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The effect of H_2SO_4 – amine clustering on chemical ionization mass spectrometry (CIMS) measurements of gas-phase sulfuric acid

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Abstract. The state-of-the art method for measuring atmospheric gas-phase sulfuric acid is chemical ionization mass spectrometry (CIMS) based on nitrate reagent ions. We have assessed the possible effect of the sulfuric acid molecules clustering with base molecules on CIMS measurements using computational chemistry. From the computational data, three conclusions can be drawn. First, a significant fraction of the gas-phase sulfuric acid molecules are very likely clustered with amines if the amine concentration is around or above a few ppt. Second, some fraction of these acid-amine clusters may not be charged by the CIMS instrument, though the most reliable computational methods employed predict this fraction to be small; on the order of ten percent or less. Third, the amine molecules will evaporate practically immediately after charging, thus evading detection. These effects may need to be taken into account in the interpretation of atmospheric measurement data obtained using chemical ionization methods. The purpose of this study is not to criticize the CIMS method, but to help understand the implications of the measured results.

1 Introduction

Measurements of nanometer-sized clusters and their molecular precursors in the atmosphere are faced with a dilemma. On one hand, most clusters and single molecules relevant to gas-to-particle nucleation are likely to be electrically neutral, with ions and charged clusters playing only minor roles (Kulmala et al., 2007). On the other hand, all accurate and currently available techniques for measuring chemical composition require the detected species to be electrically charged. Thus, to obtain information on neutral molecules or clusters, they must first be charged via some process. If the charging mechanism is too energetic (for example, corona charging), all types of clusters or molecules certainly can be charged, but many of them are likely broken up in the process, and entirely new and artificial ions and corresponding clusters types may also be formed. Alternatively, if the process is more "gentle" and selective, the charging probability will depend on the chemical composition of the molecule or cluster, and some species of interest may perhaps not be charged. Also, even if the charging itself does not directly break up a cluster, some molecules may still evaporate between charging and eventual mass spectrometric detection. Thus, understanding of neutral molecules or clusters based on measurements of charged species requires understanding of charging probabilities and possible changes in chemical composition resulting from the charging process. Fortunately, at least part of the required information (such as energy differences between neutral and charged molecular clusters with similar composition) can be calculated by quantum chemical methods, provided that the clusters are small and the participating molecules "well-behaved" in terms of their electronic structure.

One particular case in which the dependence of charging probability on cluster composition can significantly affect measurement results is chemical ionization mass spectrometry, CIMS. Nitrate ion CIMS, in which H_2SO_4 is selectively ionized to HSO_4^- by NO_3^-/HNO_3 mixtures,

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is the state-of-the-art method to measure ambient sulfuric acid concentrations (Eisele and Tanner, 1993; Berresheim et al., 2000). As sulfuric acid is considered the single most important chemical species for atmospheric gas-to-particle nucleation (Weber et al., 1996; Kulmala et al., 2004, 2007; Sipilä et al., 2010), accurate sulfuric acid concentration data is crucial for understanding atmospheric new-particle formation. The selectivity of the CIMS process is based on the fact that H_2SO_4 is one of the few atmospheric species with greater acidity than HNO_3. Some exceptions exist, e.g. malonic acid, hydroiodic acid and methane sulfonic acid, but these are typically assumed not to interfere with the H_2SO_4 measurement. Based on the moderately large difference in the vacuum proton affinities of HSO_4^- and NO_3^-, and on the well-known bulk acidity (pKa) values of H_2SO_4 and HNO_3, it is expected that given constant instrumental conditions (such as NO_3^- concentration, charging time, etc.), a constant fraction of the sulfuric acid present in air samples will be ionized in nitrate ion CIMS instruments.

This explanation for the working principle of CIMS assumes that the effects of possible NO_3^--HNO_3 clustering on the proton affinity of the main charging ion are small. Also, it does not account for the tendency of H_2SO_4 to aggregate with other molecules, producing clusters which may sometimes have proton affinities significantly higher than that of free H_2SO_4. Experimental evidence (Viggiano et al., 1997) indicates that neither NO_3^--HNO_3 clustering nor hydration (binding to water) of sulfuric or nitric acid on their own significantly affect the charging probability of sulfuric acid molecules, or the rates of the charging reactions. However, in the presence of base molecules such as ammonia or amines, a large fraction of the gas-phase sulfuric acid may be bound to base-containing clusters. These are likely to have significantly higher proton affinities than free or hydrated H_2SO_4, and will therefore be much more difficult to charge by proton removal in CIMS – type instruments. In the presence of base molecules, NO_3^--HNO_3 clustering may therefore decrease the charging probability of sulfuric acid – containing clusters. Furthermore, the base molecules are very likely to evaporate from those H_2SO_4-base clusters which are successfully charged, prior to their mass-spectrometric detection. The hypothesis that H_2SO_4 clustered with other molecules such as ammonia may not be quantitatively measured by CIMS has been suggested already by Eisele and Tanner (1993), and some experimental indications of this have been presented by Hanson and Eisele (2002). In this study, we attempt to study this issue using quantum chemistry methods. The qualitative results of this study are schematically summarized in Fig. 1.

As different CIMS instruments have different characteristics, the degree to which their H_2SO_4 measurements are affected by base molecules may be variable. In this "proof-of-concept" study, we focus on the Selected Ion CIMS (SI-CIMS) instruments used at the University of Helsinki, Finland and at the National Centre for Atmospheric Research in Boulder, Colorado (Eisele and Tanner, 1993; Tanner et al., 1997; Mauldin et al., 1998; Petäjä et al., 2009, and references therein), and estimated representative values (e.g. neutral to charged ratios for base-containing clusters) for this instrument. In the SI-CIMS discussed here (referred to as the "Helsinki University CIMS" in the following discussion), the nitrate ions are created in a nitric acid sheath flow outside the sample flow, and drawn into the sample flow electrostatically. See Fig. 2 for a simplified diagram of the instrument. Other CIMS instruments with different experimental setups may perform differently, but the general phenomenon discussed here is still relevant – base-containing sulfuric acid clusters are more difficult to charge regardless of the experimental setup.

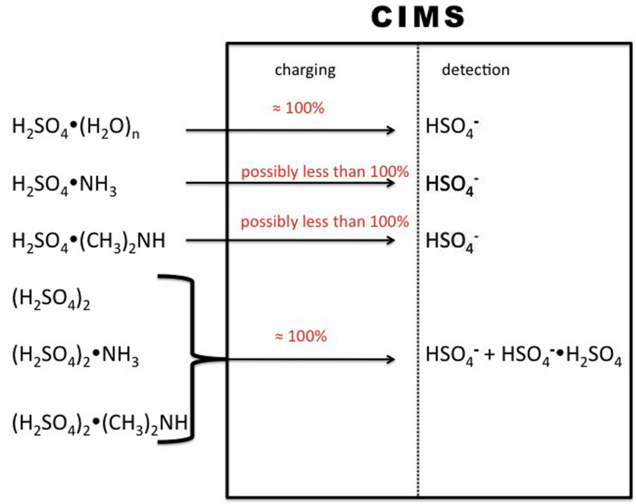

Fig. 1. Schematic of the performance of the CIMS instrument for various sulfuric acid – containing small clusters. The scheme illustrates two fundamental issues: only part of some base-containing clusters may be charged, and the base molecules will evaporate prior to detection even if the charging is successful. The qualitative estimates of charging efficiencies correspond to the Helsinki University CIMS (Petäjä et al., 2009, and references therein). See text for details.

2 Computational details

Quantum chemistry refers to numerically solving the Schrödinger equation, subject to a large number of approximations, in order to calculate parameters of chemical or physical interest. The precise details of these approximations specify the so-called "model chemistry", typically defined as a combination of a method to treat electron – electron correlation, and a set of basis functions ("basis set") used to describe the atomic and molecular orbitals of the electronic wavefunction (or the electron density in density functional methods), see e.g. Jensen (2009) for detailed descriptions. All calculations in this study were performed using the Gaussian 03 and 09 program suites (Frisch et

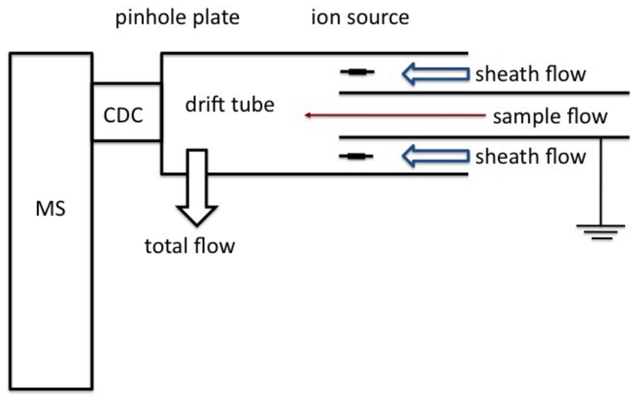

Fig. 2. A schema of the CIMS inlet. CDC and MS refer to collision-dissociation chamber and mass spectrometer, respectively.

al., 2009). Initially, we performed calculations using the PW91 density functional method (Perdew and Wang, 1992) and the 6-311++G(3df, 3pd) basis set (Mclean and Chandler, 1980; Raghavachari et al., 1980). This permitted comparison and synthesis with the large body of data on other types of charged and neutral clusters computed by Nadykto et al. (2007, 2008, 2011; see also references therein) at the exact same level. Unfortunately, even though the PW91 method has been demonstrated to predict H_2SO_4-H_2O and H_2SO_4-H_2SO_4 binding reasonably well compared to experimental results or higher-level computations, recent investigations (Kurtén, 2011) indicate that it systematically underestimates, by several kcal mol^{-1}, the binding of dimethylamine to sulfuric acid – containing clusters. Test calculations in the present study show that the same applies also to the binding of dimethylamine to HSO_4^--HNO_3 – clusters. This discovery necessitated recalculation of some cluster formation thermodynamics using the much more accurate (but also computationally very expensive) composite methods G3 (Curtiss et al., 1998) and G3MP2 (Curtiss et al., 1999). The G3 method has been shown to yield excellent results for water clusters (Dunn, 2004), and the G3MP2 method is a cost-effective approximation for G3. The most stable structures from the PW91 calculations were used as input guesses for the G3 and G3MP2 calculations.

Default energy and geometry convergence criteria were used in all calculations. Test calculations on the $(H_2SO_4)(CH_3)_2NH$ cluster indicate that the use of tight criteria (which also requires the use of an ultrafine integration grid) affect the PW91/6-311++G(3df, 3pd) binding energies by less than 0.1 kcal mol^{-1}, while increasing the computational effort by a large factor. Thus, using tighter convergence criteria was not found to be cost-effective in this study. Thermochemical parameters were computed using the standard rigid rotor and harmonic oscillator approximations (with scaling factors applied in the G3 and G3MP2 calculations as described in the corresponding method references). As the clusters studied here are relatively strongly bound, the errors due to the harmonic approximation are, while not negligible, likely to be fairly small, for example in comparison to the differences between energies computed using PW91 and G3 or G3MP2.

Computed equilibrium constants, charging efficiencies, evaporation rates and other similar parameters of interest generally depend on the exponentials of the free energies, and should thus be considered order-of-magnitude estimates rather than quantitatively accurate values. The average absolute deviations from experiment of the G3 and G3MP2 methods are slightly below 1 and 1.5 kcal mol^{-1}, respectively, for a test set of single-molecule formation enthalpies (Curtiss et al., 1998, 1999). The reliability of the reaction free energies, especially for cluster structures, is presumably somewhat worse, but the lack of consistent experimental benchmark datasets prevents a quantitative assessment of the error margins.

It should be noted that in this particular study, the largest uncertainties in assessment of the charging process itself may be related to the actual dynamics of the charging, e.g. the rate at which $NO_3^-(HNO_3)$ ions are able to displace amine molecules from (H_2SO_4)-amine clusters, rather than to the computed thermodynamics, despite the large differences between e.g. PW91 and G3MP2 results.

Proton affinities have been computed using the standard definition that the proton affinity for some species X is -1 times the enthalpy for the $X + H^+ \rightarrow XH^+$ reaction, with the enthalpy of a proton set to 1.5 RT, where R is the gas constant and T the temperature. Structures and energetics for the studied clusters are given in the Supplement.

3 Results and discussion

3.1 Charging mechanism of pure and hydrated H_2SO_4

To understand the charging processes occurring inside the CIMS instrument, we first need to know in what form the nitrate ions responsible for charging the sulfuric acid molecules (and their clusters) actually exist. The nitrate ions can exist either as free ions, or as complexes with nitric acid molecules. It cannot be ruled out that nitrate ions could cluster also with other species, e.g. organic acids, but the concentration of organic contaminants is presumably much smaller than that of HNO_3. Further speculation on this is beyond the scope of this study. All of these species can also be bound to one or more water molecules, though as shown by the data of Viggiano et al. (1997), this will likely not affect the charging process significantly.

Ignoring hydration and possible clustering with organics, the fraction of nitrate ions bound to x nitric acid molecules at equilibrium can be determined from the law of mass balance:

$$\frac{\left[NO_3^- \cdot (HNO_3)_x\right]}{\sum_{k=0}^{n}\left[NO_3^- \cdot (HNO_3)_k\right]} = \frac{[HNO_3]^x\, e^{\frac{-\Delta G_x}{RT}}}{1+\sum_{k=1}^{n}[HNO_3]^k\, e^{\frac{-\Delta G_k}{RT}}} \quad (1)$$

where the nitric acid vapor pressure $[HNO_3]$ is equal to the partial pressure of HNO_3 (p_{HNO_3}) divided by a reference pressure p_{ref} (here, 1 atm), and ΔG_k is the free energy change (computed for 1 atm reference pressure and some temperature T) for the reaction $NO_3^- + k HNO_3 \leftrightarrow NO_3^-(HNO_3)_k$. Note that as we are comparing the relative concentrations of different clusters, the absolute nitrate ion concentration does not enter the final expression. The clustering enthalpies and free energies for nitrate ions with one and two nitric acid molecules, computed at the PW91/6-311++G(3df, 3pd) level, are given in Table 1. The G3 and G3MP2 free energy values for the $NO_3^- + HNO_3$ reaction are -21.81 and $-21.03\,\mathrm{kcal\,mol^{-1}}$, respectively, indicating that the PW91 values for nitric acid – nitrate binding are qualitatively reliable, though perhaps slightly too high. If the total concentration of nitric acid is much larger than that of nitrate (i.e. the concentration of free nitric acid is not significantly depleted by clustering with nitrate), Eq. (1) can easily be used to obtain an estimate of the nitrate ion – nitric acid cluster distribution.

The quantitative extent of nitrate – nitric acid clustering will be different in different CIMS instruments, as it depends on temperature, nitric acid vapor concentration, and mixing time. In some instruments, the time between the charging of the nitric acid sheath flow and the separation of ions from the flow is rather short, and full thermodynamic equilibrium (as assumed in Eq. 1) likely cannot be assumed even for the sheath flow. In the sample flow, the nitric acid concentration is much lower than in the sheath flow, but evaporation of the smallest clusters is almost certainly too slow for a new equilibrium to be fully reached within the timescale of the charging processes. For example, the evaporation rate of $(NO_3^-)(HNO_3)$ to $NO_3^- + HNO_3$ computed from the data in Table 1 is on the order of $10^{-7}\,\mathrm{s^{-1}}$, while that of $(NO_3^-)(HNO_3)_2$ to $(NO_3^-)(HNO_3) + HNO_3$ is on the order of $10^2\,\mathrm{s^{-1}}$. Thus, even if the HNO_3 concentration in the sample flow were zero, $(NO_3^-)(HNO_3)$ ions would remain intact, while most $(NO_3^-)(HNO_3)_2$ ions might evaporate to $(NO_3^-)(HNO_3) + (HNO_3)$. Furthermore, ions with different masses are pulled from the sheath flow into the sample flow with different efficiencies, so the equilibrium cluster distribution computed for the sheath flow may not apply, even as an initial condition, for the sample flow.

As an illustrative example, at 298 K temperature and a nitric acid concentration of 600 ppb in the sheath flow, corresponding roughly to conditions of the SI-CIMS used at Helsinki University (Petäjä et al., 2009, and references therein), yields the result that only 10^{-10}% of the nitrate ions in the sheath flow actually exist as free nitrate NO_3^-, with 11 % as $NO_3^-(HNO_3)$ and 89% as $NO_3^-(HNO_3)_2$ (using Eq. (1), with x truncated to 0, 1, 2). Though the absolute values are not quantitatively reliable, both due to the errors in the equilibrium assumption and to uncertainties in the computed free energies (e.g. the G3 data indicates that PW91 may predict slightly too high NO_3^--HNO_3 clustering), the qualitative result that only a very small fraction of nitrate is present as free NO_3^- is trustworthy. This qualitative result is also verified by experimental evidence by Tanner et al. (1997) and Zhao et al. (2010), who both find the dominant ion to be $NO_3^-(HNO_3)$, with a significant but smaller (on the order of 10%) contribution of $NO_3^-(HNO_3)_2$. The difference between the computed equilibrium for the sheath flow and the measured result from the sample flow is probably partially due to evaporation of $NO_3^-(HNO_3)_2$ in the sample flow (which has a significantly lower HNO_3 concentration). Based on this, subsequent calculations have been made assuming the dominant charge carrier to be $NO_3^-(HNO_3)$. If, in some instruments, the extent of NO_3^--HNO_3 clustering in the sample flow is even larger, the charging efficiencies will be correspondingly lower.

The proton affinities of the three $NO_3^-(HNO_3)_b$ (with $b = 0,1,2$) species are shown in Table 2. The proton affinity computed for HSO_4^- is shown for comparison. Both the values for nitrate and hydrogensulfate are in reasonable agreement with the state-of-the art computational values given in the NIST Chemistry webbook (Bartmess, 2010), as well as with G3 and G3MP2 data computed here (see the Supplement for absolute enthalpy values).

A naïve interpretation of the data in Table 2 would seem to indicate that CIMS instruments should not work at all, since the dominant charge carrier $NO_3^-(HNO_3)$ is not able to remove a proton from H_2SO_4 in the gas phase. For example, the PW91-level standard Gibbs free energy change for the reaction $(H_2SO_4) + (NO_3^-)(HNO_3) \leftrightarrow (HSO_4^-) + (HNO_3)_2$ is $+9.95\,\mathrm{kcal\,mol^{-1}}$, indicating that the equilibrium for the reaction will lie strongly on the reactant side. Similar results are obtained for all charging reactions with $(NO_3^-)(HNO_3)$ as the charging ion and free HSO_4^- as an end product. Note that for reactions with different numbers of reactants and products, the choice of reference pressure will have an enormous effect on the numerical value of the free energy change. In these cases, the sign of the ΔG term cannot directly be used to infer the favorability of the reaction for an arbitrary set of reactant and product concentrations. This can be understood by noting that the equilibrium constant is also the ratio of the forward and reverse reaction rates. If the number of reactant and product molecules are different, the equilibrium constant will therefore not be dimensionless, and its numerical value will depend on the chosen system of units. For example, reaction rates and equilibrium constants computed for such reactions using 1 atm as a reference pressure will have very different numerical values from those using 1 molecule $\mathrm{cm^{-3}}$, even though the actual physical parameters – e.g. the cluster collision and evaporation rates – naturally remain identical.

Table 1. Thermochemical parameters (at the PW91/6-311++G(3df, 3pd) level) for the clustering of nitrate ions with nitric acid. All values correspond to 298 K and 1 atm reference pressure for all species.

Reaction	ΔH, kcal mol^{-1}	ΔG, kcal mol^{-1}
$HNO_3 + NO_3^- \leftrightarrow (NO_3^-)(HNO_3)$	−32.02	−23.60
$HNO_3 + (NO_3^-)(HNO_3) \leftrightarrow (NO_3^-)(HNO_3)_2$	−18.31	−9.71

Table 2. Proton affinities (at the PW91/6-311++G(3df, 3pd) level) for the hydrogensulfate ion and various nitrate ion – nitric acid clusters.

Species	Proton affinity, kcal mol^{-1}
NO_3^-	323.9
$(NO_3^-)(HNO_3)$	300.5
$(NO_3^-)(HNO_3)_2$	285.5
HSO_4^-	311.1

In the given example, the number of reactants and products happens to be the same, so the reference pressure terms cancel out.

Even though "fly-by" charging reactions are thermodynamically unfavorable, charging can (and will) occur via various clustering reactions, as noted by Viggiano et al. (1997):

$$(H_2SO_4) + (NO_3^-)(HNO_3)_b \tag{R1}$$

$$\leftrightarrow (HSO_4^-)(HNO_3)_{b+1} \tag{R1a}$$

$$\leftrightarrow (HSO_4^-)(HNO_3)_b + (HNO_3) \tag{R1b}$$

where each cluster may also bound to one or more water molecules, and b may take several values – though, as indicated by experiments of Tanner et al. (1997) and Zhao et al. (2010), the most probable value is $b = 1$. In the Helsinki University CIMS, the clusters formed in Reaction (R1a, b) are subsequently broken up in a collision dissociation chamber (CDC; see Mauldin et al., 1998 and Petäjä et al., 2009 for details) prior to the mass spectrometric detection. Thus, even though the initially formed bisulfate-containing species are mostly $(HSO_4^-)(HNO_3)$ and $(HSO_4^-)(HNO_3)_2$, the main sulfur-containing ion finally detected is HSO_4^-.

Assuming that the effect of hydration can either be ignored (as indicated by the results of Viggiano et al., 1997) or in any case accounted for via summation over all degrees of hydration, the equilibrium ratio of neutral to ionized sulfuric acid in the two mechanisms can be written as:

$$\frac{[H_2SO_4]}{\left[HSO_4^-(HNO_3)_{b+1}\right]} = \frac{1}{\left[NO_3^-(HNO_3)_b\right]K_{R1a,b}} = \frac{1}{\frac{p_{\{NO_3^-(HNO_3)_b\}}}{p_{ref}}}e^{\frac{\Delta G_{R1a,b}}{RT}} = \frac{p_{ref}}{p_{\{NO_3^-(HNO_3)_b\}}}e^{\frac{\Delta G_{R1a,b}}{RT}} \tag{2}$$

for reaction type R1a, or

$$\frac{[H_2SO_4]}{\left[HSO_4^-(HNO_3)_b\right]} = \frac{[HNO_3]}{\left[NO_3^-(HNO_3)_b\right]K_{R1b,b}} = \frac{[HNO_3]}{\left[NO_3^-(HNO_3)_b\right]}e^{\frac{\Delta G_{R1b,b}}{RT}} \tag{3}$$

for reaction type R1b. Here, $K_{R1a,b}/\Delta G_{R1a,b}$ and $K_{R1b,b}/\Delta G_{R1b,b}$ are the equilibrium constants/free energy changes for the Reaction (R1a, b), respectively, $p_{NO_3-(HNO_3)b}$ is the partial pressure of $NO_3^-(HNO_3)_b$, and $p_{ref} = 1$ atm.

The standard enthalpies and free energies for reaction types R1a and R1b with number of nitric acids $b = 0, 1$ for reaction R1a and $b = 0, 1, 2$ for Reaction (R1b) are given in Table 3.

Precise values of the ratio of ionized nitrate to nitric acid, and thus the total nitrate ion concentration, are not easy to determine in different regions of CIMS instruments, and are also likely quite different for different instruments. For the Helsinki University CIMS, an upper limit can be estimated by assuming that all the kinetic energy of all the alpha particles (roughly 5 MeV per particle) emitted by the instrument's 7.5 MBq radiation source goes into ionizing air molecules (predominantly N_2 and O_2, with ionization energies of 15.6 and 12.1 eV, respectively) in the nitric acid sheath air, which flows past the radiation source at a rate of 22 standard liters per minute, and that every electron liberated from air molecules eventually leads to the formation of NO_3^- ions, with all loss terms ignored. This would result in nitrate ion concentration in the sheath air of about 7×10^9 ions per cubic centimeter, or about 250–300 ppt. This is less than 0.05% of the original HNO_3 concentration, which indicates that the assumption of excess neutral HNO_3 in computing the nitrate ion cluster distribution is justified. Preliminary experiments using a CIMS inlet together with an atmospheric pressure interface mass spectrometer (APi-TOF; see Junninen et al., 2010, and Ehn et al., 2010) indicated a total negative ion concentration of under 10^6 cm^{-3}, which is probably somewhat more realistic. For the subsequent calculations, the upper limit of 7×10^9 cm^{-3} for the Helsinki University CIMS will nevertheless be used.

Even if all concentrations in the nitric acid sheath flow were precisely known, the application of equations 2 and 3 is still far from trivial, as the nitrate ion concentrations and nitrate – nitric acid concentration ratios required are those in the sample flow (where the proton transfer reactions actually occur), not in the sheath air. This discussion refers to a CIMS instrument of the same type as the Helsinki University CIMS, but the general principle is the same for any nitrate ion

Table 3. Thermochemical parameters (at the PW91/6-311++G(3df, 3pd) level) for the clustering reactions of sulfuric acid with nitrate– nitric acid ions. All values correspond to 298 K and 1 atm reference pressure for all species.

Reaction	ΔH, kcal mol^{-1}	ΔG, kcal mol^{-1}
$H_2SO_4 + NO_3^- \leftrightarrow (HSO_4^-)(HNO_3)$	−44.88	−35.16
$H_2SO_4 + (NO_3^-)(HNO_3) \leftrightarrow (HSO_4^-)(HNO_3)_2$	−29.06	−19.41
$H_2SO_4 + NO_3^- \leftrightarrow HSO_4^- + HNO_3$	−12.81	−14.86
$H_2SO_4 + (NO_3^-)(HNO_3) \leftrightarrow (HSO_4^-)(HNO_3) + HNO_3$	−12.87	−11.57
$H_2SO_4 + (NO_3^-)(HNO_3)_2 \leftrightarrow (HSO_4^-)(HNO_3)_2 + HNO_3$	−10.75	−9.69

CIMS – the HNO_3 and NO_3^- concentrations must be known specifically in the region where the H_2SO_4 charging occurs. As an order-of-magnitude estimate, the maximum nitrate ion concentration in the Helsinki University CIMS sample flow can presumably be taken to be that computed above for the sheath flow, 7×10^9 cm^{-3}. While the nitrate ions and ion clusters are effectively pulled from the sheath flow to the sample flow by an electric field, the neutral nitric acid in the sheath air (with a total concentration of 600 ppb in the example instrument) does not mix significantly with the sample air. Therefore, the neutral nitric acid concentration in the sample flow is difficult to estimate. The total nitric acid concentration in the sample air consists of three different contributions: minimal amounts of nitric acid mixed in from the sheath flow, background ambient nitric acid concentration (which is highly variable, but mostly in the 1–10 ppb range, see e.g. Arnold and Luke, 2007; Arnold et al., 2007; Neuman et al., 2000) and nitric acid liberated in charge transfer reactions such as reaction R1b. For the subsequent calculations, we have assumed a HNO_3 concentration in the sample air of 1 ppb, giving a ratio of 4:1 for the neutral HNO_3 to the total nitrate ion. (This intended to be a lower limit estimate – the actual ratio is very likely higher.)

Focusing on the number of nitric acids $b = 1$ case, and using the HNO_3 and $NO_3^-(HNO_3)$ concentrations computed above, gives equilibrium values of 2×10^{-5} and 1×10^{-8} for the neutral to ionized sulfuric acid ratio at 298 K for Reaction (R1a, R1b), above.

The equilibrium concentrations computed above are not directly applicable to the dynamic situation inside a CIMS instrument. Even if the upper limit ion concentration of 7×10^9 cm^{-3} is used, a sulfuric acid molecule only collides with the charging ions a few times per second (with the precise value depending on the rate coefficient assumed for the ion-molecule collision). If more realistic nitrate ion concentrations are used, the time between collisions grows to several seconds or tens of seconds – implying that only a small fraction of the H_2SO_4 molecules will actually collide with charging ions during the time spent in the drift tube. However, since the equilibrium constants in Equations 2 and 3 above are equal to the ratios of the rate coefficients of the forward and reverse reactions, their values (as well as the computed equilibrium concentration ratios) are still good indicators of the relative efficiency of different charging mechanisms, or the relative efficiency of the same charging mechanisms for different cluster types.

For example, the PW91/6-311++G(3df, 3pd) equilibrium constant for the reaction $(NO_3^-)(HNO_3) + H_2SO_4 \leftrightarrow (HSO_4^-)(HNO_3) + (HNO_3)$ is roughly 3×10^8, indicating that the reverse reaction rate coefficient is smaller than the forward reaction rate coefficient by this factor. Assuming that the forward reaction occurs at close to the ion-molecule collision limit (on the order of 10^{-9} cm^{-3} s^{-1}), this would imply a reverse rate coefficient of around 10^{-17} cm^{-3} s^{-1}. This is clearly too small to matter regardless of the HNO_3 concentration. Thus, the concentration of HSO_4^- ions detected will be linearly proportional to the concentration of pure H_2SO_4 molecules in the sample flow.

Preliminary calculations on hydrated clusters made by us (see the Supplement for computed thermodynamic parameters) indicate that hydration of the sulfuric acid by up to 3 water molecules will increase the Gibbs free energy of Reaction (R1a, b) (with $b = 1$), but by less than 2 and 6 kcal mol^{-1}, respectively. Even after accounting for hydration, the neutral to ionized sulfuric acid ratio is thus well below 10^{-3} for both charging pathways. From a dynamic viewpoint, this means that the reverse reactions of R1a and R1b, where the hydrated $(HSO_4^-)(HNO_3)_2$ clusters evaporate, or where HNO_3 combines with a hydrated $(HSO_4^-)(HNO_3)$ cluster, to reform hydrated H_2SO_4 and $(NO_3^-)(HNO_3)$, are significantly faster than for the unhydrated case, but still too slow to influence the measurement results.

For pure and hydrated sulfuric acid monomers, the nitrate – hydrogensulfate proton transfer can therefore be expected to be essentially complete, even when nitric acid – nitrate clustering is accounted for. This qualitative result presumably applies for all CIMS instruments, and is in accordance with the experimental results of Viggiano et al. (1997).

3.2 Effect of base molecules on charging probability

Sulfuric acid – containing clusters which also contain base molecules such as ammonia or amines are less likely to be negatively charged by proton exchange reactions than clusters containing only sulfuric acid and water. The fundamental reason for this is that while H_2SO_4 is a strong acid, and forms very strong hydrogen bonds with base molecules, HSO_4^- is a fairly weak acid, and does not bind particularly strongly to bases. In a computational study by Kurtén et al. (2008), it was demonstrated that the binding of H_2SO_4 to ammonia and seven different amines is significantly stronger (by several kcal mol^{-1}) than that of HSO_4^-. In other words, for base-containing clusters, the effect of the strong acidity of H_2SO_4 on the binding energies (or formation enthalpies/free energies) is greater than the electrostatic attraction associated with the net charge on HSO_4^-. On the other hand, for non-basic molecules, the opposite applies. For example, HSO_4^- binds both H_2SO_4 and H_2O much more strongly than neutral H_2SO_4 does (see e.g. Kurtén et al., 2007, 2008 and Ortega et al., 2008 for thermodynamic data). This difference in stabilities means that it is much more difficult to remove protons from base-containing clusters than from pure sulfuric acid – water clusters.

Assessment of the overall effect of H_2SO_4 – base clustering on CIMS measurements requires investigation of three partially separate issues. First, the fraction of H_2SO_4 molecules clustered with various bases at different conditions needs to be known. Second, the relative probability of a H_2SO_4-base cluster being charged in the CIMS instrument compared to a pure H_2SO_4 molecule or H_2SO_4-H_2O cluster needs to be evaluated. Third, we need to know in what form the fraction of H_2SO_4-base clusters that are charged will be measured in the final MS detection.

We have studied all of these three issues using dimethylamine as an example amine. In general, the basicity of amines, as well as the strength of their binding to a single sulfuric acid (though not necessarily to a larger, multiple-acid cluster) increases with the number of alkyl groups. The results obtained here are thus likely to apply qualitatively also to other amines, but with the effects on clustering and charging efficiency being more pronounced for tertiary amines like trimethylamine, and less pronounced for primary amines like methylamine.

3.2.1 Estimating the fraction of H_2SO_4 bound to base molecules

In principle, estimating the fraction of H_2SO_4 molecules bound to ligands such as water or base molecules for any set of ligand concentrations is a simple task once the relevant formation thermodynamics are available – se e.g. Kurtén et al. (2007) for an application to H_2SO_4-H_2O clustering. Unfortunately, while e.g. the PW91 free energies for H_2SO_4-H_2O clustering compare quite favorably with experimental and higher-level computational results, recent calculations (Kurtén, 2011) indicate that they strongly underestimate the binding between amines and H_2SO_4. In contrast, the formation thermodynamics given in Loukonen (2010) strongly overestimate the amine-acid binding, most likely due to the vibrational scaling approach used. The scaling factors in Loukonen et al. (2010) are determined based on H_2SO_4-H_2O clusters, which have a greater proportion of intermolecular to intramolecular vibrational modes compared to H_2SO_4-amine clusters. As intermolecular vibrations are, in general, much more anharmonic than intramolecular vibrations, this approach tends to overestimate the anharmonicity of the amine-containing clusters, which leads to too strong binding when the free energies are calculated using the scaled frequencies.

As none of the published datasets are sufficiently accurate for modeling the precise cluster distribution of clusters containing one H_2SO_4 molecule and a varying number of ligands, we recomputed the formation thermodynamics for $H_2SO_4(H_2O)_{1...3}$ and $H_2SO_4(H_2O)_{0...2}(X)$ clusters (with X = ammonia or dimethylamine) with the highly accurate and expensive G3 method. Truncation of the dataset to clusters of up to four molecules only was done due to computational reasons (the cpu and memory requirements of the G3 method scales with the 7th power of the number of valence electrons in the modeled clusters), and may affect the reliability of the results for very high RH values. However, for RH values below about 80%, truncation of the dataset to the trihydrate should not cause significant error (Kurtén et al., 2007), and the computed results should give a reasonable indication of the degree of acid-water and acid-base clustering. The G3 enthalpies and free energies are given in the Supplement – equilibrium concentrations for the one-acid cluster distribution can be straightforwardly computed as described above for the case of nitrate-nitric acid clustering, or in Kurtén et al. (2007) for H_2SO_4-H_2O clustering. The discussion here refers to free energies and cluster distributions computed at a temperature of 298.15 K. While the overall degree of clustering decreases with increasing temperature, the competition between water and dimethylamine for H_2SO_4 is only weakly temperature-dependent. The cluster distributions described here therefore serve as order-of-magnitude estimates also for different temperatures.

While the PW91 data (see the Supplement and Nadykto et al., 2011) would indicate negligible amine-acid clustering even for amine concentrations as high as 1 ppb, and the data from Loukonen et al. (2010) would indicate essentially complete amine-acid clustering even for concentrations below 1 ppt, the G3 method predicts moderate clustering for concentrations in the ppt range.

Three main conclusions can be drawn from the cluster distributions predicted by the G3 thermodynamics. First, the concentration of one-acid clusters containing ammonia remains very low even for ammonia concentrations as high as 100 ppb, regardless of relative humidity. This is in agreement with previous computational studies (Ortega et al., 2008;

Nadykto et al., 2007, 2011) – at least two sulfuric acid molecules are required for ammonia to attach to the clusters at typical atmospheric conditions. Second, the most common H_2SO_4-$(CH_3)_2NH$ cluster for any relative humidity above 6% is $(H_2SO_4)[(CH_3)_2NH](H_2O)$, in qualitative agreement with Loukonen et al. (2010). Third, the fraction of amine-containing clusters becomes significant as the free amine concentration reaches a few ppt. For $[(CH_3)_2NH] = 1$ ppt, the total fraction of amine-containing clusters is about 7% for RH 0% and 9% for RH 100%. At $[(CH_3)_2NH] = 10$ ppt, the amine-containing clusters begin to dominate the distribution, with total fractions of 42% at RH 0% and 50% at RH 100%.

The values above correspond to theoretical equilibrium distributions, where the formation and loss rates of sulfuric acid have been ignored. In the real atmosphere, sulfuric acid may have a lifetime as short as a few minutes, and the amine-acid equilibrium distribution may never have time to form. The hard-sphere collision rate between a (H_2SO_4) and a $(CH_3)_2NH$ molecule is about 3×10^{-10} molecules^{-1} s^{-1}. As there are no significant kinetic barriers to cross in the formation of H-bonded clusters, and energy non-accommodation plays only a minor role due to the large number of vibrational degrees of freedom of the formed cluster (Kurtén et al., 2010), the formation rate of amine-acid clusters is likely of the same order of magnitude. An amine concentration of 1 ppt thus implies that a sulfuric acid molecule collides with an amine, and forms a cluster, on average once per 140 s. For an amine concentration of 10 ppt, the time between collisions is reduced to 14 s. Thus, both kinetic and (G3) thermodynamic parameters suggest that the threshold amine concentration region for significant amine-acid clustering is in the 1–10 ppt range. Below this range, clustering will be negligible for both kinetic and thermodynamic reasons, while above it, amine-containing clusters will dominate the distribution of neutral sulfuric acid clusters.

Whether or not the H_2SO_4-amine clusters are defined to belong to the "total gas-phase sulfuric acid" is a matter of taste. For example, H_2SO_4-H_2O clusters are normally included under this definition, so logic would suggest that also H_2SO_4 clusters with other ligands should be included. On the other hand, unlike the smallest hydrate clusters, the H_2SO_4-amine clusters typically have an ion pair structure, so they could also be considered to be salt monomers rather than a different form of gas-phase H_2SO_4 like the hydrates. Nevertheless, we emphasize that unlike condensation onto larger particles or various deposition processes, acid-amine clustering is not a permanent sink of atmospheric sulfuric acid. The evaporation rates of (H_2SO_4)-$(CH_3)_2NH$ clusters are in the $10^1 \ldots 10^{-3}$ s^{-1} region depending on the water content and computational method employed. Thus, even if the term "gas-phase sulfuric acid" is defined in a way that excludes the acid-amine clusters, knowledge of their concentrations is still crucial, as they form a relatively labile reservoir of free H_2SO_4.

3.2.2 Relative charging probability of H_2SO_4-base clusters

To illustrate the effect of base molecules on the charging thermodynamics of sulfuric acid clusters, we have computed the proton affinities of the two-molecule clusters of the hydrogensulfate ion with ammonia (NH_3) and dimethylamine ($(CH_3)_2NH$). At the PW91 level, the values are 320.1 and 322.1 kcal mol^{-1}, respectively. The corresponding G3MP2 values are 317.3 and 322.0 kcal mol^{-1}, respectively. These proton affinities are around 10 kcal mol^{-1} higher than that of free HSO_4^-, and within a few kcal mol^{-1} of the value for free NO_3^-. To assess the effect of this on the charging probabilities in CIMS, we have further computed the free energies for proton transfer reactions of ammonia- and amine-containing clusters:

$$(H_2SO_4)(X) + (NO_3^-)(HNO_3)_b \tag{R2b}$$

$$\leftrightarrow (HSO_4^-)(HNO_3)_{b+1}(X) \tag{R2a}$$

$$\leftrightarrow (HSO_4^-)(HNO_3)_b(X) + (HNO_3) \tag{R2b}$$

where X is either NH_3 or $(CH_3)_2NH$.

The standard free energies for reaction types R2a and R2b with number of nitric acids $b = 1$, computed with both the PW91/6-311++G(3df, 3dp) and the G3MP2 methods, are given in Table 4. Reaction enthalpies, as well as free energies for reactions with $b = 0$ or $b = 2$, can be computed from the data given in the Supplement.

Analogously to Eqs. (2) and (3) above, we can also compute the ratio of neutral to ionized acid-base clusters for the two charging mechanisms by simply replacing H_2SO_4, $(HSO_4^-)(HNO_3)_b$ and $(HSO_4^-)(HNO_3)_{b+1}$ by $(H_2SO_4)(X)$, $(HSO_4^-)(HNO_3)_b(X)$ and $(HSO_4^-)(HNO_3)_{b+1}(X)$ in the equations.

Using the same concentration values and ratios as above, the PW91 method predicts neutral to charged ratios for the $(H_2SO_4)(NH_3)$ cluster of around 0.2 for both mechanisms, and neutral to charged ratios for the $(H_2SO_4)(CH_3)_2NH$ cluster of around 17 and 3 for reactions R2a and R2b, respectively. In contrast, the G3MP2 method predicts significantly lower values: 0.0004 and 0.002 for $(H_2SO_4)(NH_3)$, and 0.0002 and 0.002 for $(H_2SO_4)(CH_3)_2NH$, using the equations for the R2a and R2b mechanisms, respectively.

Thus, while the PW91 data predicts that as many as three out of four $(H_2SO_4)(CH_3)_2NH$ clusters remain uncharged by CIMS, the G3MP2 data indicates that despite the lowering of proton affinity caused by the base molecules, also $(H_2SO_4)(CH_3)_2NH$ clusters will be essentially completely charged given the assumed nitrate and nitric acid concentrations (see Sect. 3.3 for a sensitivity analysis). In dynamic terms, this means that PW91 predicts that the reverse reactions (where $(HSO_4^-)(HNO_3)_b(X)$ clusters either evaporate or react with HNO_3 to produce $(H_2SO_4)(X)$ and

Table 4. Reaction free energies at the PW91/6-311++G(3df, 3pd) and G3MP2 levels for the clustering reactions of sulfuric acid, sulfuric acid – ammonia and sulfuric acid - dimethylamine dimers with the nitrate - nitric acid ion. All values correspond to 298 K and 1 atm reference pressure for all species.

Reaction	ΔG, PW91, kcal mol^{-1}	ΔG, G3MP2, kcal mol^{-1}
$(H_2SO_4) + (NO_3^-)(HNO_3) \leftrightarrow (HSO_4^-)(HNO_3)_2$	−19.41	−21.85
$(H_2SO_4)(NH_3) + (NO_3^-)(HNO_3) \leftrightarrow (HSO_4^-)(HNO_3)_2(NH_3)$	−13.95	−17.71
$(H_2SO_4)(CH_3)_2NH + (NO_3^-)(HNO_3) \leftrightarrow (HSO_4^-)(HNO_3)_2(CH_3)_2NH$	−11.41	−18.27
$(H_2SO_4) + (NO_3^-)(HNO_3) \leftrightarrow (HSO_4^-)(HNO_3) + HNO_3$	−11.57	−11.09
$(H_2SO_4)(NH_3) + (NO_3^-)(HNO_3) \leftrightarrow (HSO_4^-)(HNO_3)(NH_3) + HNO_3$	−1.70	−4.61
$(H_2SO_4)(CH_3)_2NH + (NO_3^-)(HNO_3) \leftrightarrow (HSO_4^-)(HNO_3)(CH_3)_2NH + HNO_3$	−0.11	−4.68

$HNO_3^-(HNO_3)$) are rapid enough to affect the measurement results, while G3MP2 predicts them to be too slow. Since the G3MP2 method (which compares favorably with the even higher-level G3 values) can be considered to be more reliable than PW91, the latter prediction is more trustworthy, though even more accurate future calculations as well as direct measurements may be required to fully settle the issue.

In addition to the charging mechanisms described above, the base-containing clusters may be charged by a "base-exchange" mechanism, where the incoming $(NO_3^-)(HNO_3)$ cluster replaces an ammonia or amine molecule. Since $(NO_3^-)(HNO_3)$ is a base in both the Brönstedt and Lewis sense (it accepts a proton and donates an electron pair), this process is then precisely analogous to the experimentally studied replacement of ammonia by amines in ammonium bisulfate (Bzdek et al., 2010), or nitrate (Lloyd et al., 2009) clusters or bulk solutions:

$$(H_2SO_4)(NH_3)+(NO_3^-)(HNO_3) \leftrightarrow (HSO_4^-)(HNO_3)_2+(NH_3) \quad \text{(R3)}$$

$$(H_2SO_4)(CH_3)_2NH+(NO_3^-)(HNO_3) \leftrightarrow (HSO_4^-)(HNO_3)_2 +(CH_3)_2NH \quad \text{(R4)}$$

The reaction free energy for Reaction (R3) is −11.14 kcal mol^{-1} at the PW91/6-311++G(3df, 3pd) and −15.08 kcal mol^{-1} at the G3MP2 level. Similarly, the free energy for Reaction (R4) is −7.55 and −8.32 kcal mol^{-1} at the PW91 and G3MP2 levels, respectively. Thus, the base-exhange type charging reactions are strongly exothermic, and the reverse reactions will be too slow to play any role regardless of which set of computational data is used. Charging via this mechanism will therefore be determined solely by the kinetics of the base exchange. The key parameter is the "uptake coefficient" – the fraction of (H_2SO_4)(base)-$(NO_3^-)(HNO_3)$ collisions that lead to the exchange reaction. Unfortunately, the interpretation of experimental data on analogous systems is ambiguous. For the exchange of ammonia by dimethylamine in nanometer-sized (positively charged) ammonium bisulfate clusters, Bzdek et al. (2010) found uptake coefficients that were close to unity, within the experimental error margins. On the other hand, experiments on the exchange of ammonia by trimethylamine in 20–500 nm ammonium nitrate particles have found uptake coefficients of around 0.002 (Lloyd et al., 2009). It is not clear which of these results correspond most closely to the system studied here. On one hand, the nanometer-sized clusters of Bzdek et al. (2010) are clearly closest in size to the two-molecule clusters in Reactions (R3) and (R4), above. On the other hand, the H_2SO_4 – amine binding is stronger than the H_2SO_4 – NH_3 binding, and there may be a higher kinetic barrier to cross in the base exchange in the case of Reaction (R4). In the absence of either truly dynamic simulation data or experimental measurements of Reactions (R3) and (R4), the quantitative determination of the efficiency of the base-exchange charging mechanism must unfortunately remain an open question.

3.2.3 Effect of further acid molecules on charging

The above discussion has concerned clusters containing only one sulfuric acid molecule. In the atmosphere, especially during particle formation events, a significant amount of the gas-phase sulfuric acid may be found in clusters with two or more acid molecules (Zhao et al., 2010; Ehn et al., 2010). To determine whether the presence of base molecules will affect the charging probability of these clusters, we have computed proton affinities for the charged sulfuric acid dimer $HSO_4^-(H_2SO_4)$ with 0–2 dimethylamine molecules, using both the PW91/6-311++G(3df, 3pd) and G3MP2 methods. The results are given in Table 5. At the PW91 level, all two-acid clusters are predicted to have lower proton affinities than free HSO_4^-. Similar predictions are made by G3MP2, except for the case of the $HSO_4^-(H_2SO_4)[(CH_3)_2NH]_2$, for which the proton affinity is predicted to be about 6 kcal mol^{-1} higher. However, even this is still 6 kcal mol^{-1} lower than the proton affinity of $HSO_4^-(CH_3)_2NH$ cluster, and about

1 kcal mol^{-1} lower than that of $HSO_4^-(NH_3)$. From a cluster chemistry perspective, the result simply indicates that despite the presence of two base molecules, the larger cluster has at least one proton that is relatively weakly bound (and thus susceptible to removal by NO_3^- and its clusters). The proton affinities given in Table 5 indicate that all clusters with more than one sulfuric acid molecule will likely be charged by CIMS, despite the presence of amines. As the effect of base molecules on charging increases with the strength of the base, the same will apply also for clusters with multiple acid molecules and ammonia.

3.2.4 Evaporation of base molecules after charging

As shown in Sect. 3.2.1, a significant fraction of sulfuric acid molecules are likely to be bound to amines whenever the free amine concentration is in the ppt range or higher. This is especially true for clusters with two or more sulfuric acids, where the presence of an amine lowers the acid evaporation rate by up to nine orders of magnitude. However, measurements of the smallest sulfuric acid – containing clusters (e.g. APi-TOF data recently published by Ehn et al., 2010, or cluster CIMS data published by Zhao et al., 2010) do not show large amounts of amine- or ammonia-containing clusters. Since the data presented above indicates that a large part of the base-containing one-acid clusters, and all of the base-containing two-acid clusters, will be charged by CIMS, the observations would seem to contradict the computational predictions. However, this apparent contradiction is almost certainly explained by the weaker binding of base molecules to negatively charged clusters, and the consequent evaporation of base molecules shortly after charging.

From the data Ortega et al. (2008, 2009), evaporation rates of an ammonia molecule from a neutral sulfuric acid cluster (computed by assuming collision rate coefficients on the order of 3×10^{-10} molecules^{-1} s^{-1}, and applying the law of detailed balance) are on the order of 10^5 s^{-1}, 10 s^{-1} and 10^{-2} s^{-1} for a cluster containing 1, 2 and 3 sulfuric acid molecules, respectively. The corresponding values for a charged cluster (where one neutral acid is replaced by HSO_4^-) are 10^{13} s^{-1}, 10^{12} s^{-1} and 10^4 s^{-1}. Since the time between charging and detection of the clusters is inevitably considerably longer than 10^{-12} s, it is clear that no charged sulfuric acid – ammonia clusters with less than 3 acids will ever be measured, despite the fact that ammonia-containing neutral two-acid cluster might be reasonably abundant in the atmosphere. The same considerations apply for the dimethylamine-containing two-acid clusters. Based on data from Kurtén et al. (2008), the evaporation rate of $(CH_3)_2NH$ from a cluster with one and two sulfuric acids (and no water) increases from around 1 and 10^{-10} s^{-1} to 10^9 and 10^3 s^{-1}, respectively, upon charging. Similar changes are predicted by the G3MP2 data presented here. Thus, even though the presence of base molecules will not prevent the measurement of the sulfuric acid contained in two-acid clusters, the base molecules themselves will likely evade detection.

Table 5. Proton affinities (at the PW91/6-311++G(3df, 3pd) and G3MP2 levels) for clusters of the hydrogensulfate ion with sulfuric acid and/or dimethylamine.

Species	Proton affinity, PW91, kcal mol^{-1}	Proton affinity, G3MP2, kcal mol^{-1}
HSO_4^-	311.1	311.4
$HSO_4^-(CH_3)_2NH$	322.1	322.0
$HSO_4^-(H_2SO_4)$	281.8	282.1
$HSO_4^-(H_2SO_4)(CH_3)_2NH$	299.3	299.7
$HSO_4^-(H_2SO_4)[(CH_3)_2NH]_2$	310.2	315.9

3.3 Sensitivity analysis and atmospheric implications

In addition to uncertainties in the computed thermochemical parameters and the neglect of various dynamic processes, the conclusions drawn in the above sections strongly depend on the assumptions made regarding the NO_3^- concentration and the extent of nitrate ion – nitric acid clustering in the CIMS instrument, as well as the neutral nitric acid concentration in the sample flow. In the example calculations in the previous sections, made for the specific case of the Helsinki University CIMS, the nitrate ion concentration estimate represents the maximum case, while the estimated neutral nitric acid concentration in the sample flow is likely in the lower end of the range of plausible values. More realistic values for either parameter would increase the computed ratios of neutral to ionized sulfuric acid. For example, a nitrate ion concentration of 1×10^7 cm^{-3} and a neutral nitric acid concentration of 10 ppb would, together with the PW91 free energies, imply that less than one percent of $(H_2SO_4)(NH_3)$ clusters and less than 0.05% of $(H_2SO_4)(CH_3)_2NH$ clusters will be charged by the main charging ion $(NO_3^-)(HNO_3)$. On the other hand, even with these concentration values, the G3MP2 data still predicts that around 80–90% of both cluster types will still be charged (via the R2a mechanism). However, it is important to note that even the G3MP2 data predicts a deviation of the charging efficiency from unity for this (reasonable) set of nitrate and nitric acid concentrations. Furthermore, if an error margin of around 2 kcal mol^{-1} in the G3MP2 free energies is assumed, the percentage of $(H_2SO_4)(CH_3)_2NH$ clusters charged could, at worst, be as low as 25%. Thus, while quantitative predictions can not be made both due to uncertainties in the computational data and due to the lack of data on concentrations within the instrument, we can not rule out the possibility that clustering with base molecules reduces the measured HSO_4^- signal. However, this reduction is very likely less than an order of magnitude, and probably only on the order of ten percent or less.

Again, we emphasize that very different values may be obtained for different instrument setups, though the general principle is the same – base-containing one-acid clusters are more difficult to charge.

Taken together, the data in Tables 4 and 5 indicate that the effect of dimethylamine (and presumably, other amines) on measured total sulfuric acid concentrations may not be a simple or even monotonic function of the amine concentration. As the amine concentration increases, larger fractions of one-acid clusters will contain amine molecules, and may thus not be quantitatively measured by CIMS. On the other hand, increasing amine concentrations will also enhance the formation of clusters with two (or more) acid molecules (Kurtén et al., 2008; Loukonen et al., 2010), which will in turn be measured by CIMS.

To some extent, the effect of amines or ammonia on the sulfuric acid measurement may already be partially included in the calibration of the CIMS instruments. The Helsinki University CIMS (as well as many others) is calibrated by generating a known amount of OH that then oxidizes SO_2 to H_2SO_4. Since the basic contaminants will likely be present in the calibration air, their effect will partially be taken into account, depending on the relative timescales of H_2SO_4 formation and measurement and acid-base cluster formation. For amines, with typical concentrations in the ppt range, the time elapsed between the formation of the calibration H_2SO_4 and its charging (around 0.3 s in the Helsinki University CIMS) is insufficient for the acid-base cluster equilibrium to be reached, as the average time between collisions with amine molecules is in the range of 100 s. On the other hand, the effect of ammonia may partially be accounted for in the calibration, as its concentration may be large enough for the H_2SO_4 molecules to have time to collide with NH_3 prior to the charging.

In order to better quantify the effect of base molecules on the total sulfuric acid measured by CIMS, the following parameters need to be known: the percentage of nitric acid molecules that are charged to nitrate ions, the residence time of the nitrate ions in the nitric acid flow, the corresponding concentrations of different nitrate – nitric acid cluster ions in the sample flow, and the concentration of neutral nitric acid in the sample flow. These parameters likely vary among different instruments, and (at least for the sample flow neutral HNO_3 concentration) between different measurement sites. One intriguing possibility is that some differences in measured sulfuric acid concentrations are due to differences in the sensitivity toward amine contamination among different CIMS instruments. It is difficult to estimate how large these differences might plausibly be. One one hand, the CIMS charging process is mainly kinetically controlled, with $NO_3^-(HNO_3)$ as the most probable reagent ion in all instruments. Also, as discussed above, some of the effects of base contaminants are accounted for already in the calibration procedure. On the other hand, the concentration of neutral HNO_3 directly determines e.g. the rate of the reverse process of reaction R2b, and instruments with higher HNO_3 concentrations (either due to the instrument construction or the measurement site) might therefore measure somewhat lower HSO_4^- signals. The more reliable G3MP2 thermodynamics indicates that the reduction in the HSO_4^- signal caused by amine contamination might be on the order of a few tens of percent, if both the ambient amine concentration and the neutral HNO_3 concentration in the instrument are high. Thus, the maximum possible difference between instruments due to differing sensitivity toward amine contamination is likely of this magnitude, as well.

In any case, we emphasize that the results and preliminary conclusions presented here should not be considered as a quantitative solution for correcting measurement results for amine contamination, but as a presentation of potential problem issue that should be investigated experimentally in more detail.

4 Conclusions

Using computational chemistry methods, we have shown that given amine concentrations in the ppt range or higher, a significant percentage of all sulfuric acid molecules will be clustered with amines. Furthermore, some fraction of these acid-amine clusters may not, under typical operating conditions, be charged in a CIMS instrument, though more reliable computational methods predict this fraction to be relatively minor; on the order of ten percent or less. In addition to the computational method used, this prediction is extremely sensitive to assumptions made about the clustering equilibria, as well as the nitrate ion and nitric acid concentrations within the CIMS instrument. However, all computational methods predict that any base molecules will very probably evaporate from the negatively charged clusters before they are measured. We note that the effects of amine clusters may be different than that of hydration (water clustering), which has negligible effect on CIMS detection, as shown both experimentally and computationally. Further investigation is required to quantitatively assess the effect of amine contaminants on CIMS measurements.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys.net/11/3007/2011/acp-11-3007-2011-supplement.pdf.

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