A density functional study on water-sulfuric acid-ammonia clusters and implications for atmospheric cluster formation

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[1] We present results for the electronic and atomic structures of different size molecular clusters containing sulfuric acid, water, and ammonia molecules. The electronic structure calculations are performed using the DMol^3 quantum chemical program packages and the PW91 density functional. We report implications of our results for atmospheric cluster size distributions. Our calculations indicate that ammonia is bonded to the cluster structures much more strongly than water. The presence of ammonia also strengthens the binding of sulfuric acid molecules to the clusters, and significantly increases the formation of clusters containing two sulfuric acid molecules and $0-2$ water molecules. However, owing to the low overall concentration of two-acid clusters, the fraction of ammonia-containing clusters in the calculated atmospheric cluster size distribution was still very low.

1. Introduction

[2] The results obtained so far suggest that water, sulfuric acid and ammonia are the most important molecules involved in new atmospheric particle formation by nucleation [*Korhonen et al.*, 1999; *Anttila et al.*, 2005]. Atmospheric ammonia is mainly a result of emissions from NH_3- based fertilizers and industry [*Seinfeld and Pandis*, 1998], whereas sulfuric acid is produced from SO_2 emitted into the air by both natural and anthropogenic processes. A complete understanding of the chemical reactions involved in the formation of sulfate-containing aerosols from gas-phase species would have significant implications for atmospheric chemistry.

[3] The particle production rate obtained by using classical nucleation theory for sulfuric acid-water (H_2SO_4 - H_2O) reactions underestimates the production rate observed in the atmosphere severely [*Kulmala et al.*, 2004]. However, a formation mechanism involving ammonia (H_2SO_4 - NH_3 - H_2O) could explain the observed high production rates. Recent experimental observations and comparison to the results of classical nucleation theory indicate that ammonia may play a significant role in aerosol formation.

[4] Classical nucleation theory treats the clusters as bulk liquid droplets. In the water–sulfuric acid–ammonia system, the smallest stable clusters consist of only a few molecules. Thus liquid drop models describe them very inaccurately. Classical simulations [*Kathman and Hale*, 2001; *Kusaka et al.*, 1998] capture the true nature of newly formed particles as molecular clusters, but suffer from the lack of transferable interaction potentials able to describe correctly the various binding states of, for example, water and sulfuric acid. Quantum chemical methods are needed to understand properties of these clusters, where proton transfer is an essential part of bond formation.

[5] Previously, the role of ammonia in the hydrates of sulfuric acid has been computationally studied with density functional theory (DFT) calculations by *Ianni and Bandy* [1999] using the B3LYP functional and the 6-311++G(2d,2p) basis set, and by *Larson et al.* [1999], who also use B3LYP with a 6-311++G(d,p) basis set, but furthermore apply the second-order frozen-core Møller-Plesset perturbation approximation (MP2). The studied structures contained one sulfuric acid molecule and up to five water molecules. Both studies have calculated equilibrium structures, binding energies, harmonic frequencies and free energies of formation reactions. On the basis of their calculations, Ianni and Bandy concluded that ammonia does not enhance particle formation. In contrast, later experimental studies by *Hanson and Eisele* [2002] and *Ball et al.* [1999] found that ammonia significantly enhances nucleation in the water–sulfuric acid system.

[6] In order to attempt to resolve the obvious contradictions between experimental and observational results, we have carried out DFT calculations on the electronic and atomic structure of clusters containing sulfuric acid, water and ammonia molecules $(H_2SO_4)_n \cdot NH_3 \cdot (H_2O)_m$. The stud-

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ied clusters contain one ammonia molecule, $1-2$ sulfuric acids and $0-7$ water molecules. Total energies, free energies, binding energies and atmospheric cluster size distributions are derived from the results of the electronic structure calculations.

2. Computational Details

[7] Our calculations were carried out by using density functional theory within the DMol^3 program package [*Accelrys Software Inc.*, 2001; *Delley*, 1990, 2000]. In the DMol^3 calculations, the geometrical optimizations were performed with the Perdew-Wang [*Perdew et al.*, 1992] PW91 functional [*Perdew et al.*, 1996], using DNP (Double Numerical Precision) basis functions. The DNP basis functions are double numerical atomic orbitals augmented by polarization functions. The medium grid mesh points were employed for the matrix integrations. The self-consistent field calculations were carried out with convergence criteria of 10^{-6} a.u. with respect to the energy and electron density. Geometry optimizations were performed using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [*Fletcher*, 1980], with convergence criteria of 10^{-3} a.u. with respect to the gradient, 10^{-3} a.u. to the displacement and 10^{-5} a.u. to the energy.

[8] *Tssuuki and Lüthi* [2001] have claimed that for hydrogen-bound systems, the PW91 functional is superior to the B3LYP functional used in most previous studies on sulfuric acid–containing clusters. However, it should be noted that more recent studies [see, e.g., *Zhao et al.*, 2006] have found that all older "second- and third-generation" DFT functionals such as B3LYP and PW91 perform inadequately, especially for noncovalently bonded systems, when compared to modern "fourth-generation" density functionals such as MPW1B95 or PWB6K. In another study [*Kurtén et al.*, 2006] we have calculated the basis-set superposition error (BSSE) of the electronic and Gibbs free energy changes of the reaction $H_2SO_4 + NH_3 \leftrightarrow H_2SO_4 \cdot NH_3$ to be ~ 1.3 kcal mol^{-1} at the PW91/ D95++(d,p) level, which probably corresponds roughly in quality to the PW91/DNP results presented here. (It should be noted that some authors [e.g., *Delley*, 1990] argue that BSSE for numerical basis sets such as DNP is close to zero, and that a benchmarking study on hydrogen-bound complexes by *Benedek et al.* [2005] considered the DNP set to be comparable in quality to quite large triple-zeta basis sets such as 6-311+G(3df, 2pd). However, in the absence of further benchmarking studies or actual counterpoise calculations using numerical basis sets we cannot fully endorse these claims.) Thus our thermochemical results cannot be considered to be highly accurate. Nevertheless, the qualitative conclusions of our thermochemical analysis, and its atmospheric implications, are still valid. Also, our main conclusions with atmospheric implications are related to differences between free energies of different reactions, and these are much less sensitive to the method and basis set used than the free energy values themselves [*Kurtén et al.*, 2006]. It should be noted that our calculations indicate that if BSSE errors of under 0.5 kcal mol^{-1} at the DFT level are desired, basis sets of aug-cc-pV(T + d)Z quality or higher should be used. With current computer power, this is clearly unfeasible for the larger clusters studied in this paper.

3. Thermodynamic Properties

[9] To link computational results with atmospheric conditions we have calculated the entropies and the thermal contributions to the enthalpies and Gibbs free energies of the energetically most stable isomers of the clusters we studied at a temperature of 265 K and a reference pressure of vapor consisting of clusters set to $P_{ref} = 1$ atm. The values have been calculated from the PW91/DNP data on the cluster geometries and vibrational frequencies using the rigid rotor and harmonic oscillator approximations. The zero-point vibrational energy is included in the thermal part of the enthalpy term H_{therm}. The thermal contribution to the free energy, G_{therm}, is calculated from H_{therm} and the entropy S as

$$G_{therm}(T, P_{ref}) = H_{therm}(T) - TS(T, P_{ref}). \quad (1)$$

Correspondingly, the total free energy G is given by

$$G(T, P_{ref}) = G_{therm}(T, P_{ref}) + E_0, \quad (2)$$

where E_0 is the electronic energy. Similarly, the total enthalpy is given as

$$H(T) = H_{therm}(T) + E_0. \quad (3)$$

The formation free energy of a cluster with n_{sa} acid n_{am} ammonia and n_{wa} water molecules is

$$\Delta G_{cluster} = G_{cluster} - n_{sa}G_{sa,free} - n_{am}G_{am,free} - n_{wa}G_{wa,free}, \quad (4)$$

where we have defined the reference state to consist of free monomers of sulfuric acid, ammonia and water, with free energies $G_{sa,free}$, $G_{am,free}$ and $G_{wa,free}$, respectively. The equilibrium constants for cluster formation are defined as

$$K_{cluster}(T, P_{ref}) = e^{\frac{-\Delta G_{cluster}(T, P_{ref})}{RT}}. \quad (5)$$

The partial pressure of a cluster containing n_{sa} acid n_{am} ammonia and n_{wa} water molecules is then given by

$$P_{cluster} = P_{ref} \times K_{cluster} \times \left(\frac{P_{sa,free}}{P_{ref}}\right)^{n_{sa}}$$
$$\times \left(\frac{P_{am,free}}{P_{ref}}\right)^{n_{am}} \times \left(\frac{P_{wa,free}}{P_{ref}}\right)^{n_{wa}} \quad (6)$$

in terms of the partial pressures of the free, unbonded monomers $P_{sa,free}$, $P_{am,free}$ and $P_{wa,free}$.

4. Results and Discussion
4.1. Structural and Chemical Analysis

[10] The optimized, most stable PW91/DNP cluster structures are shown in Figure S1 of the auxiliary material[1]. The

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[1]Auxiliary material data sets are available at ftp://ftp.agu.org/apend/jd/ 2006jd007391. Other auxiliary material files are in the HTML.

Table 1. Thermodynamic Properties of the Most Stable Isomers of the Different Cluster Types at 265 K and 1 atm, Using the DMol[3] Program at the PW91/DNP Level[a]

Cluster							$K = e^{(-\Delta G/RT)}$	Example Conditions		
n_{sa}	n_{am}	n_{wa}	E_0, Hartrees	H_{therm}, kcal mol^{-1}	G_{therm}, kcal mol^{-1}	S, cal mol^{-1} K^{-1}	For P_{ref} = 1 atm	P(atm)	%sa	%am
0	0	1	−76.4411	15.1	3.07	45.6	1	1.63×10^{-3}	0	0
0	1	0	−56.5618	23.1	10.6	47.2	1	1.40×10^{-11}	0	100
1	0	0	−700.3448	26.6	7.7	71.2	1	1.59×10^{-13}	22.8	0
1	0	1	−776.8073	43.3	21.1	84.0	4.13×10^{2}	1.08×10^{-13}	15.4	0
1	0	2	−853.2685	59.7	34.2	96.1	5.15×10^{4}	2.19×10^{-14}	3.1	0
1	0	3	−929.7347	75.7	48.7	102.1	2.23×10^{8}	1.55×10^{-13}	22.2	0
1	0	4	−1006.1984	92.7	63.3	110.6	3.23×10^{10}	3.67×10^{-14}	5.2	0
1	0	5	−1082.6607	109.4	76.4	124.2	1.67×10^{13}	3.10×10^{-14}	4.4	0
1	0	6	−1159.1241	125.7	89.2	137.7	6.22×10^{16}	1.88×10^{-13}	26.9	0
2	0	0	−1400.7125	54.4	26.6	104.6	4.64×10^{2}	1.18×10^{-23}	0	0
2	0	1	−1477.1775	70.9	40.3	115.5	2.09×10^{6}	8.64×10^{-23}	0	0
2	0	2	−1553.6443	87.6	55.7	120.6	3.04×10^{9}	2.06×10^{-22}	0	0
2	0	3	−1630.1108	104.6	69.5	132.3	5.07×10^{13}	5.60×10^{-21}	0	0
2	0	4	−1706.5805	120.0	83.8	136.6	1.81×10^{19}	3.26×10^{-18}	0	0
2	0	5	−1783.0442	136.6	96.5	151.3	1.26×10^{23}	3.73×10^{-17}	0	0
2	0	6	−1859.5099	152.7	110.9	158.1	3.17×10^{26}	1.53×10^{-16}	0	0
2	0	7	−1935.9712	169.9	123.5	175.0	1.09×10^{29}	8.62×10^{-17}	0	0
2	0	8	−2012.4324	187.4	138.5	184.6	5.32×10^{29}	6.84×10^{-19}	0	0
1	1	0	−756.9364	50.4	28.4	83.1	1.62×10^{7}	3.61×10^{-17}	0	0
1	1	1	−833.3995	67.7	43.2	92.5	7.18×10^{8}	2.62×10^{-18}	0	0
1	1	2	−909.8657	85.3	58.0	103.3	1.83×10^{12}	1.09×10^{-17}	0	0
1	1	3	−986.3280	102.1	71.3	115.9	5.47×10^{14}	5.32×10^{-18}	0	0
1	1	4	−1062.7903	118.9	85.3	126.8	5.38×10^{16}	8.54×10^{-19}	0	0
1	1	5	−1139.2522	135.6	98.9	138.6	6.75×10^{18}	1.75×10^{-19}	0	0
2	1	0	−1457.3184	79.1	49.8	110.6	1.41×10^{15}	5.90×10^{-22}	0	0
2	1	1	−1533.7829	96.7	62.4	129.6	2.93×10^{19}	1.70×10^{-20}	0	0
2	1	2	−1610.2506	112.3	77.6	130.9	1.54×10^{23}	1.46×10^{-19}	0	0
2	1	3	−1686.7156	130.2	92.3	143.1	1.37×10^{26}	2.12×10^{-19}	0	0
2	1	4	−1763.1761	146.2	105.9	152.0	2.28×10^{27}	5.76×10^{-21}	0	0
2	1	5	−1839.6418	163.6	117.5	173.7	1.05×10^{33}	4.36×10^{-18}	0	0
2	1	6	−1916.1006	179.5	131.4	181.5	2.13×10^{33}	1.44×10^{-20}	0	0
2	1	7	−1992.5627	197.0	146.4	190.8	2.19×10^{34}	2.41×10^{-22}	0	0

[a]Thermodynamic properties comprise electronic energy E_0, thermal contribution to the enthalpy H_{therm}, thermal contribution to the Gibbs free energy G_{therm}, and entropy S. T = 265 K. The first three columns give the numbers of molecules of sulfuric acid (n_{sa}), ammonia (n_{am}) and water (n_{wa}) in the cluster. K is the equilibrium coefficient for cluster formation. The last three columns give partial pressures and the percentage of sulfuric acid and ammonia molecules bonded to various cluster types at atmospheric model conditions: RH 50% P_{am} = 14 ppt = 3.877×10^8 cm^{-3} and P_{sa} = 0.7 ppt. = 1.939×10^7 cm^{-3}. The data for (H$_2$SO$_4$)$_2 \cdot$ (H$_2$O)$_m$ clusters (with m = 0−8) is from *Ding et al.* [2003].

corresponding Cartesian coordinates are given in Table S1 of the Supplementary Material. In general, the one-acid clusters resemble those presented by *Ianni and Bandy* [1999], with two notable differences: the H-bond lengths are somewhat shorter, and proton transfer from sulfuric acid to ammonia is predicted to occur already in the H$_2$SO$_4 \cdot$NH$_3 \cdot$H$_2$O cluster, whereas Ianni and Bandy predicted that four waters were required to facilitate the transfer. Both differences can be attributed to the choice of density functional. As shown by *Kurtén et al.* [2006], PW91 consistently predicts stronger H-bonding (and thus shorter bonds) and greater hydrogen transfer ratios than B3LYP. For the two-acid clusters, proton transfer is predicted to occur even without the presence of any water molecules, and a second proton transfer (from sulfuric acid to water) is predicted to occur in the (H$_2$SO$_4$)$_2 \cdot$NH$_3 \cdot$(H$_2$O)$_2$ cluster. There are no other published results of (H$_2$SO$_4$)$_2 \cdot$NH$_3 \cdot$(H$_2$O)$_m$ cluster structures, but given the above results it would be reasonable to assume that, for example, B3LYP studies would predict a later onset of both the first and second proton transfers. Most of the two-acid cluster structures contain more than one bond between ammonia and the acid molecules, which is hardly surprising given the general affinity of acids and bases for each other.

4.2. Thermochemical Analysis

[11] The thermochemical parameters calculated at the PW91/DNP level are presented in Table 1. The PW91/DNP data for the (H$_2$SO$_4$)$_2 \cdot$(H$_2$O)$_m$ clusters (with m = 0−8) are from *Ding et al.* [2003]. All values correspond to a temperature of 265 K and a pressure of 1 atm unless otherwise stated.

[12] Figure 1 shows the Gibbs free energy for the reactions (H$_2$SO$_4$)$_n \cdot$(H$_2$O)$_m$ + NH$_3 \leftrightarrow$ (H$_2$SO$_4$)$_n \cdot$NH$_3 \cdot$(H$_2$O)$_m$, with m = 0−5 and m = 0−7 for n = 1 and n = 2, respectively. It can be seen that the ammonia molecule is strongly bonded to the sulfuric acid − water clusters, and that the binding predicted for one-acid clusters at the PW91/DNP level is several kcal mol^{-1} stronger than that predicted by *Ianni and Bandy* [1999] at the B3LYP/6-311++G(2d,2p) level (at the temperatures of 273 K and 248 K). See Table S2a in the auxiliary material for a detailed comparison. It can further be seen that the ammonia molecule is bonded much more strongly to two-acid clusters than to one-acid clusters, the difference in free energies being around −7 kcal mol^{-1} for clusters containing less than four water molecules. For the larger two-acid clusters, the absolute value of the Gibbs free energy for the addition of an ammonia molecule
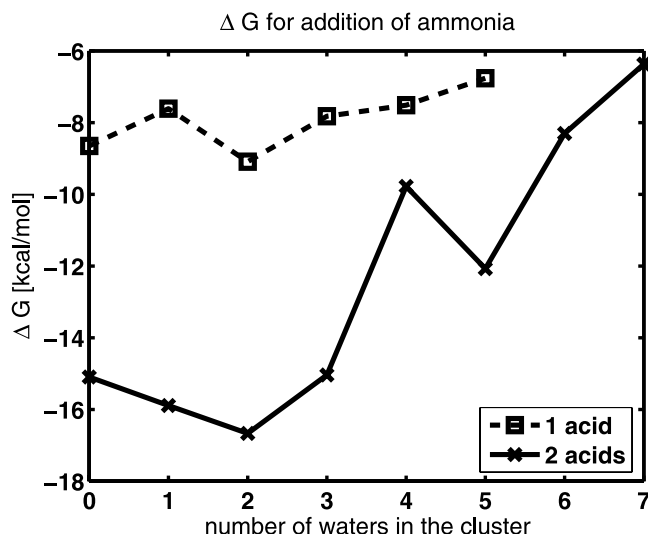
Figure 1. Gibbs free energy for the reactions $(H_2SO_4)_n \cdot (H_2O)_m + NH_3 \leftrightarrow (H_2SO_4)_n \cdot NH_3 \cdot (H_2O)_m$, with $m = 0-5$ and $m = 0-7$ for $n = 1$ (1 acid) and $n = 2$ (2 acids), respectively. $T = 265$ K, $p = 1$ atm. Values correspond to the most stable isomers.

decreases somewhat, as the ammonia molecule is increasingly bonded to water instead of acid molecules.

[13] Figure 2 shows the Gibbs free energy for the reactions $H_2SO_4 \cdot NH_3 \cdot H_2O_{m-1} + H_2O \leftrightarrow H_2SO_4 \cdot NH_3 \cdot (H_2O)_m$ and $H_2SO_4 \cdot (H_2O)_m + H_2O \leftrightarrow H_2SO_4 \cdot H_2O_{m+1}$ (with $m = 1-5$) and Figure 3 for the reactions $(H_2SO_4)_2 \cdot NH_3 \cdot H_2O_{m-1} + H_2O \leftrightarrow (H_2SO_4)_2 \cdot NH_3 \cdot (H_2O)_m$ and $(H_2SO_4)_2 \cdot H_2O_m + H_2O \leftrightarrow H_2SO_4 \cdot H_2O_{m+1}$ (with $m = 1-7$). (The indices have been chosen so that clusters containing equal numbers of molecules may be compared.) It can be seen from Figure 2 that adding an ammonia molecule to a one-acid cluster has a very small impact on the water affinity of the cluster. Furthermore, Figure 3 indicates that the presence of ammonia in two-acid clusters actually decreases the water affinity of clusters containing four, five, six or eight molecules in total. All of the Gibbs free energies for the addition of water molecules are significantly lower than those predicted by *Bandy and Ianni* [1998] for $H_2SO_4 \cdot (H_2O)_m$ clusters ($m = 0-7$) and *Ianni and Bandy* [1999, 2000] for $H_2SO_4 \cdot NH_3 \cdot (H_2O)_m$ ($m = 0-5$) and $(H_2SO_4)_2 \cdot (H_2O)_m$ ($m = 0-6$) clusters (at the temperatures of 273 K and 248 K)). See Tables S2b–S2d in the auxiliary material for a detailed comparison.

[14] Figure 4 shows the Gibbs free energy for the reactions $(H_2SO_4) \cdot NH_3 \cdot (H_2O)_m + H_2SO_4 \leftrightarrow (H_2SO_4)_2 \cdot NH_3 \cdot (H_2O)_m$ and $(H_2SO_4) \cdot (H_2O)_{m+1} + H_2SO_4 \leftrightarrow (H_2SO_4)_2 \cdot (H_2O)_{m+1}$, with $m = 0-5$. The presence of ammonia increases the acid affinity of sulfuric acid – water clusters significantly, as expected. The difference in the Gibbs free energies for the addition of a sulfuric acid molecule to clusters containing the same number of molecules is between -3.1 and -7.1 kcal mol^{-1}, except for the six-molecule case, where the difference is only -0.9 kcal mol^{-1}.

[15] In order to assess the role of ammonia in atmospheric particle formation, the most important thermochemical parameters are not the formation free energies themselves,
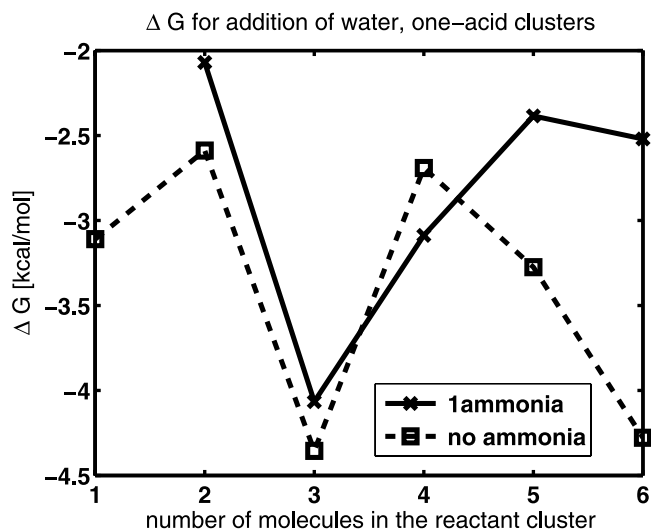

Figure 2. Gibbs free energy for the reactions $H_2SO_4 \cdot NH_3 \cdot H_2O_{m-1} + H_2O \leftrightarrow H_2SO_4 \cdot NH_3 \cdot (H_2O)_m$ and $H_2SO_4 \cdot (H_2O)_m + H_2O \leftrightarrow H_2SO_4 \cdot H_2O_{m+1}$ (with $m = 1-5$).

but the differences in the free energies of the reactions $(H_2SO_4)_n \cdot (H_2O)_m + H_2O \leftrightarrow (H_2SO_4)_n \cdot H_2O_{m+1}$ and $(H_2SO_4)_n \cdot (H_2O)_m + NH_3 \leftrightarrow (H_2SO_4)_n \cdot NH_3 \cdot (H_2O)_m$. These are plotted in Figure 5, with $m = 0-5$ and $m = 0-7$ for $n = 1$ and $n = 2$, respectively. The difference is between -4.2 and -5.5 kcal mol^{-1} for the smaller one-acid clusters, and between -5 and -12 kcal mol^{-1} for the two-acid clusters. It should be noted that though the studies of *Bandy and Ianni* [1998] and *Ianni and Bandy* [1999, 2000] predict significantly higher Gibbs free energies for all reactions studied here, the absolute values of the differences between the free energies for the $H_2SO_4 \cdot (H_2O)_m + H_2O \leftrightarrow H_2SO_4 \cdot (H_2O)_{m+1}$ and $H_2SO_4 \cdot (H_2O)_m + NH_3 \leftrightarrow H_2SO_4 \cdot NH_3 \cdot (H_2O)_m$ reactions calculated from their data (at 273 K and 248 K) are only slightly smaller than those
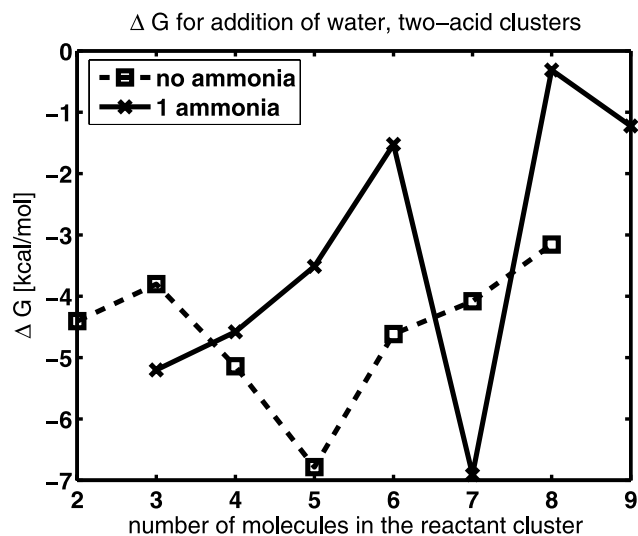

Figure 3. Gibbs free energy for the reactions $(H_2SO_4)_2 \cdot NH_3 \cdot H_2O_{m-1} + H_2O \leftrightarrow (H_2SO_4)_2 \cdot NH_3 \cdot (H_2O)_m$ and $(H_2SO_4)_2 \cdot H_2O_m + H_2O \leftrightarrow H_2SO_4 \cdot H_2O_{m+1}$ (with $m = 1-7$).
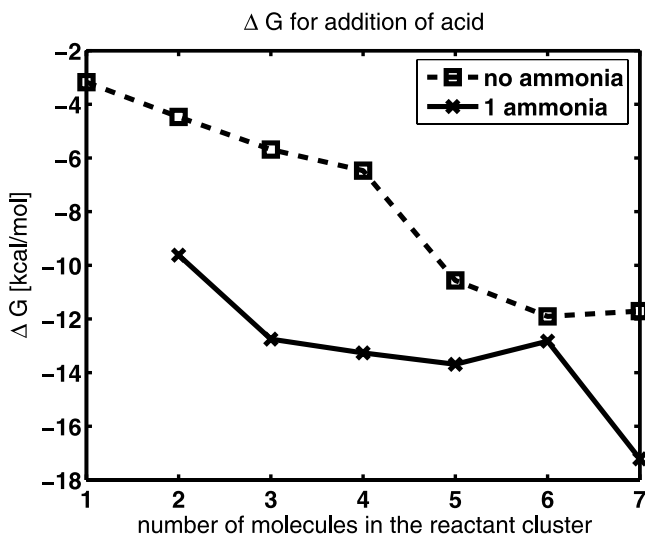
Figure 4. Gibbs free energy for the reactions $(H_2SO_4) \cdot NH_3 \cdot (H_2O)_m + H_2SO_4 \leftrightarrow (H_2SO_4)_2 \cdot NH_3 \cdot (H_2O)_m$ and $(H_2SO_4) \cdot (H_2O)_{m+1} + H_2SO_4 \leftrightarrow (H_2SO_4)_2 \cdot (H_2O)_{m+1}$, with m = 0–5.

presented here: For reactant clusters with less than five molecules, the differences calculated from their data are between −3 and −4 kcal mol^{-1} (for both the 273 K and 248 K data). For clusters with more than five molecules, the absolute values of the differences calculated from their data are actually larger than those obtained by us, but this is mainly caused by the low stability of their $H_2SO_4 \cdot (H_2O)_5$ and $H_2SO_4 \cdot (H_2O)_6$ clusters.

4.3. Cluster Size Distribution and Atmospheric Implications

[16] We have tabulated the equilibrium cluster distribution for typical atmospheric conditions with RH 50%, $P_{am} = 14$ ppt $= 3.877 \times 10^8$ cm^{-3}, $P_{sa} = 0.7$ ppt $= 1.939 \times 10^7$ cm^{-3} and T = 265 K. These values are given in Table 1. (See tables S3a to S3n in the Supplementary Information for cluster size distributions obtained in a variety of different conditions.) The water saturation vapor pressure given by *Seinfeld and Pandis* [1998] is used to convert relative humidity to vapor pressure of water. Atmospheric measurements on the concentrations of sulfuric acid or ammonia yield the total number of molecules bonded to small clusters. Thus the known pressures P_{am} and P_{sa} are the pressures corresponding to the total number of ammonia or acid molecules in all clusters, not the partial pressures of the free molecules entering equation (6). Concentrations of free molecules are solved iteratively from the cluster distribution (equation (6)) with conditions:

$$P_{am} = \sum_{clusters} P_{cluster} n_{am}, \qquad (7)$$

$$P_{sa} = \sum_{clusters} P_{cluster} n_{sa}, \qquad (8)$$

$$P_{wa} = \sum_{clusters} P_{cluster} n_{wa}. \qquad (9)$$

Table 1 also shows the percentage of sulfuric acid or ammonia molecules bonded to each cluster type. The pressure of water molecules is so much higher than the partial pressures of the clusters that the total water pressure and free water pressure do not differ significantly. In our example conditions, the same applies to ammonia.

[17] The equilibrium constants derived from our calculations predict that about 1/5 of the sulfuric acid molecules are free, while the rest are mainly bonded to clusters containing one acid and three or six water molecules. In contrast to our results, the earlier studies of *Bandy and Ianni* [1998], *Ianni and Bandy* [1999, 2000] and *Re et al.* [1999] found no significant formation of sulfuric acid-water clusters. However, regarding the role of ammonia in nucleation, our results are, at a first glance, consistent with those of *Ianni and Bandy* [1999], and indicate that the concentration of ammonia-containing clusters is negligible compared to the concentration of sulfuric acid −water clusters. The main reason for this is that the atmospheric concentration of water is so much larger than that of ammonia. As mentioned in the previous section, and demonstrated in Figure 5, the PW91/DNP free energies of formation (from molecular precursors, at 265 K) of clusters containing one acid and one ammonia molecule are ∼4.2–5.5 kcal mol^{-1} lower than those of the corresponding clusters without ammonia. Thus the equilibrium constants for the formation of acid-ammonia-water clusters are (from equation (5), at 265 K) 3000–34,000 times larger than for acid-water clusters containing an equal number of molecules. However, since the concentration of water in the atmosphere is around 10^8 times larger than that of ammonia, the concentration of ammonia-containing clusters is still negligible owing to the law of mass action (equation (6)). At a temperature of 265 K, the difference in formation free energies required to exactly balance the 10^8 – fold difference in water vapor and ammonia concentrations is 9.7 kcal mol^{-1}. As shown in Figure 5, this is significantly larger than that calculated for
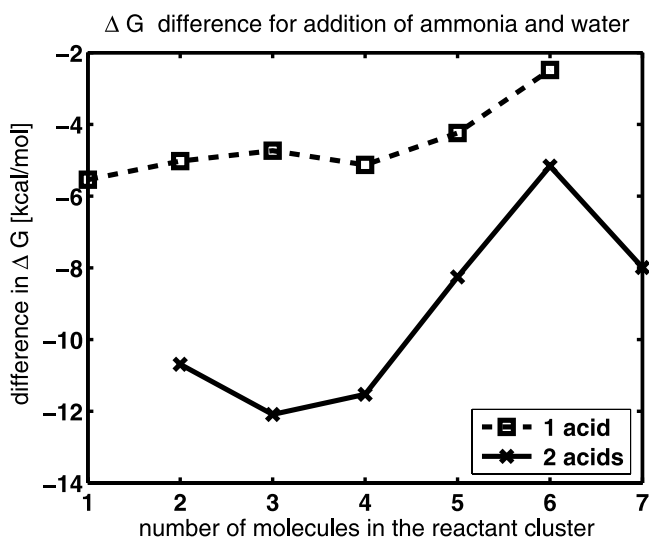

Figure 5. Differences between the Gibbs free energies of the reactions $(H_2SO_4)_n \cdot (H_2O)_m + NH_3 \leftrightarrow (H_2SO_4)_n \cdot NH_3 \cdot (H_2O)_m$ and $(H_2SO_4)_n \cdot (H_2O)_m + H_2O \leftrightarrow (H_2SO_4)_n \cdot H_2O_{m+1}$ with m = 0–5 and m = 0–7 for n = 1 (1 acid) and n = 2 (2 acids), respectively.

any of the one-acid clusters in this study. However, for the two-acid clusters this is not always the case. For the two-acid clusters, the difference in free energies of formation between ammonia-containing $H_2SO_4 \cdot (NH_3) \cdot (H_2O)_m$ and ammonia-free $H_2SO_4 \cdot (H_2O)_{m+1}$ clusters of the same size is between -10 and -12 kcal mol^{-1} for m = 0–2. This difference is large enough to overcome the domination of the law of mass action, and, for example, the concentrations of $(H_2SO_4)_2 \cdot (NH_3) \cdot (H_2O)$ and $(H_2SO_4)_2 \cdot (NH_3) \cdot (H_2O)_2$ clusters are 80 and 28 times larger than those of the corresponding $(H_2SO_4)_2 \cdot (H_2O)_2$ and $(H_2SO_4)_2 \cdot (H_2O)_3$ clusters, respectively. However, this effect is not visible in the partial pressure column of Table 1 owing to the low overall concentration of two-acid clusters. Also, the distribution of two-acid clusters is dominated by the larger five to seven water clusters, for which the fraction of ammonia-containing clusters is negligible. It is possible that the addition of a second ammonia molecule would be necessary to enhance the formation of the larger two-acid clusters.

[18] To assess the dependence of our results on the ambient conditions, we have performed a sensitivity analysis with respect to the four environmental variables (T, RH, P_{am} and P_{sa}). First, we varied each variable in both directions with the other variables kept fixed. The results (presented in Tables S3a–S3h in the auxiliary material) indicate that varying RH by 30% in either direction, or changing the sulfuric acid concentration by an order of magnitude, did not greatly affect the qualitative aspects of the cluster distribution, though the absolute concentrations naturally changed significantly. However, decreasing the temperature by 20 K or increasing the ammonia concentration by an order of magnitude caused a significant increase in the concentration of ammonia-containing clusters, though their proportion of the total distribution still remained small. We then carried out further calculations to determine under which conditions the concentration of two-acid clusters becomes greater than that of the one-acid clusters, and under which conditions the fraction of ammonia-containing two-acid clusters becomes significant. Tables S3i–S3m in the auxiliary material indicate that for the two-acid clusters to dominate the distribution, the concentration of sulfuric acid must be increased by 4 orders of magnitude, or the sulfuric acid concentration by two and the ammonia concentration by 1 or 2 orders of magnitude. These sulfuric acid concentrations are unrealistic, and the results probably reflect the limitations of our data set (e.g., with respect to the number of water or ammonia molecules). Similarly, as shown by Table S3n in the auxiliary material, both a significant decrease in temperature and an order-of-magnitude increase in the ammonia concentration are required for the ammonia-containing clusters to dominate even the two-acid cluster distribution. These conditions are probably not representative of any real atmospheric conditions, with the possible exception of some regions of the Antarctic Ocean downwind of penguin colonies [*Weber et al.*, 1998].

[19] Presumably, nucleation studies using data sets with thermochemical parameters for clusters containing more than two acid molecules, and possibly also more than one ammonia molecule, would reveal further information about the role of ammonia in new-particle formation. Our calculations therefore do not support the conclusion drawn by *Ianni and Bandy* [1999] that ammonia does not take part in

atmospheric particle formation. However, further work with both larger clusters and more reliable methods (for example, better functionals) will be required to reproduce the experimental evidence [*Ball et al.*, 1999], which indicates that adding ammonia to water-sulfuric acid vapor mixture enhances nucleation significantly.

5. Conclusions

[20] The thermochemical parameters of clusters containing one ammonia molecule, 1–2 sulfuric acids and 0–7 water molecules were computed at the PW91/DNP level. Our calculations indicate that the presence of ammonia significantly lowers the formation free energies of sulfuric acid–water clusters. Especially the binding of a second sulfuric acid molecule to a existing cluster is enhanced. Our calculations predict significantly lower free energies of formation than earlier B3LYP studies, indicating a dependence of the results on the functional and basis set used. In contrast to earlier studies, we observe a significant increase in the concentrations of some cluster size classes upon the addition of ammonia molecules. However, under realistic environmental conditions the fraction of ammonia-containing clusters in the total cluster distribution is still negligible. Further work with larger clusters will be required to conclusively demonstrate the role of ammonia in atmospheric particle formation.

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