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T. Kurtén, L. Torpo, M. R. Sundberg, V.-M. Kerminen, H. Vehkamäki, et al.. Estimating the NH₃:H₂SO₄ ratio of nucleating clusters in atmospheric conditions using quantum chemical methods. *Atmospheric Chemistry and Physics*, 2007, 7 (10), pp.2765-2773. hal-00296240

HAL Id: hal-00296240

<https://hal.science/hal-00296240>

Submitted on 18 Jun 2008

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Estimating the NH₃:H₂SO₄ ratio of nucleating clusters in atmospheric conditions using quantum chemical methods

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Received: 31 January 2007 – Published in Atmos. Chem. Phys. Discuss.: 23 February 2007

Revised: 14 May 2007 – Accepted: 18 May 2007 – Published: 25 May 2007

Abstract. We study the ammonia addition reactions of H₂SO₄·NH₃ molecular clusters containing up to four ammonia and two sulfuric acid molecules using the ab initio method RI-MP2 (Resolution of Identity 2nd order Møller-Plesset perturbation theory). Together with results from previous studies, we use the computed values to estimate an upper limit for the ammonia content of small atmospheric clusters, without having to explicitly include water molecules in the quantum chemical simulations. Our results indicate that the NH₃:H₂SO₄ mole ratio of small molecular clusters in typical atmospheric conditions is probably around 1:2. High ammonia concentrations or low temperatures may lead to the formation of ammonium bisulfate (1:1) clusters, but our results rule out the formation of ammonium sulfate clusters (2:1) anywhere in the atmosphere. A sensitivity analysis indicates that the qualitative conclusions of this study are not affected even by relatively large errors in the calculation of electronic energies or vibrational frequencies.

1 Introduction

In most atmospheric conditions, particle formation by nucleation is thought to involve sulfuric acid and water, with possible contributions from ions, ammonia or some organic species. Experimental studies have indicated that the presence of ammonia has a clear nucleation-enhancing effect (Ball et al., 1999) in the sulfuric acid - water system. However, previous estimates of NH₃:H₂SO₄ mole ratios in atmospheric nucleating clusters have varied widely. Predictions of theoretical studies have ranged from zero (corresponding to no nucleation enhancement by ammonia) to 1:1 or even 2:1, corresponding to ammonium bisulfate and ammonium sulfate formation, respectively. Quantum chemical studies

(Ianni and Bandy, 1999) have predicted low values for the NH₃:(H₂SO₄)-ratio, while state of the art thermodynamics (Clegg et al., 1998) predicts extensive ammonium bisulfate formation (Vehkamäki et al., 2004). Older versions of the classical nucleation theory indicated that ammonia enhances H₂SO₄-H₂O nucleation very strongly (Napari et al., 2002), while the updated models result in more modest, but still significant enhancement (Anttila et al., 2005).

Our PW91/DNP study (Kurtén et al., 2007) on two-acid clusters containing up to one ammonia and up to seven water molecules predicted the fraction of ammonia-containing two-acid clusters in ambient conditions¹ to be quite low. However, ammonia was observed to significantly enhance the addition of sulfuric acid molecules to the clusters, and preliminary unpublished MPW1B95 calculations² on three-acid clusters demonstrate that the enhancement increases with the number of sulfuric acid molecules. This might tentatively indicate a lower limit of around 1:3 or 1:4 for the NH₃:(H₂SO₄) mole ratio in atmospheric conditions. In this study, we have extended the analysis along the ammonia co-ordinate in order to complete the picture of the role of ammonia in ternary nucleation.

We apply an accurate ab initio method to study the thermochemistry of (H₂SO₄)_y·(NH₃)_y (y=0–4) molecular clusters and investigate reactions potentially relevant to atmospheric nucleation by calculating their Gibbs free energies. Using the derived cluster distributions, we further estimate an upper limit for the NH₃:(H₂SO₄) – ratio in atmospheric conditions.

¹Cluster distributions were derived at a temperature of 265 K, a RH of 50%, an ammonia partial pressure of 14 ppt and a sulfuric acid partial pressure of 0.7 ppt.

²Torpo, L., Kurtén, T., Vehkamaki, H., Laasonen, K., and Kulmala, M.: The significance of ammonia in growth of atmospheric nanoclusters, in preparation, 2007.

2 Computational details

Previous quantum chemistry studies (Ianni and Bandy, 1999; Kurtén et al., 2007; Larson et al., 1999; Ianni and Bandy, 2000; Re et al., 1999; Bandy and Ianni, 1998; Ding et al., 2003) on sulfuric acid – ammonia – water clusters have mainly used various density functionals (e.g. B3LYP or PW91) to treat the exchange-correlation of electrons. Currently, all generally available density functionals are, by construction, unable to accurately treat electron dispersion (see e.g. Jensen, 2007), which plays a moderately important role in hydrogen bonding. This is a major reason for the large differences observed between the experimental formation free energies for sulfuric acid-water clusters (Hanson and Eisele, 2000) and the computed values (see e.g. Kurtén et al., 2006). There are two main pathways to obtain accurate thermochemistry for hydrogen-bonded clusters. One approach is to use density functionals that are sufficiently well parametrized to replicate binding energies of various benchmarking sets of weakly bound clusters, despite the physically inaccurate treatment of dispersion. Another alternative is to use correlated wavefunction-based methods such as Møller-Plesset (MP) perturbation theory (Møller and Plesset, 1934) or coupled-cluster methods. Unfortunately, the computational cost of even the most affordable correlated wavefunction-based method, MP2, is normally orders of magnitude greater than that of density functional methods. However, the recently developed and implemented (Weigend and Häser, 1997) resolution of identity (RI) approximation MP2 (RI-MP2) produces binding energies that are essentially identical to MP2, at a small fraction of the computational effort (Weigend et al., 1998). In this study we have used the RI-MP2 method implemented in the Turbomole program suite (Ahrlrichs et al., 1989; Häser and Ahrlrichs, 1989; Turbomole version 5.8) for all calculations.

For structure optimization and numerical frequency calculations, we have used the augmented correlation-consistent basis set of valence double-zeta quality (Dunning Jr. et al., 2001) aug-cc-pV(D+d)Z. The electronic energies are then calculated at these geometries using the larger triple-zeta aug-cc-pV(T+d)Z basis set. The corresponding auxiliary basis sets needed for the RI expansion are given by Weigend et al. (2002). From the aug-cc-pV(D+d)Z and aug-cc-pV(T+d)Z energies, basis-set limit (denoted as aug-cc-pV(∞ +d)Z) energies can be extrapolated using the formula of Helgaker et al. (1997):

$$E(X) = E(\infty) + AX^{-3} \quad (1)$$

where $E(\infty)$ is the basis-set limit energy, A is a constant, $X=2$ for the aug-cc-pV(D+d)Z set and $X=3$ for the aug-cc-pV(T+d)Z set. The purpose of the extrapolation is to remove both basis-set superposition errors and basis-set incompleteness errors, and thus provide a more reliable estimate of the basis-set limit than that given e.g. by the counterpoise correction of Boys and Bernadi (1970). Test calculations up to

the RI-MP2/aug-cc-pV(5+d)Z level carried out in connection with our recent high-level study on small neutral and ionic sulfuric acid – water clusters³ indicate that for the RI-MP2 method, basis-set effects beyond the aug-cc-pV(T+d)Z level are relatively small (well under 0.5 kcal/mol in terms of the binding energy per molecule). Neglect of higher-order correlation may cause some errors but these are also likely to be relatively small.

The convergence with respect to the electronic energy in the self-consistent field (SCF) step was 10^{-7} a.u. (atomic units), and the convergence with respect to the gradient was 10^{-4} a.u. For the numerical frequency calculations, a step-size of 0.01 a.u. and a SCF convergence limit of 10^{-8} a.u. were used. Thermal contributions to the enthalpies and entropies are computed using the rigid rotor and harmonic oscillator approximations.

To obtain the initial geometries for the moieties under study, a Monte Carlo-based conformational search installed in Spartan '02 (Wavefunction Inc., 2002) was first applied. The search was carried out by semiempirical methods using the AM1 basis. Since the chosen level of theory was low, several structures for each stoichiometry were subsequently optimized at the B3LYP/6-31G* level using the Gaussian 03 program suite (Frisch et al., 2004). The most stable structures from this optimization were then selected for the accurate RI-MP2 computations. For the (H₂SO₄)₂·(NH₃)₄ stoichiometry, several structures were optimized at the RI-MP2 level in order to ensure that the final energies (and corresponding NH₃:H₂SO₄ ratios) are representative.

3 Results and discussion

Modeling the hydration of sulfuric acid – ammonia clusters is problematic. In typical atmospheric conditions, two-acid clusters can be bound to as many as seven or eight water molecules according to our recent PW91/DNP study (Kurtén et al., 2007). The addition of water molecules to the clusters increases the computational effort in two ways. First, the CPU time and memory required for one energy, or gradient, evaluation increases as an n:th power of the system size. For the RI-MP2 method used in this study, this so-called scaling coefficient n is around 4. For example, with the aug-cc-pV(D+d)Z basis set, a (H₂SO₄)₂·NH₃·(H₂O)₈ cluster contains about 1.6 times as many basis functions as a (H₂SO₄)₂·(NH₃)₄ cluster, implying approximately a 6-fold increase in the computing time for each energy evaluation. For numerical frequency calculations (required for the computing of free energies), the scaling is even worse, as the hydrated (H₂SO₄)₂·NH₃·(H₂O)₈ cluster possesses more than 1.8 times the number of normal modes as the unhydrated (H₂SO₄)₂·(NH₃)₄ cluster, and each normal mode requires

³Kurtén, T., Noppel, M., Vehkämäki, H., Salonen, M., and Kulmala, M.: Quantum chemical studies of hydrate formation of H₂SO₄ and HSO₄⁻, in press, Boreal Env. Res., 2007.

Table 1. The computed reaction Gibbs free energies, in units of kcal mol⁻¹, for the addition of one ammonia molecule to various clusters, with monomer pressures of 1 atm.

reaction	ΔG , kcal/mol
H ₂ SO ₄ + NH ₃ ↔ H ₂ SO ₄ ·NH ₃	-8.7 ^a -5.3 ^b
H ₂ SO ₄ ·H ₂ O + NH ₃ ↔ H ₂ SO ₄ ·NH ₃ ·H ₂ O	-7.6 ^a -4.4 ^b
H ₂ SO ₄ ·(H ₂ O) ₂ + NH ₃ ↔ H ₂ SO ₄ ·NH ₃ ·(H ₂ O) ₂	-9.1 ^a -4.3 ^b
H ₂ SO ₄ ·(H ₂ O) ₃ + NH ₃ ↔ H ₂ SO ₄ ·NH ₃ ·(H ₂ O) ₃	-7.8 ^a -3.6 ^b
H ₂ SO ₄ ·(H ₂ O) ₄ + NH ₃ ↔ H ₂ SO ₄ ·NH ₃ ·(H ₂ O) ₄	-7.5 ^a -4.2 ^b
H ₂ SO ₄ ·(H ₂ O) ₅ + NH ₃ ↔ H ₂ SO ₄ ·NH ₃ ·(H ₂ O) ₅	-6.8 ^a -5.7 ^b
(H ₂ SO ₄) ₂ + NH ₃ ↔ (H ₂ SO ₄) ₂ ·NH ₃	-15.1 ^a
(H ₂ SO ₄) ₂ ·H ₂ O + NH ₃ ↔ (H ₂ SO ₄) ₂ ·NH ₃ ·H ₂ O	-15.9 ^a
(H ₂ SO ₄) ₂ ·(H ₂ O) ₂ + NH ₃ ↔ (H ₂ SO ₄) ₂ ·NH ₃ ·(H ₂ O) ₂	-16.7 ^a
(H ₂ SO ₄) ₂ ·(H ₂ O) ₃ + NH ₃ ↔ (H ₂ SO ₄) ₂ ·NH ₃ ·(H ₂ O) ₃	-15.0 ^a
(H ₂ SO ₄) ₂ ·(H ₂ O) ₄ + NH ₃ ↔ (H ₂ SO ₄) ₂ ·NH ₃ ·(H ₂ O) ₄	-9.8 ^a
(H ₂ SO ₄) ₂ ·(H ₂ O) ₅ + NH ₃ ↔ (H ₂ SO ₄) ₂ ·NH ₃ ·(H ₂ O) ₅	-12.1 ^a
(H ₂ SO ₄) ₂ ·(H ₂ O) ₆ + NH ₃ ↔ (H ₂ SO ₄) ₂ ·NH ₃ ·(H ₂ O) ₆	-8.3 ^a
(H ₂ SO ₄) ₂ ·(H ₂ O) ₇ + NH ₃ ↔ (H ₂ SO ₄) ₂ ·NH ₃ ·(H ₂ O) ₇	-6.4 ^a

^a At the PW91/DNP level and 265 K, Kurtén et al. (2007).^b At the B3LYP/6-311++G(2d,2p) level and 273 K, Ianni and Bandy (1999).

two energy evaluations. Second, the number of possible bonding patterns (cluster conformers) increases combinatorially with the number of molecules. Finding a decent representative minimum energy configuration (the so-called configurational sampling problem) thus becomes prohibitively difficult as the cluster size increases. Also, as the degree of water-water bonding grows, the clusters become increasingly floppy (i.e. the number of very low frequency vibrational modes grows), and the harmonic oscillator and rigid rotor approximations become less reliable. Fortunately, an analysis of previous quantum chemical results (Ianni and Bandy, 1999; Kurtén et al., 2007) indicates that though the energetics of individual water addition reactions vary significantly, the average free energy for the addition of several water molecules to a sulfuric-acid-ammonia cluster is only weakly dependent on the ammonia content of the cluster. Similarly, the binding of ammonia to the clusters is weakly dependent on the water content. The free energies for the addition of ammonia to various clusters calculated in previous studies are presented in Table 1. The differences between the results of Ianni and Bandy (1999) and Kurtén et al. (2007) are related mainly to the density functionals used in the studies: the B3LYP functional used by Ianni and Bandy tends to underpredict binding energies for sulfuric acid – water clusters while the PW91 functional used by Kurtén et al. tends to somewhat overpredict them (Kurtén et al., 2006). The differences between B3LYP and PW91 results on sulfuric acid – ammonia – water clusters have been extensively discussed by Kurtén et al. (2006, 2007) and Nadykto et al. (2007).

It can be seen from Table 1 that the effect of water molecules on the addition free energies of ammonia is rel-

atively weak at least for the first few water molecules. The effect is also to some extent systematic: the addition of water molecules tends to somewhat decrease the binding of ammonia to the cluster. (The deviations from this pattern may be related to configurational sampling issues rather than true chemical effects.) This is reasonable from a chemical point of view. The binding between sulfuric acid and ammonia is much stronger than that between sulfuric acid and water or ammonia and water. Thus, the binding of a few water molecules to the cluster is unlikely to significantly disrupt the bonding pattern of the sulfuric acid – ammonia core. However, as the number of water molecules increases, the core will eventually start to dissolve, and both the acid and ammonia molecules will be bonded mainly to water molecules.

The addition of ammonia to an unhydrated (H₂SO₄)_x·(NH₃)_y core thus represents the minimum case with respect to the free energy (i.e. the most negative values for ΔG are obtained for the unhydrated or almost unhydrated cluster), and hydration will probably only serve to decrease the H₂SO₄-NH₃ binding. Therefore, cluster distributions derived for the (H₂SO₄)_x·(NH₃)_y system with no water present represent the maximum case with respect to the amount of ammonia molecules bound to the clusters. While the competition of water molecules with ammonia will lead to lower NH₃:(H₂SO₄) mole ratios in the real atmosphere, there exist, to our knowledge, no mechanisms which would tend to lead to greater ratios than that predicted for this reference case. NH₃:(H₂SO₄) ratios calculated from these distributions at some temperatures and partial pressures will thus yield useful upper limits for atmospheric cluster distributions.

Table 2. The electronic energy E_0 (in Hartree), thermal contribution to the enthalpy H_{term} (in kcal mol⁻¹) and entropy S_{term} (in cal (Kmol)⁻¹) from calculations at T=298 K. $E_{0\text{DZ}}$ and $E_{0\text{TZ}}$ (a.u.) correspond to the aug-cc-pV(D+d)Z and aug-cc-pV(T+d)Z basis sets, respectively. All values are computed using the RI-MP2 method.

species	$E_{0\text{DZ}}$ hartree	$E_{0\text{TZ}}$ hartree	H_{term} kcal/mol	S_{term} cal/Kmol
NH ₃	-56.40765	-56.47724	23.99	49.80
(H ₂ SO ₄) ₂	-1398.38942	-1399.25446	57.58	113.04
(H ₂ SO ₄) ₂ ·NH ₃	-1454.84352	-1455.78118	84.13	119.73
(H ₂ SO ₄) ₂ ·(NH ₃) ₂	-1511.28801	-1512.29423	110.75	131.42
(H ₂ SO ₄) ₂ ·(NH ₃) ₃	-1567.71964	-1568.79619	136.35	147.29
(H ₂ SO ₄) ₂ ·(NH ₃) ₄	-1624.15452	-1625.30224	162.14	155.60

Table 3. The electronic and free energies of ammonia addition reactions, in kcal mol⁻¹, with electronic energies extrapolated to the RI-MP2/aug-cc-pV(∞ +d)Z level and thermal contributions computed at the RI-MP2/aug-cc-pV(D+d)Z level. All values correspond to a temperature of 298 K and monomer pressures of 1 atm.

Reaction	ΔE_0	ΔG (298 K)
(H ₂ SO ₄) ₂ +NH ₃ \leftrightarrow (H ₂ SO ₄) ₂ ·(NH ₃)	-31.85	-16.39
(H ₂ SO ₄) ₂ ·(NH ₃) + NH ₃ \leftrightarrow (H ₂ SO ₄) ₂ ·(NH ₃) ₂	-22.20	-8.18
(H ₂ SO ₄) ₂ ·(NH ₃) ₂ + NH ₃ \leftrightarrow (H ₂ SO ₄) ₂ ·(NH ₃) ₃	-15.71	-3.94
(H ₂ SO ₄) ₂ ·(NH ₃) ₃ + NH ₃ \leftrightarrow (H ₂ SO ₄) ₂ ·(NH ₃) ₄	-18.50	-4.28

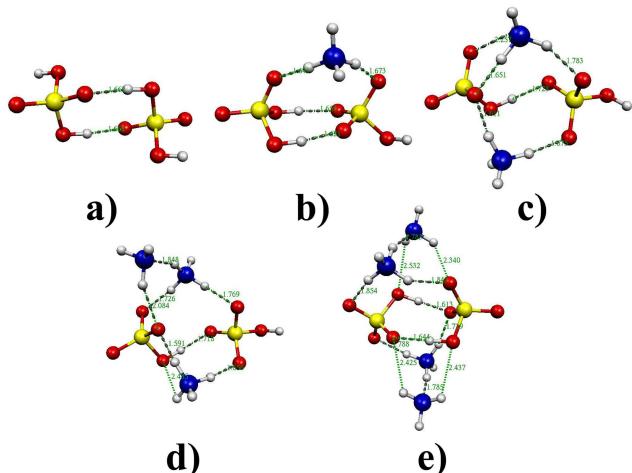


Fig. 1. The optimized structures of the clusters in this study.

- (a) (H₂SO₄)₂
- (b) (H₂SO₄)₂·(NH₃)
- (c) (H₂SO₄)₂·(NH₃)₂
- (d) (H₂SO₄)₂·(NH₃)₃
- (e) (H₂SO₄)₂·(NH₃)₄.

The hydrogen bonds are displayed with dotted lines. Some relevant bond lengths and other interatomic distances (in Ångström) are given in green. Color coding: white=hydrogen, red=oxygen, yellow=sulfur and blue=nitrogen.

3.1 Structural and thermochemical data

The cluster structures studied here are shown in Fig. 1. The clusters have been drawn using the MOLEKEL 4.3 visualization package (Portmann, 2002). The corresponding electronic energies, enthalpies and entropies are presented in Table 2. The cartesian coordinates for the most stable cluster structures are given in the auxiliary information (<http://www.atmos-chem-phys.net/7/2765/2007/acp-7-2765-2007-supplement.pdf>). The electronic and standard Gibbs free energies for the ammonia addition reactions (at 298 K and reactant pressures of 1 atm) are given in Table 3.

It can be seen from Table 3 that the free energy of the ammonia addition reactions increases steadily with the number of ammonia molecules. Thus, while the addition of the first ammonia molecule is strongly exothermal, the third and fourth addition reactions are close to endothermal.

The mode of intermolecular interaction in the sulfuric acid dimers varies depending on the number of attached ammonia molecules (see Fig. 1). In the pure dimer [structure a)] each sulfuric acid has two “outer” and two “inner” hydrogen atoms. The latter atoms form a typical hydrogen bonding system found e.g. in organic acids. In structure b), an attached ammonia molecule has taken one of the two outer hydrogens. However, when the number of the ammonia molecule increases to two, one of the inner hydrogen atoms is also taken. In structure d), the remaining inner hydrogen still

Table 4. Relative concentrations of different two-acid cluster types at different temperatures and ammonia concentrations.

	T=298 K [NH ₃]=1 ppt	T=298 K [NH ₃]=100 ppt	T=298 K [NH ₃]=10 ppb	T=298 K [NH ₃]=1 ppm
(H ₂ SO ₄) ₂	48.792%	0.944%	0.009%	0
(H ₂ SO ₄) ₂ ·NH ₃	51.208%	99.046%	99.009%	50.198%
(H ₂ SO ₄) ₂ ·(NH ₃) ₂	0	0.010%	0.982%	49.763%
(H ₂ SO ₄) ₂ ·(NH ₃) ₃	0	0	0	0.039%
(H ₂ SO ₄) ₂ ·(NH ₃) ₄	0	0	0	0
	T=273 K [NH ₃]=1 ppt	T=273 K [NH ₃]=100 ppt	T=273 K [NH ₃]=10 ppb	T=273 K [NH ₃]=1 ppm
(H ₂ SO ₄) ₂	0.937%	0.009%	0	0
(H ₂ SO ₄) ₂ ·NH ₃	99.060%	99.767%	81.706%	4.244%
(H ₂ SO ₄) ₂ ·(NH ₃) ₂	0.002%	0.223%	18.292%	95.025%
(H ₂ SO ₄) ₂ ·(NH ₃) ₃	0	0	0.001%	0.717%
(H ₂ SO ₄) ₂ ·(NH ₃) ₄	0	0	0	0.014%
	T=248 K [NH ₃]=1 ppt	T=248 K [NH ₃]=100 ppt	T=248 K [NH ₃]=10 ppb	T=248 K [NH ₃]=1 ppm
(H ₂ SO ₄) ₂	0.004%	0	0	0
(H ₂ SO ₄) ₂ ·NH ₃	99.910%	92.095%	10.425%	0.101%
(H ₂ SO ₄) ₂ ·(NH ₃) ₂	0.086%	7.905%	89.481%	86.814%
(H ₂ SO ₄) ₂ ·(NH ₃) ₃	0	0	0.094%	9.076%
(H ₂ SO ₄) ₂ ·(NH ₃) ₄	0	0	0	4.009%

participates in the intermolecular hydrogen bonding between the sulfuric acid moieties. There is also an intermolecular interaction between an ammonia molecule and the vicinal ammonium cation. In structure e), the inner hydrogen still remains, and there are two similar ammonia – ammonium dimers approximately on the opposite sides of the sulfuric acid dimer.

3.2 Cluster distributions

The computed free energies can be used to derive cluster size distributions given some ambient monomer pressures. Specifically, the relative fraction of two-acid clusters bound to n ammonia molecules is:

$$\frac{[(\text{H}_2\text{SO}_4)_2 \cdot (\text{NH}_3)_n]}{\sum_{k=0}^4 [(\text{H}_2\text{SO}_4)_2 \cdot (\text{NH}_3)_k]} = \frac{[\text{NH}_3]^n e^{-\frac{\Delta G_n}{RT}}}{1 + \sum_{k=1}^4 [\text{NH}_3]^k e^{-\frac{\Delta G_k}{RT}}} \quad (2)$$

where the ammonia vapor pressure [NH₃] is given in atmospheres and ΔG_n is the free energy change for the reaction $(\text{H}_2\text{SO}_4)_2 + n \text{NH}_3 \Rightarrow (\text{H}_2\text{SO}_4)_2 \cdot (\text{NH}_3)_n$. (Note that as we are comparing the relative concentrations of two-acid clusters, the sulfuric acid concentration does not enter the final expression.) Table 4 shows the relative concentrations of the five studied cluster types for three temperatures and four ammonia concentrations; 1 ppt–1 ppm. The concentrations were chosen to span the range of measured atmospheric values. According to Seinfeld and Pandis (1998), typical atmospheric ammonia concentrations in continental air are

around 0.1–10 ppb. In a recent (spring 2005) campaign at the Hytiälä measurement station (Riipinen et al., 2007), ammonia concentrations in the range 10^9 – 10^{11} cm⁻³ were measured, corresponding to mixing ratios of about 0.04–4 ppb. Similarly, results from the BIOFOR campaign (Kulmala et al., 2001) in 2001 yielded average ammonia mixing ratios of 49 ppt and 52 ppt in spring and summer, respectively.

The results are shown in Table 4. It can be seen that the two-acid clusters of our hypothetical unhydrated cluster distribution are bound to at least one ammonia molecule in almost all conditions. The ammonium bisulfate dimer (H₂SO₄)₂·(NH₃)₂ is formed in high ammonia concentrations or low temperatures, but the ammonium sulfate dimer (H₂SO₄)₂·(NH₃)₄ is not formed in any atmospherically relevant conditions. It should be noted that these values relate to the very first steps of gas-to-particle nucleation only: ammonium sulfate clusters may be produced in the atmosphere by other mechanisms (e.g. growth processes), which are beyond the scope of this study.

3.3 Sensitivity analysis

Error analysis of previous studies (Kurtén et al., 2006) indicates that far-reaching atmospheric conclusions drawn from relatively small differences in computed thermochemical data may be unreliable. Though the RI-MP2/aug-cc-pV(T+d)Z data should be reliable (more so than previous density functional data), our thermochemical parameters may be contaminated by several error sources. Basis-set superposition errors not accounted for by the extrapolation

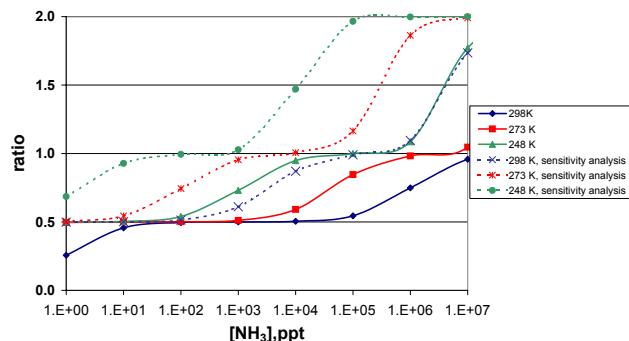


Fig. 2. Average NH₃:H₂SO₄ mole ratios as a function of the ammonia concentration, at three different temperatures. Solid lines correspond to the RI-MP2/aug-cc-pV($\infty+d$)Z//RI-MP2/aug-cc-pV(D+d)Z data with harmonic frequencies. Dashed lines correspond to the sensitivity analysis data, in which vibrational frequencies have been scaled by 0.75 and a further term of -2 kcal/mol has been added to each ammonia addition reaction energy.

procedure of Eq. (1) would tend to decrease the computed Gibbs free formation energies (i.e. exaggerate the stability of the clusters) compared to the real values, while the neglect of vibrational anharmonicity would tend to increase them. Conformational sampling may cause problems in two ways. First, we can not be certain that our studied cluster structures correspond to the global minimum geometries. Second, especially the largest (H₂SO₄)₂·(NH₃)₄ cluster possesses some very low vibrational frequencies, indicating that treating the cluster as a single structure vibrating harmonically around some minimum energy geometry may cause large errors in the thermochemistry. Moreover, our assumption that the binding of water molecules will tend to decrease the H₂SO₄-NH₃ binding might at least in some conditions be incorrect, and the atmospheric NH₃:H₂SO₄ mole ratios could therefore be greater than those predicted here.

The effects of these error sources on our atmospheric conclusions were estimated by recomputing the cluster size distributions using formation energetics that have been modified in two ways. First, we have scaled the vibrational frequencies by a factor of 0.75, which is somewhat lower than the factors computed in our previous study (see the footnote on page 4) on small ionic clusters using accurate anharmonic thermochemical expressions, and significantly lower than the scaling factors usually used at the MP2 level (which are obtained by using the anharmonic fundamental frequencies in the expressions derived for harmonic oscillators, and are usually around 0.94–0.96, see e.g. Foresman and Frisch, 1996). This should be more than enough to account for vibrational anharmonicity. Second, we have assumed that the calculated electronic energy change for each ammonia addition reaction is too positive by 2 kcal/mol. (Thus, the electronic energy change for the (H₂SO₄)₂ + 4 NH₃ => (H₂SO₄)₂·(NH₃)₄ reaction used in the sensitivity analysis is 8 kcal/more more

negative than that computed from Table 3.) This is intended to give an upper limit to the correction for all possible errors relating, for example, to the configurational sampling, the omission of higher-order correlation, and the binding of water molecules to the cluster. (It should be noted that any basis-set superposition error not corrected by the extrapolation procedure would tend to act in the opposite direction). The energetics used for the sensitivity analysis are given in the auxiliary information (<http://www.atmos-chem-phys.net/7/2765/2007/acp-7-2765-2007-supplement.pdf>).

The results of the sensitivity analysis are presented graphically in Fig. 2. The solid lines correspond to the average NH₃:H₂SO₄ mole ratio (computed as a weighted sum of the relative concentrations) for two-acid clusters computed from the original data in Tables 2 and 3. The dashed lines are the corresponding mole ratios computed with the data from the sensitivity analysis. We expect that the upper limits to the real atmospheric mole ratios will lie somewhere between the two lines, as the systematic errors assumed in the sensitivity analysis are rather extreme. The step-function-like behavior of the curves is explained by the fact that the mole ratio is a sum of polynomial terms, with e.g. the relative fraction of (H₂SO₄)₂·NH₃ depending on [NH₃], the relative fraction of (H₂SO₄)₂·(NH₃)₂ on [NH₃]² and so on.

The dashed curves predict somewhat greater mole ratios (with e.g. significant amounts of ammonium bisulfate forming at around 2 orders of magnitude lower ammonia concentrations for each temperature), but mole ratios of 3:2 or higher are still not reached in any atmospherically realistic conditions. We thus conclude that ammonium sulfate dimer clusters are very unlikely to form by gas-to-particle nucleation in the atmosphere. While this does not directly prove anything about the composition of larger cluster structures (containing more than two sulfuric acid molecules), it is a strong indication that in nucleating molecular clusters, NH₃:H₂SO₄ mole ratios significantly greater than 1:1 are unlikely.

3.4 Comparison to experimental and classical simulation results

Extensive experimental information on the NH₃ to H₂SO₄ mole ratio in the atmosphere is only available for bulk samples consisting of a large number of particles with diameter below 1 μm . In these samples, the NH₃ to H₂SO₄ mole ratio (in experimental studies usually expressed as the NH₄⁺ to SO₄²⁻ mole ratio) depends in a complicated manner on the relative magnitudes of regional ammonia and sulfur emissions, on the conversion of gaseous sulfur compounds to particulate sulfate, and on the removal rate of gaseous and particulate compounds from the atmosphere. In continental areas, the most important ammonia source is agriculture, whereas in marine areas gaseous ammonia originates mainly from the oceans (Bouwman et al., 1997). The principal sulfate precursor over the continents is sulfur dioxide

(SO₂) with its largest emissions taking place in industrial regions (see e.g. Berglen et al., 2004). Over marine areas, aerosol sulfate is being produced from gaseous dimethylsulfide (DMS) originating from natural biological activities in the oceans (Kettle and Andreae, 2000). The conversion of SO₂ and DMS to aerosol sulfate takes place via photochemical reactions in the gas phase followed by H₂SO₄ condensation, and by aqueous-phase reactions taking place in clouds or wet aerosol particles (Berglen et al., 2004). Acidic sulfate aerosols rapidly take up gaseous ammonia if available. If there is ammonia in excess of that needed to neutralize all particulate sulfate, which corresponds to a NH₄⁺:SO₄²⁻ mole ratio of 2:1, also ammonium nitrate (and other ammonium salts) may be formed, leading to NH₄⁺:SO₄²⁻ mole ratios larger than 2:1 (Adams et al., 1999; Feng and Penner, 2007).

Observed NH₄⁺ to SO₄²⁻ mole ratios display a large variability in fine (<2.5 µm diameter) lower-tropospheric aerosols. Over continental mid-latitudes, these ratios are commonly in the range 1:1–2:1, even though larger ratios can be observed close to agricultural areas (Malm et al., 2004; Schaap et al., 2004). Ratios close to or even below 1:1 are frequently observed over Arctic or sub-Arctic regions (Richard et al., 2002). In the marine boundary layer, NH₄⁺ to SO₄²⁻ mole ratios are practically always below 2:1, with typical values being in the range 1:2–3:2 (Bates et al., 2001; Virkkula et al., 2006). Ratios smaller than unity are typical for the Southern Ocean, and ratios approaching zero, indicative of almost pure H₂SO₄-H₂O aerosols, have been measured in Antarctic air masses (O'Dowd et al., 1997).

Macroscopic model simulations confirm the above patterns and show a few additional features (Adams et al., 1999; Feng and Penner, 2007). For example, NH₄⁺ to SO₄²⁻ mole ratios are predicted to be close to or above 2:1 over most low-latitude continental regions. Due to the lack of significant ammonia sources, substantially lower ratios are expected to be found in remote continental areas as well as in the free troposphere.

The experimental values described above are completely dominated by particles very much larger than the molecular clusters studied here. Neutral particles below 2.5 nm in diameter (corresponding to ca. 100–200 molecules) or so can not be detected at all with present instrumentation (McMurtry, 2000), though there have been some improvements recently (Kulmala et al., 2005). Single-particle composition measurements are only possible for particles in the 10 nm size range (corresponding to ca 10⁵ molecules) or larger (Nash et al., 2006). In contrast, the clusters studied here contain only up to 6 molecules (perhaps 10–20 when hydration is accounted for) and are below 1 nm in diameter. Also, the computational methods used to calculate thermochemical parameters in this study are based on the assumption that the translational, rotational and vibrational contributions to the entropy and enthalpy of the molecular clusters can be calculated as if they

were large gas-phase molecules. In the larger particles, ammonium sulfate may exist in the solid phase, and the thermochemistry determining the NH₃:(H₂SO₄) mole ratios may be quite different. For example, crystallization processes may favor pure ammonium bisulfate or ammonium sulfate over more ammonium-poor mixtures, even though the latter are more stable in the gas phase. Large differences between the chemical composition of small clusters (where all molecules are typically “on the surface”) and bulk liquids or solids are not uncommon in physical chemistry, examples include surface enrichment by surfactants. (See for example Chen et al., 2002, where this is studied in the context of water-ethanol nucleation.) This corresponds to the fact that the strength of the Kelvin effect is different for different molecular species. Since ammonia has a high vapor pressure (compared to sulfuric acid) it is more difficult for it to accumulate in small clusters.

Our computational results indicate that the NH₃:(H₂SO₄) mole ratio for molecular clusters formed in the very first steps of atmospheric nucleation is not likely to be greater than 1:1. This does not contradict the measurement results (which in turn do not cast doubt on the validity of the computations), but simply indicates that the chemical composition of nucleating particles is different from that of larger particles. Thus, using e.g. ammonium sulfate as a model for the chemical or physical properties of nucleating molecular clusters may not be justified, even though experimental evidence indicates that it is in many conditions a good model species for predicting the properties of larger particles.

4 Conclusions

We have studied (H₂SO₄)₂·(NH₃)_y (with y=0–4) clusters at the RI-MP2/aug-cc-pV(T+d)//RI-MP2/aug-cc-pV(D+d)Z-level in order to determine an upper limit to the NH₃:H₂SO₄ mole ratio of small molecular clusters in atmospheric conditions. Our calculations indicate that depending on the temperature, ammonia concentrations of around 10–10 000 ppb are required for the ratio to reach 1:1 (corresponding to ammonium bisulfate). Ratios of 2:1 (corresponding to ammonium sulfate) are unlikely to be found anywhere in the atmosphere. A sensitivity analysis indicates that errors in the computational method might lead to an overestimation of the ammonia concentration required for ammonium bisulfate to form by at most 2 orders of magnitude. However, the finding that ammonium sulfate molecular clusters do not form in the atmosphere is insensitive even to relatively large systematic errors.

Acknowledgements. The authors thank the Scientific Computing Center (CSC) in Espoo, Finland for computing time, and the Academy of Finland for financial support.

Edited by: B. Kärcher

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