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Chemical ionization mass spectrometry (CIMS) may not measure all gas-phase sulfuric acid if base molecules are present

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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. Using computed proton affinities and reaction thermodynamics for the relevant charging reactions, we show that in the presence of strong bases such as amines, which tend to cluster with the sulfuric acid molecules, a significant fraction of the total gas-phase sulfuric acid may not be measured by a CIMS instrument. If this is the case, this effect has to be taken into account in the interpretation of atmospheric sulfuric acid measurement data, as well as in intercomparison of different CIMS instruments, which likely have different susceptibilities to amine-sulfuric acid clustering.

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 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

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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, 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. (Atmospheric concentrations of other acids stronger than HNO_3 are typically assumed to be much lower than that of H_2SO_4.) Based on the moderately large difference in the vacuum proton affinities of HSO_4^- and NO_3^-, and on the well-known bulk acidity (pK_a) 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. Some experimental indications of this have been presented by Hanson and Eisele (2002). In the presence of base molecules, NO_3^--HNO_3 clustering may decrease the charging probability of sulfuric acid – containing clusters. We have explored the possible consequences of this issue on the charging efficiency of CIMS using quantum chemistry methods. We also briefly discuss a related but separate issue affecting the final measured results, namely the evaporation of base molecules between the charging and the actual detection. 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 is likely 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. charging 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. Given information on the required parameters (e.g. NO_3^- and HNO_3 concentrations), the supplied thermodynamics and equations can be used to estimate charging ratios for any nitrate ion CIMS.

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 al., 2009), 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) with default energy and geometry convergence criteria. Thermochemical parameters were computed using the standard rigid rotor and harmonic oscillator approximations. 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. The computational approach used here is cost-effective (e.g. MP2 or CBS-QB3 energy calculations on the largest clusters studied here would, while perhaps desirable, be rather costly), provides at least qualitative reliability, and also permits comparison and synthesis with the large body of data on other types of charged and neutral clusters computed by Nadykto et al. (2007, 2008; see also references therein) at the exact same level. In general, quantum chemical free energies calculated for medium-sized (containing at most a few hundred electrons) clusters using appropriate methods are reliable to within about 1–2 kcal/mol, at least in the case of strongly bound clusters such as those studied here.

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. It should be noted that in this particular study, the largest uncertainties are probably related to the estimated concentrations of nitrate ions (and the ratio of nitrate ions to neutral nitric acid) in the region of the CIMS instrument where the proton transfer reactions take place, as well as to the neglect of various dynamic processes, rather than to the computed thermodynamics. Before these parameters can be better constrained, higher-level calculations of thermodynamic parameters would not significantly improve our understanding of the issues studied here.

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 $1.5RT$, 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 in CIMS

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:

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

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 $NO_3^- + kHNO_3 \Leftrightarrow NO_3^-(HNO_3)_k$. 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 are given in Table 1. 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 $(NO_3^-)(HNO_3)$ computed from the data in Table 1 is on the order of $10^{-7}\,s^{-1}$, while that of $(NO_3^-)(HNO_3)_2$ is on the order of $10^2\,s^{-1}$. 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, 298 K temperature and 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 actually exist as free nitrate NO_3^-, with 11.2% as $NO_3^-(HNO_3)$ and 88.8% 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, the qualitative result that only a 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 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 $NO_3^-(HNO_3)_n$ (with n=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), validating that the method used is at least qualitatively reliable for these species and cluster types (see computational details section).

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 standard Gibbs free energy change for the reaction $(H_2SO_4)+(NO_3^-)(HNO_3)\Leftrightarrow(HSO_4^-)+(HNO_3)_2$

is +9.95 kcal/mol, 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. In the given example, the number of reactants and products happens to be the same, so the reference pressure terms cancel out). However, as noted by Viggiano et al. (1997), charging can (and will) occur via various clustering reactions:

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

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

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

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 Reactions (R1a) and (R1b) 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 ratio of unionized to ionized sulfuric acid in the two mechanisms can be written as:

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

for reaction type (R1a), or

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

for reaction type (R1b). Here, $K_{\mathrm{R1a,b}}/\Delta G_{\mathrm{R1a,b}}$ and $K_{\mathrm{R1b,b}}/\Delta G_{\mathrm{R1b,b}}$ are the equilibrium constants/free energy changes for the reactions $(\mathrm{H_2SO_4})+(\mathrm{NO_3^-})(\mathrm{HNO_3})_b \Leftrightarrow (\mathrm{HSO_4^-})(\mathrm{HNO_3})_{b+1}$ and $(\mathrm{H_2SO_4})+(\mathrm{NO_3^-})(\mathrm{HNO_3})_b \Leftrightarrow (\mathrm{HSO_4^-})(\mathrm{HNO_3})_b+(\mathrm{HNO_3})$, respectively, $p_{\{\mathrm{NO_3^-(HNO_3)b}\}}$ is the partial pressure of $\mathrm{NO_3^-(HNO_3)_b}$, and $p_{\mathrm{ref}}=1$ 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 $\mathrm{N_2}$ and $\mathrm{O_2}$, 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 $\mathrm{N_2}$ or $\mathrm{O_2}$ molecules eventually leads to the formation of $\mathrm{NO_3^-}$ 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 $\mathrm{HNO_3}$ concentration, which indicates that the assumption of excess neutral $\mathrm{HNO_3}$ 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; 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. We recommend other CIMS users repeat these calculations using appropriate NO_3^- and HNO_3 concentration estimates.

Even if all concentrations in the nitric acid sheath flow were precisely known, the application of Eqs. (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 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, $7\times10^9\,\mathrm{cm}^{-3}$. The neutral nitric acid concentration in the sample flow is difficult to estimate, as the neutral nitric acid in the sheath air (with a total concentration of 600 ppb in the example instrument) does not have time to mix completely with the sample air. The total nitric acid concentration in the sample air consists of three different contributions: 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 assuming a neutral HNO_3 concentration of 1 ppb and a total nitrate ion concentration, assumed to be in the form of $NO_3^-(HNO_3)$, of 250 ppt, gives equilibrium values of 2×10^{-5} and 1×10^{-8} for the unionized to ionized sulfuric acid ratio at 298 K for Reactions (R1a) and (R1b), above. (Naturally, in a real instrument, there will probably not be time for the full equilibrium to be established, but the concentration of HSO_4^- ions detected will still be linearly proportional to the concentration of H_2SO_4 in the sample flow, as the evaporation rates of pure HSO_4^--HNO_3 clusters are so low.) 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 Reactions (R1a) and (R1b) (with b=1), but by less than 2 and 6 kcal/mol, respectively. Even after accounting for hydration, the unionized to ionized sulfuric acid ratio is thus well below 10^{-3} for both charging pathways. 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) 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; 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.

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 ($(CH_3)_2NH$), and found them to be 320.07 and 322.06 kcal/mol, respectively. These proton affinities are 9 and 11 kcal/mol higher than that of free HSO_4^-, and within 2 and 4 kcal/mol 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:

$$(H_2SO_4)(X) + (NO_3^-)(HNO_3)_b \quad \text{(R2)}$$

$$\Leftrightarrow (HSO_4^-)(HNO_3)_{b+1}(X) \quad \text{(R2a)}$$

$$\Leftrightarrow (HSO_4^-)(HNO_3)_b(X) + (HNO_3) \quad \text{(R2b)}$$

where X is either NH_3 or $(CH_3)_2NH$. Free energies for these reactions with b=0, 1 for Reaction (R2a) and b=0, 1, 2 for Reaction (R2b) are listed in Table 4. Analogously to Eqs. (2) and (3) above, we can also compute the ratio of unionized 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. Note that this approach disregards a potential mechanism by which the $(H_2SO_4)(X)$ cluster could be charged even though Reactions (R2a) and (R2b) themselves are rather unfavorable. If the transient complex formed directly from the collision of $(H_2SO_4)(X)$ and $(NO_3^-)(HNO_3)_b$ lives long enough for an amine molecule to evaporate before the reverse reaction occurs, the resulting $(H_2SO_4)(NO_3^-)(HNO_3)_b$ cluster would likely quickly rearrange to give $(HSO_4^-)(HNO_3)_{b+1}$ (or $(HSO_4^-)(HNO_3)_b$+$(HNO_3)_b$), which is fairly stable. Given the strength of the H_2SO_4-base binding, this process seems somewhat improbable, but it may play a role in determining the final quantitative charging ratios. Experimental or first-principles molecular dynamics studies on $(H_2SO_4)(X)$+$(NO_3^-)(HNO_3)_b$ collisions and may thus be warranted if more quantitative charging probabilities are required.

Assuming for simplicity that b=1, and using the same concentration values and ratios as above, we obtain for the $(H_2SO_4)(NH_3)$ cluster charging ratios of 0.24 and 0.22 for Reactions (R2a) and (R2b), respectively. Thus, both charging mechanism will leave about a fifth of $(H_2SO_4)(NH_3)$ clusters uncharged. For the $(H_2SO_4)(CH_3)_2NH$ cluster, the corresponding ratios are 17.1 and 3.3 for mechanism (R2a) and (R2b), respectively. This indicates that only less than one fourth of $(H_2SO_4)(CH_3)_2NH$ clusters will be charged, and hence measured by CIMS.

The significance of this result for measurements of total atmospheric gas-phase sulfuric acid depends on the total percentage of sulfuric acid molecules bound to ammonia or amines under atmospheric conditions. The thermodynamic data computed by Loukonen et al. (2010) for $(H_2SO_4)(X)_{0...1}(H_2O)_{0...5}$ clusters (where $X=NH_3$ or $(CH_3)_2NH$) can be used to estimate this percentage if thermodynamic equilibrium and constant gas-phase NH_3 and $(CH_3)_2NH$ concentrations are assumed, using the same approach as in Eq. (1) above. The results of such an analysis are somewhat surprising: even for very low (around 1 ppt) gas-phase amine concentrations, and for any relative humidity below 100%, over 98% of one-acid clusters at thermodynamic equilibrium contain dimethylamine. Given the charging ratios computed above, CIMS could thus be underestimating the true gas-phase sulfuric acid concentrations by over a factor of four due to H_2SO_4-amine clustering. On the other hand, even if the amine concentration is set to zero, and the ammonia concentration to a relatively high value of 10 ppb, the relative humidity must decrease below 8% for the fraction of ammonia-containing one-acid clusters to exceed 10%. The effect of ammonia on CIMS measurements in realistic atmospheric conditions is thus likely fairly low, though it may be moderately important in extremely dry conditions in the laboratory. (For example, at an RH of 1%, and if no amines are present, about half of the one-acid clusters contain ammonia.) Some indication of this is given by the experimental results of Tanner and Eisele (1995). It must be cautioned that the assumptions of constant gas-phase amine concentrations and thermodynamic equilibrium are very probably not valid for very low amine concentrations. If the amine concentration is on the same order of magnitude as the sulfuric acid concentration (e.g. 1 ppt corresponds to about 2.5×10^7 molecules cm^{-3}) the formation of amine-acid clusters will significantly deplete the gas-phase amine pool, and the fraction of amine-containing clusters will be significantly lower than computed assuming constant gas-phase concentrations. Also, the time between collisions for an H_2SO_4 molecule with amine molecules at ppt-range concentrations is of the same order of magnitude (around 100 s) as the total lifetime of sulfuric acid. The assumption of thermodynamic equilibrium may therefore tend to exaggerate the real fraction of amine-bound H_2SO_4. It should especially be noted that the equilibrium assumption is likely to give strongly erroneous results in experimental setups (such as some calibration experiments, see Sect. 2.4) where sulfuric acid is formed in situ.

3.3 Effect of further acid molecules on charging

The above discussion has concerned clusters containing only one sulfuric acid molecule. In the atmosphere, especially during nucleation 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. The results are given in Table 5. From the data in Tables 2 and 5, all two-acid clusters have lower proton affinities than free HSO_4^-. This is perhaps somewhat surprising for the case of the $HSO_4^-(H_2SO_4)[(CH_3)_2NH]_2$ cluster, as one might intuitively have expected it to have a proton affinity very close to the $HSO_4^-(CH_3)_2NH$ cluster, which has the same acid-base ratio. 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 be easily 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.

3.4 Sensitivity analysis and atmospheric implications

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 amine concentration increases, larger fractions of one-acid clusters will contain amine molecules, and will 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.

In addition to uncertainties in the computed thermochemical parameters, the neglect of various dynamic processes and the further assumptions made in estimating the fraction of one-acid clusters containing base molecules, 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 unionized to ionized sulfuric acid. For example, a nitrate ion concentration of $1\times10^7\ \mathrm{cm}^{-3}$ and a neutral nitric acid concentration of 10 ppb would 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 $(NO_3^-)(HNO_3)$. 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 much more difficult to charge.

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 differences in sulfuric acid concentrations measured by different CIMS instruments are due to differences in their sensitivity toward amine contamination. In any case, we emphasize that the results and preliminary conclusions presented here should not be considered a criticism of the CIMS method for measuring sulfuric acid, nor 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.

3.5 Evaporation of base molecules after charging

A counter-argument to a significant effect of amine contaminants on measured sulfuric acid concentrations is that measurements on 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 in Table 5 indicate that base-containing clusters with two (or more) acids will be charged by CIMS, and the data by Loukonen et al. (2010) indicate that almost all of the neutral two-acid clusters will contain a base molecule, the observations would seem to contradict the computational predictions. However, this apparent contradiction is very probably 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 $3\times10^{-10}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$, and applying the law of detailed balance) are on the order of $10^5\,\mathrm{s^{-1}}$, $10\,\mathrm{s^{-1}}$ and $10^{-2}\,\mathrm{s^{-1}}$ 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 $\mathrm{HSO_4^-}$) are $10^{13}\,\mathrm{s^{-1}}$, $10^{12}\,\mathrm{s^{-1}}$ and $10^4\,\mathrm{s^{-1}}$. 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. Similar considerations apply for the dimethylamine-containing two-acid clusters. Based on data from Kurtén et al. (2008), the evaporation rate of $\mathrm{(CH_3)_2NH}$ from a cluster with two sulfuric acids increases from $10^{-10}\,\mathrm{s^{-1}}$ to $10^3\,\mathrm{s^{-1}}$ upon charging. 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.

4 Conclusions

Using computational chemistry methods, we have shown that nitrate-based chemical ionization instruments may not, under typical operating conditions, charge all clusters containing one sulfuric acid molecule and an amine molecule. However, 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. Ammonia-containing clusters will be charged more easily, but a moderate fraction may still remain uncharged. Clusters with multiple acid molecules will, on the other hand, be charged regardless of the presence of base molecules. However, the base molecules will very probably still evaporate before the clusters are measured. We note that the effects of amine clusters are very 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, and on the differences among different CIMS instruments.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/10/30539/2010/ acpd-10-30539-2010-supplement.pdf.

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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	ΔG, kcal/mol
$HNO_3+NO_3^- \Leftrightarrow (NO_3^-)(HNO_3)$	−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
NO_3^-	323.9
$(NO_3^-)(HNO_3)$	300.5
$(NO_3^-)(HNO_3)_2$	285.5
HSO_4^-	311.1

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	ΔG, kcal/mol
$H_2SO_4+NO_3^- \Leftrightarrow (HSO_4^-)(HNO_3)$	−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

Table 4. Thermochemical parameters (at the PW91/6-311++G(3df,3pd) level) for the clustering reactions of sulfuric acid-ammonia and sulfuric acid-dimethylamine dimers with nitrate-nitric acid ions. All values correspond to 298 K and 1 atm reference pressure for all species.

Reaction	Δ*H*, kcal/mol	Δ*G*, kcal/mol
$(H_2SO_4)(NH_3)+(NO_3^-)\Leftrightarrow(HSO_4^-)(HNO_3)(NH_3)$	−35.98	−25.30
$(H_2SO_4)(CH_3)_2NH+(NO_3^-)\Leftrightarrow(HSO_4^-)(HNO_3)(CH_3)_2NH$	−33.99	−23.70
$(H_2SO_4)(NH_3)+(NO_3^-)(HNO_3)\Leftrightarrow(HSO_4^-)(HNO_3)_2(NH_3)$	−27.61	−13.95
$(H_2SO_4)(CH_3)_2NH+(NO_3^-)(HNO_3)\Leftrightarrow(HSO_4^-)(HNO_3)_2(CH_3)_2NH$	−24.97	−11.41
$(H_2SO_4)(NH_3)+(NO_3^-)\Leftrightarrow(HSO_4^-)(NH_3)+HNO_3$	−3.82	−5.30
$(H_2SO_4)(CH_3)_2NH+(NO_3^-)\Leftrightarrow(HSO_4^-)(CH_3)_2NH+HNO_3$	−1.83	−2.35
$(H_2SO_4)(NH_3)+(NO_3^-)(HNO_3)\Leftrightarrow(HSO_4^-)(HNO_3)(NH_3)+HNO_3$	−3.97	−1.70
$(H_2SO_4)(CH_3)_2NH+(NO_3^-)(HNO_3)\Leftrightarrow(HSO_4^-)(HNO_3)(CH_3)_2NH+HNO_3$	−1.97	−0.11
$(H_2SO_4)(NH_3)+(NO_3^-)(HNO_3)_2\Leftrightarrow(HSO_4^-)(HNO_3)_2(NH_3)+HNO_3$	−9.29	−4.23
$(H_2SO_4)(CH_3)_2NH+(NO_3^-)(HNO_3)_2\Leftrightarrow(HSO_4^-)(HNO_3)_2(CH_3)_2NH+HNO_3$	−6.65	−1.70

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

Species	Proton affinity, kcal/mol
$HSO_4^-(CH_3)_2NH$	322.06
$HSO_4^-(H_2SO_4)$	281.77
$HSO_4^-(H_2SO_4)(CH_3)_2NH$	299.34
$HSO_4^-(H_2SO_4)[(CH_3)_2NH]_2$	310.19

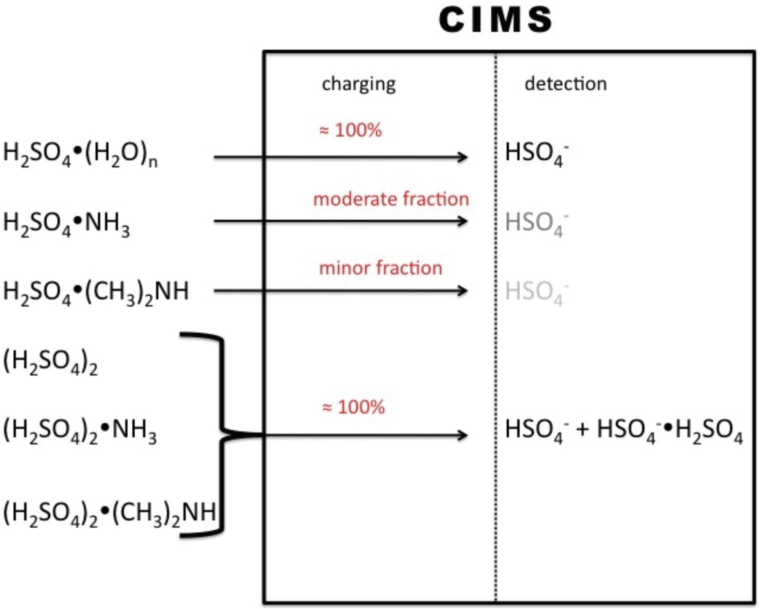

Fig. 1. Schematic of the performance of the CIMS instrument for various sulfuric acid-containing small clusters. The scheme illustrates two fundamental issues: only part of some base-containing clusters may be charged, and the base molecules will evaporate prior to detection even if the charging is successful.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

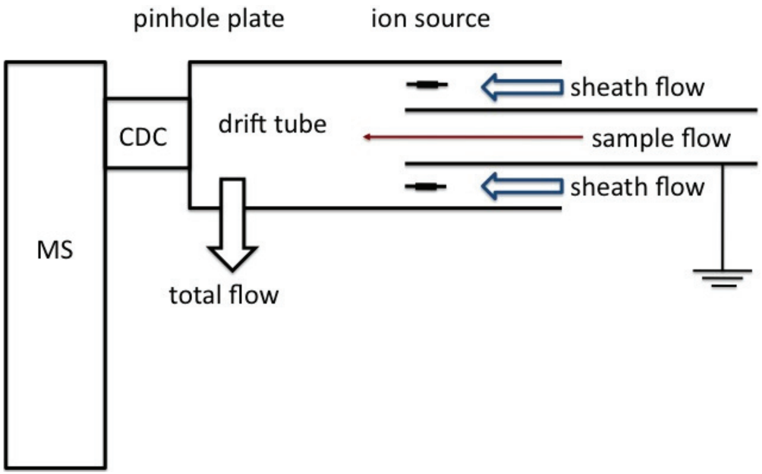

Fig. 2. A schema of the CIMS inlet. CDC and MS refer to collision-dissociation chamber and mass spectrometer, respectively.