric chemistry, the common usage is that an aerosol refers to the particulate component. Particles emitted directly into the atmosphere are called primary aerosols while those formed in the atmosphere through conversion of a gas to a particle are called secondary aerosols. Secondary aerosol nucleation begins with the formation of small precritical clusters that then grow to form an aerosol. Experimental sampling of aerosols is limited to those larger than 3 nm,[1] which restricts experimental data about small clusters. There are numerous theoretical models for aerosol formation, but they are not appropriate for modeling small cluster formation because they use bulk properties to describe the aerosol.

None of the current models of aerosol formation have been completely successful in matching environmental data.[2] It is known that water clusters are capable of absorbing significant amounts of energy,[3] and these clusters are not yet included in climate models due to the lack of data about their formation.[4] Detailed computational thermodynamics, such as those calculated in this study, can be useful in modeling the initial steps of aerosol growth by determining the equilibrium constants for cluster formation. Past computational studies of small aerosol clusters have often relied on input structures with limited conformational sampling. Although this may be appropriate for small water clusters with a limited number of conformers, such a procedure will be unlikely to sample the most relevant conformers as more waters are added. Achieving convergence for a large cluster system can be difficult, and incomplete sampling may result in inaccurate calculated cluster energies. In addition, some studies have relied on DFT calculations, which, although less computationally expensive, are generally less accurate for water clusters held together by London dispersion forces.[5]

The ammonium ion is primarily produced in the atmosphere from the agricultural release of ammonia,[6] which is converted to the cation by reaction with water or other atmospheric species. Ammonium in the atmosphere is known to play a major role in the deposition of nitrogen in the environment,[7] the control of acidity in precipitation,[8] and the formation of potentially dangerous fine aerosol particles.[9] Three structures for $NH_4^+(H_2O)_4$ have been detected in a free jet expansion in a vibrational predissociation spectroscopic experiment with an estimated internal temperature of approximately 130−170 K.[10,11] The main structure is the canonical structure with the four waters bound individually to each hydrogen on the ammonium cation.[12] The same spectroscopic experiment resulted in the identification of at least three isomers for $NH_4^+(H_2O)_5$. The $NH_4^+(H_2O)_5$ minimum energy structure has been reported in the literature,[13] and both minimum structures in electronic energy and free energy have been detected experimentally.[10] The $NH_4^+(H_2O)_6$ free energy structure minimum has also been detected experimentally;[10] this structure differs from the minima found through more recent ab initio calculations.[14–17] Kim and co-workers have published an extensive comparison of B3LYP, MP2, and CCSD(T) binding energies, enthalpies, and free energies at 100 and 150 K for $NH_4^+(H_2O)_n$ clusters.[15] They calculated complete basis set (CBS) limit MP2 and CCSD(T) calculations with aug-cc-pVnZ basis sets (n = D, T). Calvo and co-workers have investigated $NH_4^+(H_2O)_{5−19}$ clusters using the B3LYP/6-311++G(d,p) method;[16] and Zhao, Meot-Ner, and Gonzalez have used a Monte Carlo search combined with a computationally efficient density functional-based tight-binding method to search many conformations of $NH_4^+(H_2O)_{4−8}$ clusters.[17] As we shall show below, covering the conformational space of the ammonium−water clusters is exceedingly difficult, and the above-mentioned scientists did not locate the experimental free energy minima for the $NH_4^+(H_2O)_6$ cluster.[10]

In this paper, we report high-level, second-order Møller−Plesset perturbation theory (MP2) calculations, with a two-point extrapolation to the complete basis set limit (CBS), of structures and energies for $NH_4^+(H_2O)_n$ clusters, for n = 1−10 and

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TABLE 1: A Comparison of Extrapolation Methods on the Thermodynamics of Formation of NH$_4^+$H$_2$O Clusters at the MP2/CBS//MP2/6-31G* Level of Theory

extrapolation method	ΔE_0, kcal/mol	ΔG^0_{298}, kcal/mol
2-point: aug-cc-pVDZ, aug-cc-pVTZ	−18.85	−13.80
2-point: aug-cc-pVTZ, aug-cc-pVQZ	−18.87	−13.82
3-point: aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ	−18.86	−13.81
BSSE 2-point: aug-cc-pVDZ, aug-cc-pVTZ	−18.64	−13.59
BSSE 2-point: aug-cc-pVTZ, aug-cc-pVQZ	−18.76	−13.71
BSSE 3-point: aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ	−18.69	−13.64

comment on the implications of these results for secondary ion nucleation of aerosols. An extensive molecular dynamics search generated 100−300 trial structures for each cluster that were subsequently used as input structures for MP2 calculations.

Methods

Because verified minima have been reported for NH$_4^+$(H$_2$O)$_{1-4}$, energies for formation of these clusters at the MP2/CBS//MP2/ 6-31G* and MP2/CBS//MP2/aug-cc-pVDZ levels were calculated from reported literature structures.[12] Each of the larger cluster simulations, 5−10 waters, began by using molecular dynamics to sample different cluster configurations. These simulations were run with the Amber 9 MD suite of programs[18] at constant *N, V, P* at the highest possible temperature where a 10 ns (ns) MD simulation completed without fragmentation of the NH$_4^+$(H$_2$O)$_n$ cluster. After a 0.5 ns heating stage, 50 structures were initially extracted from even intervals of the last 9.5 ns production run. Each structure was run through a geometry optimization using Gaussian 03[19] at the MP2/6-31G* level. Test calculations included in the Supporting Information show MP2/6-31G* to be both accurate and relatively efficient, in agreement with previous results on water clusters.[20,21] The frequencies from optimized structures were scaled by 0.9646 and used to obtain entropies and free energies.[22] A single-point calculation with the aug-cc-pVDZ basis set was then completed for all optimized structures with a tight convergence criteria. Every low-energy structure, defined as within 2 kcal/mol of the minimum energy structure, had an additional single-point calculation completed with the aug-cc-pVTZ basis set. The ΔE_{el}, ΔE_0, ΔG^0_{242}, and ΔG^0_{298} values for the reaction were then calculated and recorded using both basis sets. These values were extrapolated to the complete basis set limit using a two-point DZ and TZ least-squares fit.[23] The extrapolation eliminated the need for basis set superposition error corrections.[24] All values are reported for the standard state of 1 atm. Following the completion of this process, another set of 50 structures was extracted and compared to the first. If no new low-energy structure was found, we judged that our low energy structure was the minimum. If a lower-energy structure was found, additional sets of 50 structures were extracted until a lower energy structure was not found. In the application of this process to the six largest ammonium clusters ($n = 6-10$), it was never necessary to extract more than 300 structures.

We calculated an estimated concentration of these clusters by solving for the equilibrium values using published data on ammonium levels at an agricultural site in North Carolina,[6] a concentration of water that reproduced 100% humidity,[25] a standard state of 1 atm of pressure, and temperatures of 242 and 298 K. The water concentrations were obtained from the Clausius−Clapeyron equation for saturated water vapor at 242 and 298 K, yielding values of 0.000 023 9 and 0.001 30 M, respectively. The ammonium concentration used was 1.84 × 10^{-6} g/m^3, or 1.02 × 10^{-10} M.[6] These calculations assume that the system is at equilibrium, contains only ammonium and water,

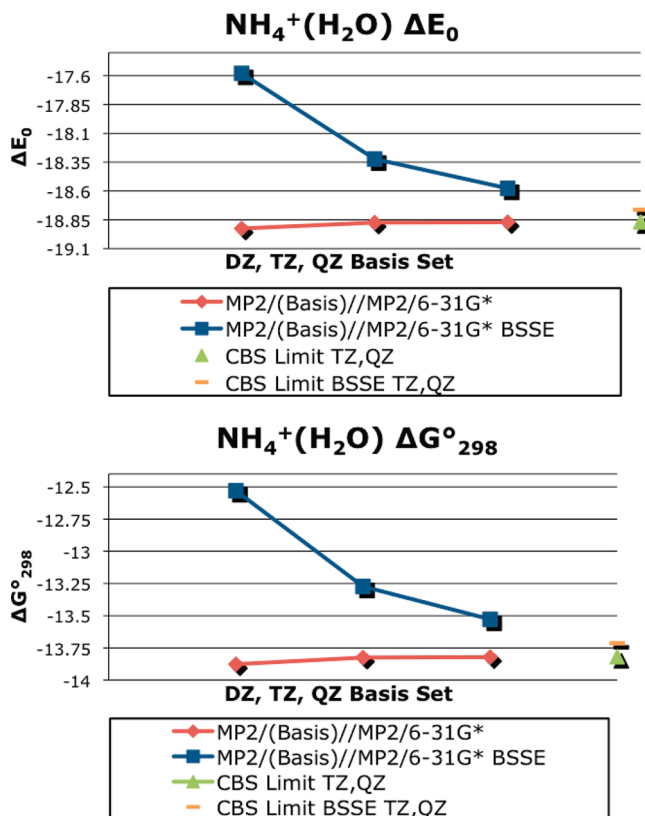**Figure 1.** A comparison of extrapolation methods and BSSE-corrected calculations on the thermodynamics of formation of NH$_4^+$H$_2$O clusters. The BSSE corrections using the aug-cc-pVDZ level of theory overestimate the error significantly. Extrapolations with and without correction for BSSE converge on the same final energies.

that the ammonium does not leave the system, and that the concentration of water is constant. For this system as defined, we have 10 equilibrium equations, included in the Supporting Information, and one unique solution that satisfies all these equations, including the feedback from all cluster formations.
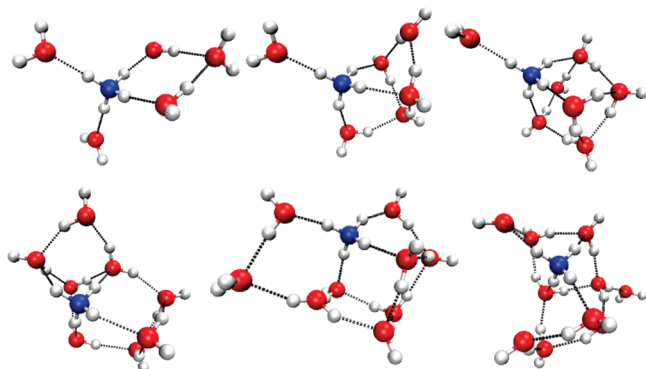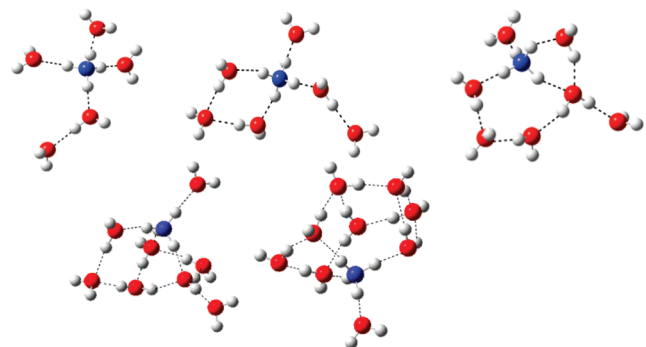
Results

Table 1 compares 2- and 3-point extrapolation methods, both with and without correction for basis set superposition error (BSSE), for formation of the NH$_4^+$(H$_2$O) cluster. Figure 1 shows that correction for BSSE with a double-ζ basis set overestimates the error significantly and that extrapolation to the MP2 CBS is essentially the same for BSSE-corrected and noncorrected values of energy and free energy.

Table 2 includes calculated values of ΔE_{el}, ΔE_0, and ΔG^0 for reactions of the ammonium cation with successive additions of water at standard conditions at ground level. The table also includes ΔG^0 values calculated at a temperature (242 K) and saturated water concentration corresponding to an altitude near the upper reaches of the troposphere, as well as the estimated concentration of clusters at the bottom and top of the tropo-

TABLE 2: Thermodynamic Data for the Reaction $NH_4^+(H_2O)_{n-1} + H_2O > NH_4^+(H_2O)_n$ Using MP2/CBS//MP2/6-31G* Values[a]

N	ΔE_{el}	ΔE_0	ΔG_{298}^0	concn[b]	ΔG_{242}^0	concn[c]	exptl[d] ΔG^0; 298, 242 K
1	−20.59	−18.85	−13.85	1.14×10^2	−14.86	2.11	−13.1; −14.4
2	−17.15	−15.33	−7.50	1.13×10^6	−9.16	2.30×10^5	−7.6; −8.9
3	−14.68	−13.02	−5.47	3.70×10^8	−6.93	2.45×10^8	−6.0; −7.1
4	−12.60	−11.23	−4.94	4.90×10^{10}	−6.17	5.34×10^{10}	−4.0; −5.4
5	−13.13	−9.89	−1.21	1.19×10^{10}	−2.65	7.71×10^9	−2.8; −4.2
6	−14.32	−10.63	0.68	1.20×10^8	−1.44	9.01×10^7	−2.5; −3.8
7	−11.36	−6.61	2.54	5.28×10^4	0.71	1.20×10^4	
8	−10.63	−8.58	−0.73	5.77×10^3	−2.53	1.36×10^3	
9	−14.17	−11.42	1.34	19.1	−1.48	17.2	
10	−12.76	−9.73	−0.43	1.26	−2.28	1.15	

[a] All energies in kcal/mol, and all concentrations in clusters/cm³. Standard state of 1 atm. [b] Calculated assuming $[NH_4^+] = 1.02 \times 10^{-10}$ M, $[H_2O] = 1.30 \times 10^{-3}$ M, and $T = 298$ K. [c] Calculated assuming $[NH_4^+] = 1.02 \times 10^{-10}$ M, $[H_2O] = 2.39 \times 10^{-5}$ M, and $T = 242$ K. [d] ΔG^0 at each temperature calculated from the average of the most reliable values for ΔH^0 and ΔS^0 from the NIST Tables, ref 26.

Figure 2. Low E_{el} clusters of $NH_4^+(H_2O)_n$, where $n = 5-10$.

Figure 3. Low G_{298} clusters of $NH_4^+(H_2O)_n$, where $n = 5-9$.

sphere. Included in Table 2 are the average of acceptable values[26] for ΔG_{242}^0 and ΔG_{298}^0 for formation of clusters containing one to six waters.[26–30] Figures 2 and 3 show the computed minimum electronic and Gibbs free energy structures for $NH_4^+(H_2O)_n$, where $n = 5-10$. The Gibbs free energy structures are the same at 242 and 298 K.

The $NH_4^+(H_2O)_5$ low-energy structure has been previously reported in the literature from computational and experimental studies,[13] but the free energy minimum has been detected only experimentally.[10] Our electronic energy minimum for $NH_4^+(H_2O)_6$ agrees with the high-level calculations of Kim but not with the DFT studies of other researchers, stressing the importance of high-level calculations.[14–17] The $NH_4^+(H_2O)_6$ free-energy structure minimum has also been detected experimentally[10] and is more favorable by about 1 kcal/mol than other free-energy structures reported from computational studies.[14–17] The very extensive study of the $NH_4^+(H_2O)_6$ cluster by Kim and co-workers[15] and earlier work by Lee and co-workers[10] find a different structure to be the free energy minimum. Specifically, structure 6I in Figure 3 of Lee et al[10] is equivalent to the high

level structure 6b in Figure 1 of Kim et al,[15] and the structure 6III in Figure 3 of Lee et al[10] is equivalent to the high-level structure we display in Figure 2. Experimental results demonstrate that the Kim et al. structure predominates at low temperatures, whereas our structure displayed in Figure 2 is one of the predominate isomers at higher temperatures.[10] It is also likely that Kim had reduced sampling because all of their MP2 and CBS calculations proceeded from their B3LYP minima.[5] Direct comparison via rmsd comparisons is not possible because the previously reported structures are not available. Our structures are available as Supporting Information for future researchers to compare their results.

The structures for 7−10 water ammonium clusters exhibit organized geometric patterns, and as more water molecules are added, the waters tend to form more of a cage around the central ammonium molecule. In general, the lowest-free-energy structures contain the fewest number of bonds for the system, resulting from the entropic cost, and the lowest-energy structures contain the most bonds for the system. This structural pattern is similar to that observed by Calvo, but our high-level calculations provide us with more confidence in our minima. The low-energy structure for $NH_4^+(H_2O)_{10}$ is a minimum in both electronic and free energy.

Discussion

Validation of Methodology. A key aspect of this study is how accurate we expect the numbers to be, given the assumptions made in this work. We believe we have made a good attempt to capture all the conformers through the method of running 100−300 MD structures through an MP2/6-31G* geometry optimization for the larger clusters ($n = 5-10$). For the smaller clusters ($n = 1-4$), we compared the MP2/CBS// MP2/6-31G* results with those for MP2/CBS//MP2/aug-cc-pVDZ and found that differences in ΔE_{el}, ΔE_0, and ΔG_{298}^0 were generally within 0.5 kcal/mol, with the differences decreasing as n increased. For example, for $n = 4$, there is no difference in ΔE_{el}, less than 0.1 kcal/mol difference in ΔE_0, and a 0.4 kcal/mol difference in ΔG_{298}^0 (data in the Supporting Information). All $NH_4^+(H_2O)_{n=5-10}$ structures from the MD simulations were geometry-optimized at the MP2/6-31G* level, and frequencies were scaled to obtain accurate entropic data. Single-point calculations at the MP2/aug-cc-pVDZ level identified all structures within 2 kcal/mol of the minimum, and additional single point calculations at the MP2/aug-cc-pVTZ level allowed for extrapolation to the MP2 CBS limit for all structures within 2 kcal/mol of both the zero point energetic and free-energy minimums. Evaluating the energies and free energies is de-

Atmospheric Implications for $NH_4^+(H_2O)_x$ Clusters

J. Phys. Chem. A, Vol. 114, No. 12, 2010 **4269**

pendent on ensuring that the extrapolation scheme is adequate, as is establishing whether the extrapolation routines compensate for BSSE.

As shown in Table 1, extrapolation of the zero point energy for formation of the $NH_4^+(H_2O)$ cluster from NH_4^+ and H_2O is -18.9 kcal/mol using a two-point extrapolation with double- and triple-ζ basis sets, a two-point extrapolation with triple- and quadruple-ζ basis sets, and using a three-point extrapolation with double-, triple-, and quadruple-ζ basis sets. The same extrapolations after first correcting for BSSE yields values of -18.6, -18.8, and -18.7 kcal/mol. Extrapolation of the free-energy difference for formation of the $NH_4^+(H_2O)$ cluster is -13.8 kcal/mol for all three extrapolations, and these same three extrapolations after correcting for BSSE yield values of -13.6, -13.7, and -13.6 kcal/mol. Figure 1 shows that correcting for BSSE at the MP2/aug-cc-pVDZ level dramatically overestimates the error, calling into question the common practice of computing the BSSE and using one-half the BSSE correction in determining the final energy. Clearly, the correct amount of BSSE correction to include is basis-set-dependent. The two graphs in Figure 1 clearly show that two-point extrapolations with or without BSSE corrections give the same answers to within 0.1 or 0.2 kcal/mol. Xantheas has shown this same phenomena for water clusters, where BSSE corrected and uncorrected energies yield the same final energies for formation of clusters of 2−6 waters[24] and formation of the D_{2d} and S_4 water octamers.[31] In addition, either two-point extrapolation (DZ/TZ or TZ/QZ) is equivalent to the DZ/TZ/QZ three-point extrapolation.

Errors in free energies are introduced by the use of scaled harmonic versus anharmonic MP2 frequencies. We have shown that these potential errors are small relative to formation of water clusters[20,21,25,32,33] and estimate that these errors will not affect the location of minimum free energy structures because of the large number of configurations that have been sampled. It is somewhat surprising that MP2/6-31G*-scaled frequencies are as good as anharmonic MP2 frequencies with the Dunning basis sets, yet we have shown this is true for water clusters.[33] This is no doubt why our previous calculations of water clusters based on MP2/6-31G* are better than those using the G3 method,[34] which is based on scaled HF/-31G* frequencies.[5,20,21,25,32,33] Calculations on sulfur are more problematic, however, and MP2/6-31G* cannot be trusted for $CS_2(H_2O)_n$ clusters.[35] Nevertheless, for a small, positive ion such as NH_4^+, it is reasonable to expect decent results for clusters of this ion with water using MP2/6-31G*-scaled frequencies.

Molecular dynamics simulations produced large numbers of different configurations for each cluster. Each simulation was run at successively higher temperatures until the cluster broke apart, at which point the preceeding run at the highest tolerated temperature was used for further analysis. The temperatures are not real, since the cluster size is small and molecular dynamics use classical force fields. For the $n = 5$ water cluster, using a temperature of 250 K, we produced a total of 200 structures that were geometry-optimized with the MP2/6-31G* method and subject to single-point calculations with the aug-cc-pVDZ and aug-cc-pVTZ basis sets. We found four structures within the absolute minimum in zero-point energy and in free energy. For the $n = 6$ cluster, using a temperature of 200 K, we produced a total of 300 structures that were geometry-optimized with the MP2/6-31G* method and evaluated further with the DZ and TZ basis sets. There were no structures within 2 kcal/mol of the free energy minimum and eight structures within 2 kcal/mol of the zero point energy minimum. For the $n = 7$

cluster, using a temperature of 170 K, we examined 300 structures by this same process. We found seven structures within 2 kcal/mol of the free energy minimum and no structures within 2 kcal/mol of the zero point energy minimum. For the $n = 8$ cluster, using a temperature of 130 K, we examined 100 structures, and found four within the 2 kcal/mol cutoff in free energy and seven within the same cutoff in zero point energy. For the $n = 9$ cluster, using a temperature of 140 K, we examined 200 structures. Three structures were within 2 kcal/mol of the free energy minimum, and two structures were within 2 kcal/mol of the zero point energy minimum. For the $n = 10$ cluster, using a temperature of 150 K, we examined 100 structures; three were within 2 kcal/mol of the free energy minimum, and three were within 2 kcal/mol of the zero point energy minimum. Overall, we found that the number of structures that were within 2 kcal/mol of either minimum was quite small, indicating that a more detailed conformational analysis that includes Boltzmann averaging will probably not change the big picture in what is reported below.

Equilibrium calculations assume that by using the free energies for cluster formation, and initial concentrations of water and the ion in question, the final concentrations of each cluster can be determined. Garrett and co-workers have discussed the treatment of dissociative states in the calculation of the partition function of the weakly bound water dimer system.[36] Their approach is complicated because there is no unique procedure to constrain the phase space of the dimer, and the values of the dimer partition function change by over 2 orders of magnitude, depending on the choice of constraint.[36] Saykally and co-workers have made extensive spectroscopic measurements combined with a global analysis of the ground state data to refine the description of the excited vibration rotation tunneling states of the water dimer.[37,38] Leforestier and co-workers have determined the equilibrium constant for the water dimer over the temperature range of 190−390 K by using a flexible potential energy surface fitted to spectroscopic data.[39] The experimental value for the water dimer equilibrium constant over the limited and high (for atmospheric chemistry purposes) temperature range of 358−386 K was measured from thermal conductivity experiments of Curtiss and co-workers,[40] yielding a ΔG_{358}^0 of 3.1 kcal/mol. Assuming that ΔH does not change significantly from 358 to 298 K, we have used the Curtiss values to estimate the experimental value for ΔG_{298}^0 to be 1.95 kcal/mol, which is in excellent agreement with values (1.7−2.1 kcal/mol) calculated using high-level quantum chemistry approaches.[25] Therefore, we think our approach yields reliable estimates for free energies and, thus, equilibrium constants and the resulting concentrations for the ammonium−water clusters.

Analysis of Results. Experimentally, three structures for $NH_4^+(H_2O)_4$ have been found in a free jet expansion with an estimated internal temperature of approximately 130−170 K.[10,11] The predominant structure is the canonical structure with the four waters bound individually to each hydrogen on the ammonium cation.[12] The same vibrational predissociation spectroscopic experiment located at least three isomers for $NH_4^+(H_2O)_5$, with the structure reported in this paper in Figure 2 the most abundant form at the lowest temperatures (the same as structure 5II in ref 10). Our free energy minimum displayed in Figure 3 was also found in the beam experiment, increasing in abundance at higher temperatures (structure 5I in ref 10). As noted previously, the ring closing process to form $NH_4^+(H_2O)_5$ (Figure 2) from $NH_4^+(H_2O)_5$ (Figure 3) will be entropically disfavored at higher temperatures.[13]

The thermodynamic values from our method agree with the literature results for the smaller ammonium−water clusters within experimental uncertainty (Table 2). This, combined with the ability of the MP2/CBS method to predict the predominate clusters found experimentally,[10] provides confidence in the thermodynamic quantities we obtained for the larger clusters as well. The cluster concentrations, which come directly from the cluster thermodynamics, provide the clearest picture of how water and ammonium will interact. They demonstrate that at room temperature, clusters with up to 10 waters will form, albeit in very small quantities because of the small amount of ammonium ion initially present. The large negative value for the formation of the $NH_4^+(H_2O)$ cluster ensures that in our atmosphere, any production of the ammonium ion will lead to cluster formation with water. There is a clear peak in the distribution, with clusters of four and five waters being the most abundant. In addition, all of the ammonium ions in the system will be bound in some sort of water cluster.

The uneven nature of the thermodynamics after $NH_4^+(H_2O)_5$ is quite interesting. The experimental free energy values for formation of $NH_4^+(H_2O)_n$ from $NH_4^+(H_2O)_{n-1}$ at 298 K decrease from −6 kcal/mol for $n = 3$, to −4 kcal/mol for $n = 4$, to −2.8 kcal/mol for $n = 5$, to −2.5 kcal/mol for $n = 6$; yet, the calculated MP2/CBS free energies continue to get more positive to $n = 7$, then begin oscillating for $n = 8-10$. The calculated oscillating results could be real, suggesting that even numbered water clusters are more favorably bound to the ammonium ion, or it could mean that a more detailed conformational analysis needs to be completed with a Boltzmann distribution to completely capture the experimental thermodynamic results. Finally, it could mean that the error bars for the experiments reported in the NIST database are becoming larger at higher values of n. Further work investigating these potential sources of error is underway.

It is unclear what the fate of initially formed clusters is in the atmosphere, and it is worth pointing out some of the possibilities here. As the $NH_4^+(H_2O)_n$ clusters rise in the atmosphere, the water concentration decreases, which favors formation of smaller clusters. On the other hand, ΔG^0 becomes more favorable as clusters rise because of falling temperature. Assuming that all the NH_4^+ in the atmosphere produced from agricultural sites continues to rise to the top of the troposphere, these two opposite effects result in no net change in the peak distribution of water clusters with this concentration scenario. It is not clear whether this is, indeed, the case, that clusters continually rise in the atmosphere, so it may be that our calculations of cluster concentration are better suited to the situation closest to the Earth, near the point sources for ammonium production. Nevertheless, we expect that the initial stages of aerosol formation in a pure ammonium−water system are seeded by $NH_4^+(H_2O)_{n=3-6}$ clusters. Clearly, changes in the initial concentrations of NH_4^+ or water in the atmosphere can potentially change the cluster distribution. Our results presented here use the published experimental concentration of NH_4^+ measured over a year's time at an agricultural site in North Carolina.[6] Under these conditions, the pure ammonium−water system is not expected to increase in cluster size, and other small clusters, such as hydrated sulfate or nitrate, may be important in increasing overall cluster size. Alternatively, already established aerosols may absorb small species such as the ammonium−water clusters presented here.

This work is a preliminary step toward understanding how aerosols grow from small clusters. It is quite likely that ammonium clusters grow larger through the addition of other hydrated chemical species, such as sulfates or nitrates. Walker and co-workers, in their measurements of ambient ammonia and ammonium aerosol at three sites in North Carolina found that the aerosols contained significant amounts of nitrate, sulfate, and chloride anions.[6] We are currently calculating larger clusters using RI-MP2 and will include conformational analysis in such a way as to include all the lowest-free-energy structures in each cluster. However, our methodology has provided accurate and valuable insight into ammonium water clusters and can easily be expanded to larger clusters and other cluster systems. Continued work is essential to determine whether the $NH_4^+(H_2O)_n$ binary system is a critical component of secondary aerosol formation in the atmosphere.

Conclusion

The energies and free energies of formation of $NH_4^+(H_2O)_{1-10}$ were calculated using a mixed molecular dynamics/quantum mechanics methodology at the MP2/CBS//MP2/6-31G* level of theory. The thermodynamic results agree with available literature values and improve upon previous computational studies. The concentration of these clusters in the atmosphere has been estimated on the basis of the free-energy values and saturated concentrations of water and measured concentrations of ammonium ion present above an agricultural site in North Carolina. These data reveal that all ammonium present in the atmosphere will be in a water cluster, and under these conditions, the vast majority of ammonium will be clustered with four or five water molecules. More data must be gathered on larger cluster systems to determine whether this binary system will be important on an atmospheric scale and the degree to which quantum-based cluster estimates agree with experimental measurements.

Supporting Information Available: Optimized geometries, thermodynamic corrections, electronic energies, enthalpies, and free energies in Hartrees for all structures reported in this paper. A comparison of the MP2 two-point extrapolation on the MP2/6-31G* geometries versus the MP2/aug-cc-pVDZ geometries. The equations used to estimate the final concentrations of all clusters at two temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Atmospheric Implications for $NH_4^+(H_2O)_x$ Clusters

J. Phys. Chem. A, Vol. 114, No. 12, 2010 **4271**

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