We thank the reviewer for carefully reading our manuscript and for providing constructive comments, which have improved the quality and clarity of our manuscript. The reviewers' comments are repeated in full below, with our replies indicated after each comment in blue font. Text which has been added to the manuscript is shown in red font.

Before we give our detailed replies to all comments we want to indicate one major change that has been implemented.

After the manuscript was published we realized that the relative humidity (RH) which was used in the data analysis was taken as the RH over ice instead of supercooled water (note that the reported experiments include only conditions where the temperature was 248 K or colder). Since Hanson and Lovejoy (2006) used the RH over supercooled water it is necessary to refer the data from this study also to water, which shifts the relative humidities to lower values.

As requested by the referee (comment (21)) we have added a new figure to the manuscript (new Figure 6, see page 3 in this document), which shows the dependence of the sulfuric acid dimer evaporation rate as a function of the RH for two temperatures (208 and 223 K). Figure 6 also shows power law fit curves for each of the two data sets, indicating that the evaporation rates decrease with a power of p = -1 at 208 K and with p = -1.6 at 223 K. Because the new RH values do not correspond to 20% RH the evaporation rates cannot be directly compared to the data by Hanson and Lovejoy (2006). Therefore, the data points from Figure 6 that are closest to 20% RH were interpolated to 20% and these data are then used in Figure 7 (previously Figure 6) to obtain the fit parameters dH and dS. Using the updated data the fit parameters are now dH = -20.1±1.2 kcal mol^{-1} and dS = -46.7±5.2 cal mol^{-1} K^{-1}. The new values are somewhat different from the data by Hanson and Lovejoy (2006) who reported dH = -18.3±1.8 kcal mol^{-1} and dS = -39.5±7.8 cal mol^{-1} K^{-1} but still agree within errors. On the other hand the new data agree very well with quantum chemical calculations taking into account the effect of water on the formation of sulfuric acid dimers (Ding et al., 2003). Ding et al. (2003) report dH = -21.1 kcal mol^{-1} and dS = -51.7 cal mol^{-1} K^{-1} for the reaction of $(H_2SO_4)(H_2O)_2$ + $(H_2SO_4)(H_2O)$. Comparison between the data by Ding et al. (2003) and from this study is now included and the data (from quantum chemistry and measurements) are now shown in a new Table 2 (the previous Table 1 is now Table 4).

Additional small changes:

- The colors of the symbols in Figure 4 and Figure 5 have changed because the RH now represents the relative humidity over supercooled water.
- RH has also been updated in the context of Figure 10 (previously Figure 9 but since the new Figure 6 has been inserted the number has been adjusted). Because the pure sulfuric acid dimer evaporation rates are now changed slightly (due to the new fit parameters discussed above), the evaporation rates for the H_2SO_4•NH_3 cluster are somewhat different. This results also in updated values for dH and dS. These are now dH = -16.1±0.6 kcal mol^{-1} and dS = -26.4±2.6 cal mol^{-1} K^{-1}. The previously reported values were dH = -16.1 kcal mol^{-1} and dS = -26.2 cal mol^{-1} K^{-1}; therefore the change is relatively small.
- The dashed black line has been removed from Figure 7 (previously Figure 6)
- A new Table (Table 2) has been added; this table compares thermodynamic data of the formation of sulfuric acid dimers in the binary system; the previous Table 1 is now labeled Table 4 (see later comments).

Besides the addition of Figure 6 and the updated thermodynamic data, parts of the text have been modified. Section 3.3 now includes discussion of the new Figure 6. This discussion replaces the last part of Section 3.3 (starting with line 8 on page 13977):

"We converted equilibrium constants reported by Hanson and Lovejoy (2006) to evaporation rates using equation (8). Hanson and Lovejoy (2006) determined evaporation rates at 20% RH; while our measurements were made at different RHs. Because RH has a significant influence on the dimer evaporation further analysis is necessary to make the two data sets comparable.

Figure 6 shows the evaluated dimer evaporation rates as a function of the relative humidity (with respect to supercooled water) for two different temperatures (208 and 223 K). The rates from this study are based on the data shown in Figures 4 and 5 and equation (5). The data were fitted by simple power law fits and the slopes of $p = -1$ (at 208 K) and $p = -1.6$ (at 223 K) indicate that the evaporation rates decrease significantly with increasing RH. Qualitatively this is in agreement with a previous experiment (Hanson and Lovejoy, 2006) and quantum chemical calculations (Ding et al., 2003). However, Hanson and Lovejoy (2006) reported $p = -0.5$, where the exponent p has an uncertainty of ±100%. Our data indicate a somewhat stronger influence of RH on the evaporation rates, which also seems to be dependent on temperature.

The evaporation rates from Figure 6 with RH between 10 and 30% were normalized to 20% RH using the reported slopes. Figure 7 shows the data from this study and from Hanson and Lovejoy (2006). Fitting the combined data set for 20% RH gives the following formulation for the equilibrium constant

$$K_{eq} = \frac{1}{\mathrm{Pa}} \cdot exp\left(\frac{(10109 \pm 609)\ K}{T} - (35.03 \pm 2.61)\right). \qquad (9)$$

The black line in Fig. 7 shows the dimer evaporation rates derived from equation (9). The uncertainties in equation (9) are based on 95% confidence intervals. Overall, the two data sets are, within errors, consistent with one another, and yield dH = -20.1±1.2 kcal mol^{-1} and dS = -46.7±5.2 cal mol^{-1} K^{-1}. We caution that in this study the assumption is made that dH does not vary with temperature; generally this variation should, however, be small. These data are slightly different than what has been reported by Hanson and Lovejoy (2006). However, our data agree within errors with results from quantum chemical calculations, taking into account the effect of water vapor (Ding et al., 2003). According to measurements by Hanson and Eisele (2000) and quantum chemical calculations (Temelso et al., 2012; Henschel et al. 2014) the sulfuric acid monomer and dimer can contain water molecules. Therefore, the data from Ding et al. (2003) taking into account the effect of water vapor are relevant for this study. Table 2 shows a comparison between different studies dealing with the sulfuric acid dimer formation. Regarding the effect of water vapor it should be noted that our experimentally determined evaporation rates represent an average for dimers containing different numbers of water molecules. The exact distribution of water associated with the dimers will be a function of relative humidity and temperature, which cannot be taken into account explicitly in this study."

Study	dH (kcal mol^{-1})	dS (cal mol^{-1} K^{-1})	$k_{2,e}$ at 208 K (s^{-1})	$k_{2,e}$ at 223 K (s^{-1})
this study (20% RH)	-20.1±1.2	-46.7±5.2	0.15	3.9
Hanson and Lovejoy (20% RH)	-18.3±1.8	-39.5±7.8	0.32	6.0
$(H_2SO_4)(H_2O) + (H_2SO_4)(H_2O)$[a]	-17.8	-48.3	89.3	1550
$(H_2SO_4)(H_2O)_2 + (H_2SO_4)(H_2O)$[a]	-21.1	-51.7	0.17	5.0
$(H_2SO_4)(H_2O)_2 + (H_2SO_4)(H_2O)_2$[a]	-25.6	-55.7	2.4×10^{-5}	1.5×10^{-3}

Table 2. Thermodynamic properties (dH and dS) and evaporation rates of the sulfuric acid dimer from this study and from the literature. [a]Literature data from Ding et al. (2003).

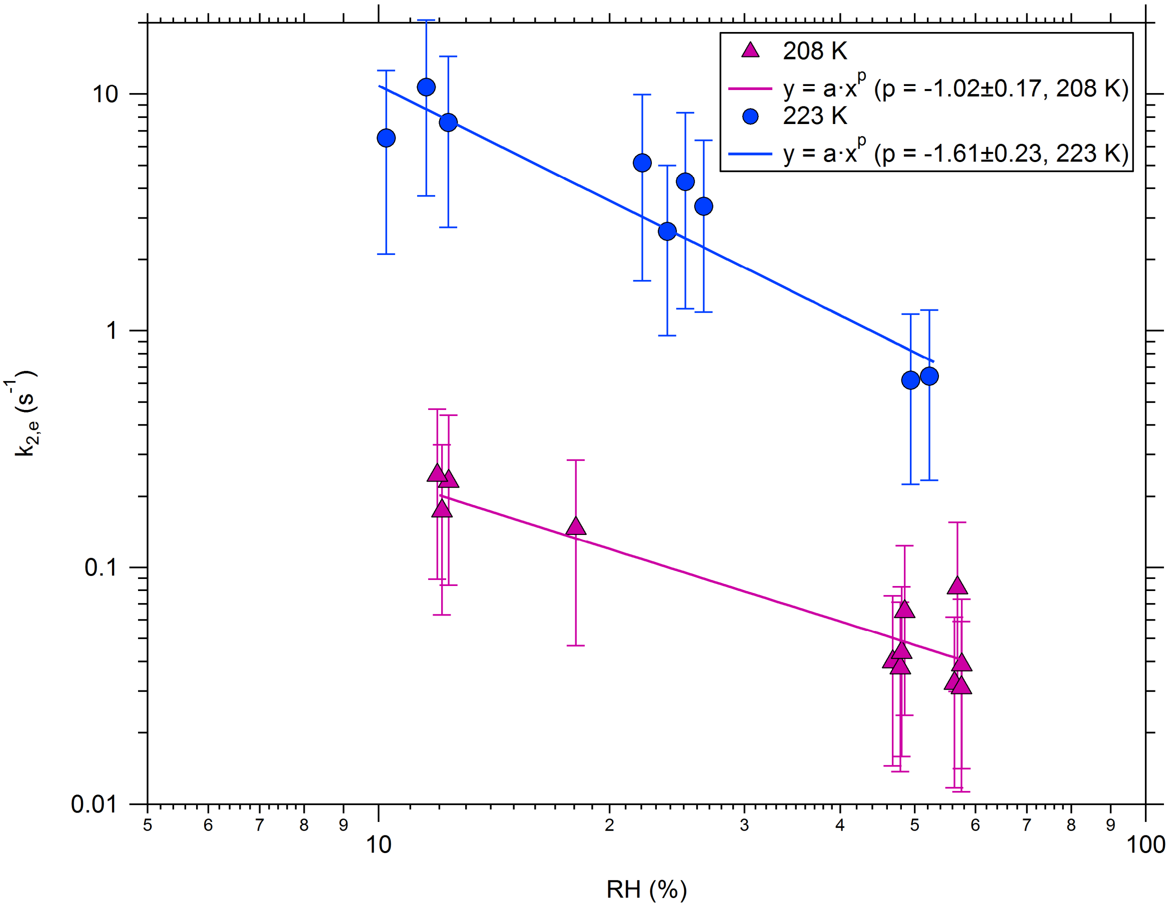


Fig. 6. Dimer evaporation rate as a function of the RH for two different temperatures (208 and 223 K). Power law fit curves are shown and the slopes *p* are indicated in the figure legend.

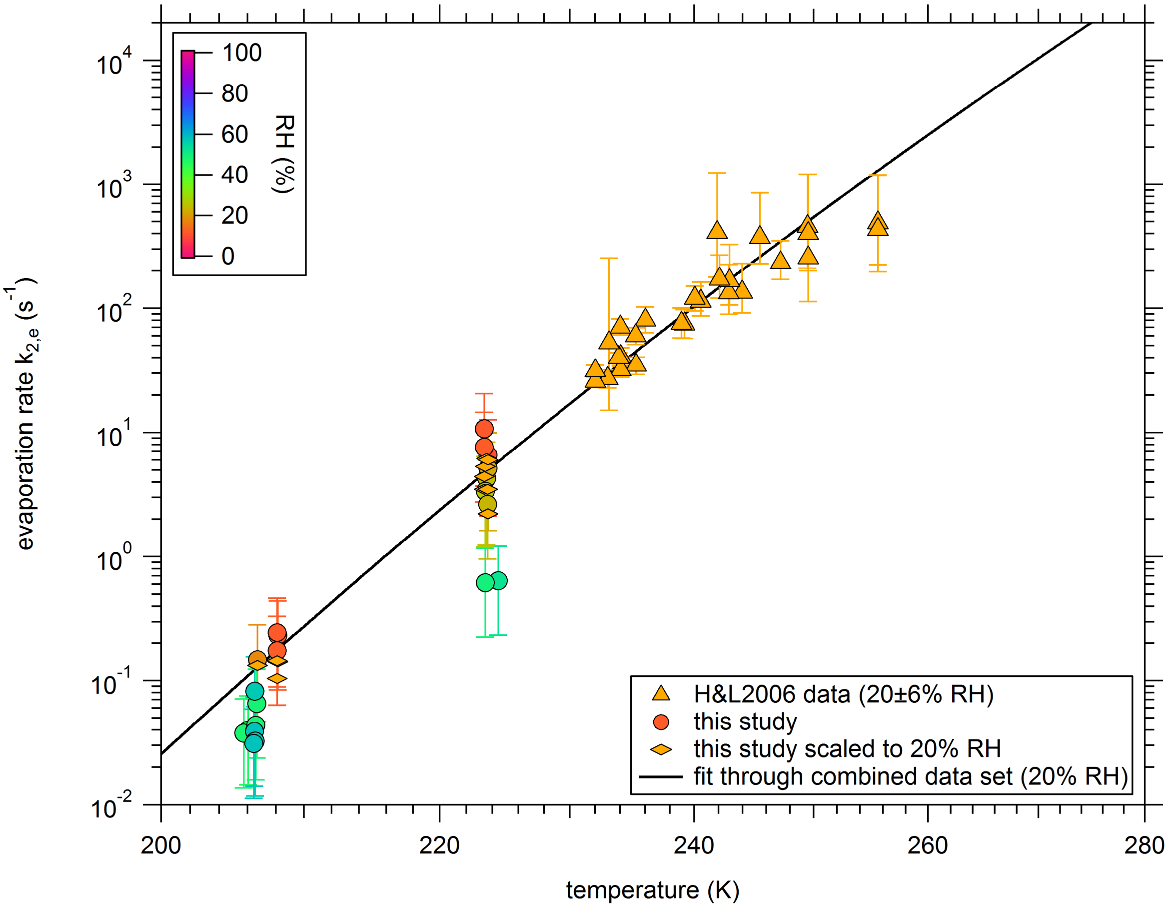


Fig. 7. Comparison of the sulfuric acid dimer evaporation rates from this study (circles) and from the literature (triangles, see Hanson and Lovejoy, 2006) as a function of temperature. The color code indicates the relative humidity during the experiments. Diamond symbols represent the data from this study scaled to 20% RH. The solid line shows a best fit through the data with the thermodynamic properties dH = -20.1±1.2 kcal mol^{-1} and dS = -46.7±5.2 cal mol^{-1} K^{-1} at 20% RH.

Referee #1:

The authors present interesting and valuable low temperature data for dimer formation in sulphuric acid-water and sulphuric acid-ammonia-water systems. The experimental data is accompanied with model calculations which contain several assumptions that appear unjustified or inconsistent. The sensitivity of the conclusions and the derived thermochemical parameters (two-acid cluster and one acid-one ammonia cluster formation enthalpies and entropies) to these assumptions needs to be assessed before the paper can be accepted for publication. Below are my detailed comments to the manuscript, starting with comments related to three major issues gathered together and followed by additional comments ordered by page number of the manuscript.

Major point 1: I find it very hard to believe that the net collision rate (combination of the collision rate and subsequent reaction rate) between two sulphuric acid molecules is higher than that between a bisulphate ion and sulphuric acid (Page 13969, lines 1-7). This situation likely results from the use of collision/reaction rates from different sources for the two processes where they have been determined differently and based on different assumptions. While both values may be of the correct order of magnitude, comparison seems to imply that at least one of them is not very accurate. The enhancement to the collision rate due to ion-dipole interaction should be larger than that due to dipole-dipole interaction (given that one of the collision partners is the same in both cases and the other is as similar as a neutral molecule and an ion can be). The reaction rate of the bisulphate ion and sulphuric acid is taken from Zhao et al (2010), where it was concluded that the clustering reaction did not proceed at the collision limit (at ~278 K). On the other hand, the clustering reaction between two neutral sulfuric acid molecules is now assumed to proceed at the collision limit. How is this assumption justified? It seems very counter-intuitive, as the chemistry after the collision is very similar in these two cases except that the neutral cluster is less strongly bound than the charged one. It also seems inconsistent to assume that sulphuric acid reacts with the nitrate ion at the collision rate (Page 13965, line 3), but with bisulphate ion with a lower rate (Page 13966, lines 11-13). Furthermore, both the neutral-neutral and neutral-ion collision rates have uncertainties. The Chan and Mozurkevich (2001) formula for the enhancement factor is derived based on a fit to experiments with 50-100 nm particles colliding with another particle of the same size. Extrapolating the parameterization from particle sizes in the continuum regime to molecules and clusters in the free molecular regime can result in fairly large errors/uncertainties. Other studies (Marlow 1980) have also found a stronger size dependence, and also a stronger dependence on whether the colliding parties are of the same size or different size, than given by the formula of Chan and Mozurkevich (2001). On the other hand, the observations of Zhao et al. could also be explained for instance by dimer (HSO_4^-)(H_2SO_4) evaporation instead of the effective collision+reaction rate between the bisulphate ion and the sulphuric acid molecule being lower than the theoretical ion-dipole collision rate. Thus, before the paper can be accepted, the authors must either a) amend the assumptions so that the ion+acid collision+reaction rate is higher (or at least equal) to the corresponding rate for acid+acid and repeat all the simulations and analysis with the new values or b) provide a fundamental explanation how such a situation could arise that the combined rate is higher for the acid+acid collision than for ion-acid collision, and also show how sensitive their results are to this counterintuitive assumption.

The reviewer criticizes that the neutral-neutral collision rate between two H_2SO_4 molecules (~1x10^{-9} cm^3 s^{-1} including an enhancement factor due to London-van der Waals forces) is faster than the charged-neutral collision rate between bisulfate and H_2SO_4 (8x10^{-10} cm^3 s^{-1} according to Zhao et al., 2010). We have outlined our arguments for these choices in detail in the following; these lead us to the conclusion that the used rate constants are appropriate for this study. However, detailed discussion is now included in the manuscript in order to clearly state why we have used these values and why we think they do not significantly influence the outcome of this study.

Discussion point 1: Value of the collision rate between H_2SO_4 and H_2SO_4

The collision rate (including the van der Waals correction factor) has been reported as ~1x10^{-9} cm^3 s^{-1} in the ACPD manuscript. However, this value was rounded up and we should have reported the exact value, which is, e.g. 6.9x10^{-10} cm^3 s^{-1} at 208 K. This value consists of two factors; the collision rate calculated from kinetic gas theory (2.83x10^{-10} cm^3 s^{-1} at 208 K) and the enhancement factor due to London-van der Waals forces (2.45 at 208 K). For a higher temperature (298 K) the calculated collision rate is 3.64x10^{-10} cm^3 s^{-1} and the van der Waals factor is 2.27 (overall collision rate is 8.26x10^{-10} cm^3 s^{-1}). The value of 3.64x10^{-10} cm^3 s^{-1} agrees well with a literature value provided by Ortega et al. (2012). Therefore, when using the exact values (which have been used for all calculations in the present study) the neutral-neutral and the charged-neutral collision rate are about the same or somewhat lower (when temperature is low as it is the case here).

Furthermore, we argue that the exact value of the neutral-neutral collision rate is not crucial for deriving the thermodynamic data (d*H* and d*S*) from Fig. 7 (previously Figure 6) for the binary (H_2SO_4-H_2O) system (see below). However, the value of the London-van der Walls enhancement factor used in the current study is considered as a best estimate which is justified in the following:

The overall collision rate is the product of the collision rate calculated from Fuchs theory (denoted as $K_{1,1}$ for two sulfuric acid monomers) and an enhancement factor due to London-van der Waals forces (denoted as $G_{1,1}$) calculated according to Chan and Mozurkewich (2001). The enhancement factor for two monomers is calculated as ~2.3. Other previous studies have reported similar values, e.g., factors of 1.98 (McMurry, 1980) and 1.95 (van Dingenen and Raes, 1990) for the same chemical systems. No study has yet determined the neutral-neutral collision rate of two sulfuric acid monomers experimentally; therefore, extrapolation of the data from larger sizes is necessary. We have used the equations provided by Chan and Mozurkewich (2001). The theory by Marlow (1980) results in a somewhat larger enhancement factor and a stronger size dependency. However, the size dependency does not matter in this case because only collisions between two equal-sized monomers are considered and for such a case the two studies result in similar values.

We also want to highlight that the value of the neutral-neutral collisions only matters if one wants to calculate the actual evaporation rates of a neutral dimer (as shown in Fig. 7 (previously Figure 6)). We have used the same collision rate (including the van der Waals enhancement factor) both for our data and the data from Hanson and Lovejoy (2006). If, e.g., the enhancement factor would be neglected ($G_{1,1}$ taken as 1) all evaporation rates (circles and triangles) would be shifted downwards by the same factor (approximately by a factor of 2.3).

Using equations (5) and (8) from the manuscript

$$k_{2,e} = \frac{0.5 \cdot G_{1,1} \cdot K_{1,1} \cdot N_1^2}{N_2} \tag{5}$$

$$k_{2,e} = 0.5 \cdot \frac{G_{1,1} \cdot K_{1,1}}{k_B \cdot T \cdot 10^6 \cdot K_{eq}} \tag{8}$$

it can be shown that the equilibrium constant does not depend on the value of $G_{1,1} \bullet K_{1,1}$

$$K_{eq} = \frac{1}{k_B \cdot T \cdot 10^6} \cdot \frac{N_2}{N_1^2}.$$

This means that the fitted parameters dH = -20.1 kcal mol^{-1} and dS = -46.7 cal mol^{-1} K^{-1} would still be valid. The calculation of evaporation rates from the fit values for K_{eq} can therefore, in principle, be made using different assumptions for $G_{1,1}$•$K_{1,1}$ than the ones made in this study by other researchers. In order to explain this we have made the following adjustments to the text.

(a) Section 2.4: The exact values for the collision rate and the van der Waals enhancement factor at 208 K are provided. Furthermore, the text at the end of this section was adjusted and now reads:

"Comparison of the rate constants used for the reactions between HSO_4^- and H_2SO_4 (Section 2.3) and between H_2SO_4 and H_2SO_4 yields that the neutral-neutral collision rate is about the same as the charged-neutral collision rate. This is due to the relatively large enhancement factor from London-van der Waals forces for the neutral-neutral rates (McMurry, 1980; Chan and Mozurkevich, 2001) and the observation that the reaction between the bisulfate ion and sulfuric acid seems not to proceed at the collisional rate (Zhao et al., 2010). Further discussion about the consequences this has on the present study is provided in Section 3.8."

(b) Section 3.8 (uncertainties discussion, previously section 3.7): The following text has been added to the discussion.

"The exact values of dimer evaporation rates depend on the choice of $G_{1,1}$•$K_{1,1}$, i.e., on the overall collision rate between two neutral dimers and is therefore subject to an additional uncertainty because this value is based on theoretical calculations. However, the thermodynamic data derived in this study does not depend on the value of $G_{1,1}$•$K_{1,1}$ because both the data from this study and the one from Hanson and Lovejoy (2006) in Fig. 7 were calculated using the same factors. Therefore, when deriving dH and dS the collision rate cancels out in the calculations (cf. equations (5) and (8))."

Discussion point 2: Value of charged-neutral collision rate (k_{21})

While the actual value of the neutral-neutral collision rate is not important for the evaluation of the thermodynamic data of dimer formation (see point 1 above) the value of the reaction rate between HSO_4^- and H_2SO_4 (denoted as k_{21}) is important.

Our current assumption is that this value is $k_{21} = 8\times10^{-10}$ cm^3 s^{-1}. This value is taken from observations made by Zhao et al. (2010) regarding their measurements with a Chemical Ionization Mass Spectrometer (CIMS) similar to the one used in the present study. An upper maximum limit for the reaction between HSO_4^- and H_2SO_4 is 2×10^{-9} cm^3 s^{-1} (Chen et al., 2012), which is a factor of 2.5 higher than the currently used value and results from charged-neutral collision theory. When using the faster collision-limited rate constant (2×10^{-9} cm^3 s^{-1}), all dimer concentrations (N_2) would need to be increased by a factor of 2.5. This would decrease all dimer evaporation rates from this study by the same factor (cf. equation (5)), while leaving the evaporation rates from Hanson and Lovejoy (2006) unaffected. Therefore, the overall fit parameters for the data in Fig. 7 (previously Fig. 6) would change to different values (dH = -23.0±1.6 kcal mol^{-1} and dS = -58.5±6.9 cal mol^{-1} K^{-1} instead of dH = -20.1±1.2 kcal mol^{-1} and dS = -46.7±5.2 cal mol^{-1} K^{-1}). For this reason use of an accurate value of k_{21} is crucial.

Argument 2a:

A publication by Viggiano et al. (1985) supports the assumption of a reaction rate for HSO_4^- and H_2SO_4 below the collision limit. They found a rate of 2.6x10^{-10} cm^3 s^{-1} for the reaction between NO_3^- and HNO_3 at the high-pressure limit. This reaction is considered to be similar to the reaction between HSO_4^- and H_2SO_4 and therefore indicates the possibility of a reaction rate below the charged-neutral collision limit.

Argument 2b: Faster rate of k_{21} results in unphysical high dimer concentrations.

As mentioned above, when assuming that the charged-neutral collision occurs at the collision limit, all dimer concentrations should be moved up by a factor of 2.5. This would also move the concentrations from Fig. 9 (previously Fig. 8) towards higher values, which would exceed the maximum possible dimer concentration expected from the kinetic limit (solid black line). Such high concentrations would, however, be unphysical.

Argument 2c: Re-evaluation of k_{21} from a CI-APi-TOF calibration in the laboratory.

The use of k_{21} is necessary because the absolute detection efficiency of the sulfuric acid dimers (HSO_4^- •H_2SO_4) is not known due to the unknown transmission efficiency at masses higher than the sulfuric acid monomer (*m*/*z* 97, HSO_4^-) for the CIMS. However, in the mean time we have calibrated the CI-APi-TOF regarding its mass-dependent transmission efficiency according to a similar method than the one described in the literature (Kangasluoma et al., 2013). When using the known transmission efficiencies for the sulfuric acid monomer and dimer, the reaction rate k_{21} can be evaluated from calibration measurements where the measured dimers result almost exclusively from ion-induced clustering. Using this method the reaction rate k_{21} was evaluated as 8.9×10^{-10} cm^3 s^{-1}, which is close to the currently used value of 8×10^{-10} cm^3 s^{-1} and significantly lower than the rate from charged-neutral collision theory.

Taken together, we think there are enough reasons not to change the used values for the neutral-neutral and charged-neutral collision rates. However, we have made the following adjustments to the manuscript to further support our decisions and to discuss the involved uncertainties.

The following text has been added to the error discussion in section 3.8 (previously section 3.7):

"In contrast to the exact value of $G_{1,1}$•$K_{1,1}$ the charged-neutral collision rate k_{21} between HSO_4^- and H_2SO_4 is important because its value scales the dimer concentrations and evaporation rates from this study while leaving the data from Hanson and Lovejoy (2006) unaffected. The reported value of $8x10^{-10}$ cm^3 s^{-1} for k_{21} from Zhao et al. (2010) suggests that this charged-neutral reaction is not proceeding at the collision limit (value of ~$2x10^{-9}$ cm^3 s^{-1}). When using the faster reaction rate for the charged-neutral collision limit some of the dimer concentrations would exceed the kinetic limit (cf. Fig. 9, upper panel) because all dimer concentrations would need to be scaled up by a factor of 2.5; therefore the faster rate seems to be implausible. However, using the upper limit for the collision rate results in d*H* = -23.0±1.6 kcal mol^{-1} and d*S* = -58.5±6.9 cal mol^{-1} K^{-1}."

Major point 2: The assumption that ammonia-containing dimers and trimers cannot evaporate leads to the evaporation rate of the one sulphuric acid-one ammonia cluster being a fitting parameter that very straightforwardly controls the dimer concentration. There is no guarantee that this fitting procedure gives a truthful estimate for this evaporation rate if the assumptions made are not correct. Similarly, in the binary system only the dimer evaporation rate is used as a fitting parameter while all other evaporation rates are set to zero. Before the paper can be accepted, the authors should test the sensitivity of their results for the cluster formation enthalpies and entropies to these assumptions by simulating also a system where evaporation of (at least some of the) larger clusters is allowed.

We agree that the assumptions made in the model have an influence on the resulting evaporation rate of the H_2SO_4•NH_3 cluster. This will be discussed further below and further discussion regarding this topic is included in the revised version of the manuscript.

However, regarding the formation of dimers in the binary system we argue that the (slow) evaporation of the larger clusters very likely has an insignificant influence on the obtained results (see justification further below).

Page 13959 lines 13-15: “For the ternary system the formation of H_2SO_4•NH_3 is very likely an essential step in the formation of sulfuric acid dimers“. In atmospheric conditions the cluster mentioned is not very stable according to any of quantum chemical results available in the literature, and thus assuming that this is the essential (rate limiting?) step does not seem justified.

For the ternary system with ammonia at low temperature the modeled fraction of [H_2SO_4•NH_3] to [H_2SO_4] can be significant (e.g. at 210 K and 3x10^6 cm^{-3} total sulfuric acid the [H_2SO_4] is 2x10^6 and [H_2SO_4•NH_3] is ~1x10^6 cm^{-3} when [NH_3] is 2x10^8 cm^{-3} according to our model). At higher temperature (248 K) for [H_2SO_4] of 1x10^7 cm^{-3} and [NH_3] = 2x10^8 cm^{-3}, the [H_2SO_4•NH_3] is 2.16x10^4 cm^{-3} and [H_2SO_4] is 9.98x10^6 cm^{-3}. However, for both temperatures the pathway via H_2SO_4•NH_3 dominates the formation of dimers. At the higher temperature (248 K) the pure dimer concentration ([$(H_2SO_4)_2$]) is 1.04x10^2 cm^{-3}, while the [$(H_2SO_4)_2$•NH_3] is 1.66x10^4 cm^{-3}. The rate of production for $(H_2SO_4)_2$•NH_3 via the H_2SO_4•NH_3 cluster is a factor of 8 higher than via $(H_2SO_4)_2$. This relates also to comment (27) made by the reviewer. Adjustments made to the text according to this comment are implemented in the context of comment (27).

Page 13961 lines 10-12: the authors should justify why is it crucial to know the evaporation rate of the dimer, but it is ok to assume evaporation rates of trimer and all larger clusters to be zero. Is this actually justified?

This assumption refers mainly to the ternary system at low temperatures (248 K and colder). It is based on previous measurements made by Hanson and Eisele (2002) for the ternary system who concluded that the critical cluster in the ternary system very likely contains two sulfuric acid molecules at a temperature of 275 K. We have no direct information about all the relevant clusters (which include different numbers of water molecules) but can only refer to other literature data which indicate that the assumptions made in the model seem to be appropriate. The arguments are listed in the following:

Argument 1: Dimer of sulfuric acid including ammonia.

Both, measurement and quantum chemical calculations suggest that a sulfuric acid dimer containing one ammonia molecule is essentially stable against evaporation at the relevant temperatures of this study (Hanson and Eisele, 2002; Ortega et al., 2012).

Argument 2: Trimer of sulfuric acid including ammonia.

Thermodynamic data from quantum chemical calculations are available for sulfuric acid trimers including ammonia (Ortega et al., 2012). Based on this data we list calculated evaporation rates for the relevant clusters (containing 3 sulfuric acid molecules A and between 1 and 3 base (ammonia) molecules B) in the following:

A evaporation from $SA_3.B_1$: 1034 s^{-1} (at 300 K) and 0.70 s^{-1} (at 248 K)
B evaporation from $SA_3.B_1$: 5.83×10^{-5} s^{-1} (at 300 K) and 1.49×10^{-9} s^{-1} (at 248 K)

A evaporation from $SA_3.B_2$: 0.047 s^{-1} (at 300 K) and 3.11×10^{-6} s^{-1} (at 248 K)
B evaporation from $SA_3.B_2$: 0.065 s^{-1} (at 300 K) and 7.33×10^{-6} s^{-1} (at 248 K)

A evaporation from $SA_3.B_3$: 4.23×10^{-8} s^{-1} (at 300 K) and 3.73×10^{-4} s^{-1} (at 248 K)
B evaporation from $SA_3.B_3$: 2.74 s^{-1} (at 300 K) and 7.24×10^{-14} s^{-1} (at 248 K)

These data indicate that the trimer containing two bases has the overall slowest evaporation rate since both the acid (A) and the base (B) evaporate rather slowly. The other cluster configurations (with only one base or with three bases) have either a fast evaporation rate regarding an acid or regarding a base molecule. However, if a base evaporates from the $SA_3.B_3$ cluster it results in a $SA_3.B_2$ cluster, which has an overall very slow evaporation rate. Therefore, the quantum chemistry data suggest that only the $SA_3.B_1$ cluster can be regarded as relatively unstable. This indicates that at relatively low ammonia concentration the trimer could evaporate at a significant rate if it is not turned into a trimer containing two base molecules. The base concentrations of this study are ~1×10^8 cm^{-3}, which results in a forward reaction rate from $A_3.B_1$ to $A_3.B_2$ of ~0.05 s^{-1}. This is not very far away from the evaporation rate of an acid from the A_3B_1 cluster (0.7 s^{-1}). In this context it is also important to note that the effect of water vapor is not taken into account in the Ortega et al. (2012); water is expected to lower the evaporation rate. This is supported by data from Herb et al. (2011), which suggest that the evaporation rate of A_3B_1 clusters is lowered in the presence of water vapor. Therefore, it seems plausible that the base containing trimer has a relatively low evaporation rate when temperature is low (248 K and lower) and the base concentration is relatively high (> ~10^8 cm^{-3}).

Argument 3:

Based on an acid-base model (similar to the one in the present study) Jen et al. (2014) evaluated an effective evaporation rate for sulfuric acid trimers containing ammonia of 0.4 s^{-1} at 300 K (see also Chen et al., 2012). Assuming that the evaporation rates decrease with decreasing temperature it seems plausible that the trimer evaporation rate would become negligible for the low temperature conditions of this study.

Overall, we think that our assumptions are appropriate but agree that more discussion is necessary to explain the limitations of our model and the involved uncertainties. Some discussion on this topic is already present in section 3.8 (previously section 3.7). Furthermore, we have added the following after line 24 on page 13982 (also following comment (28) made by the referee, see below):

"The quantum chemistry data from Ortega et al. (2012) support the assumption that a trimer containing at least two bases is relatively stable (evaporation rate below 0.1 s^{-1} at 300 K). However, it predicts that the trimer containing only one ammonia molecule has a high evaporation rate regarding an acid molecule (~1000 s^{-1} at 300 K); additional ammonia in the trimer will lower the evaporation rates. For this reason the trimer concentration will strongly depend on the ammonia concentration, which controls the cluster distribution. Therefore, the Chen et al. (2012) value can be regarded as a best estimate for the overall trimer evaporation rate for their experimental conditions. Herb et al. (2011) also simulated the effect that one water molecule has on the acid evaporation rate from $(H_2SO_4)_3(NH_3)_1(H_2O)_{0,1}$ clusters. While the water molecule lowers the evaporation rate the absolute evaporation rate is higher (2.9×10^4 s^{-1} at 300 K) than for the Ortega et al. (2012) data."

Page 13968, lines 4-5: "The second term is significantly smaller than the first term, so it can be neglected in the following discussion." The authors simply assume that the trimer evaporation is zero. What is this assumption based on? How confident are the authors of this choice? How much would it affect the results and conclusions to let also the trimers (and possible larger clusters) to evaporate?

We are not arguing that the trimer (and larger cluster) evaporation rate(s) are zero, we are only saying that the contribution of the second term on the RHS of the following equation is negligible compared to the first term:

$$k_{2,e} = \frac{0.5\cdot G_{1,1}\cdot K_{1,1}\cdot N_1^2}{N_2} + \frac{k_{3,e}\cdot N_3}{N_2} - \left(k_{2,w} + k_{dil} + \sum_{i=1}^{n} G_{2,i}\cdot K_{2,i}\cdot N_i\right). \tag{4}$$

Without using any of the data from the current study we can use the dimer and trimer evaporation rates from Hanson and Lovejoy (2006) in order to estimate the contributions from the two terms on the evaporation rate. E.g. at 210 K the evaporation rate of the dimer is 0.1 s^{-1} while the trimer evaporation rate is $1\mathrm{x}10^{-3}$ s^{-1}. Since, generally the trimer and the dimer concentrations are of a similar value (with the trimer concentration being somewhat lower than the dimer concentration, see Hanson and Lovejoy, 2006) the second term on the RHS is smaller than $1\mathrm{x}10^{-3}$ s^{-1}. Now adding $1\mathrm{x}10^{-3}$ s^{-1} to the dimer evaporation rate of 0.1 s^{-1} makes a one percent change, which is much lower than the error in the dimer evaporation rate. At a higher temperature (248 K) this error is still smaller than 2%; therefore, the second term can be neglected for the analysis.

Page 13969, lines 23-24: how sensitive is the SAWNUC model to the assumption that only dimers and sometimes trimers can evaporate. The authors should run the code with evaporation for larger cluster turned on using some literature estimates for the evaporation rates, and see how much the results change?

The figure on the next page shows a sensitivity study of the SAWNUC results towards the trimer evaporation rate for 208 and 223 K. The black lines show the simulations under the assumption that the trimer evaporation rate is zero. These data are the same as in Fig. 4 and Fig. 5 of the manuscript. The red lines use trimer evaporation rates from Hanson and Lovejoy (2006). It can be seen that for the data of this study (colored circles as shown in Fig. 4 and Fig. 5) the trimer evaporation has no significant influence on the evaluated dimer evaporation rates. This indicates that as soon as the dimer evaporation rate is equal to or larger than the trimer evaporation rate, the effect of trimer evaporation becomes essentially insignificant.

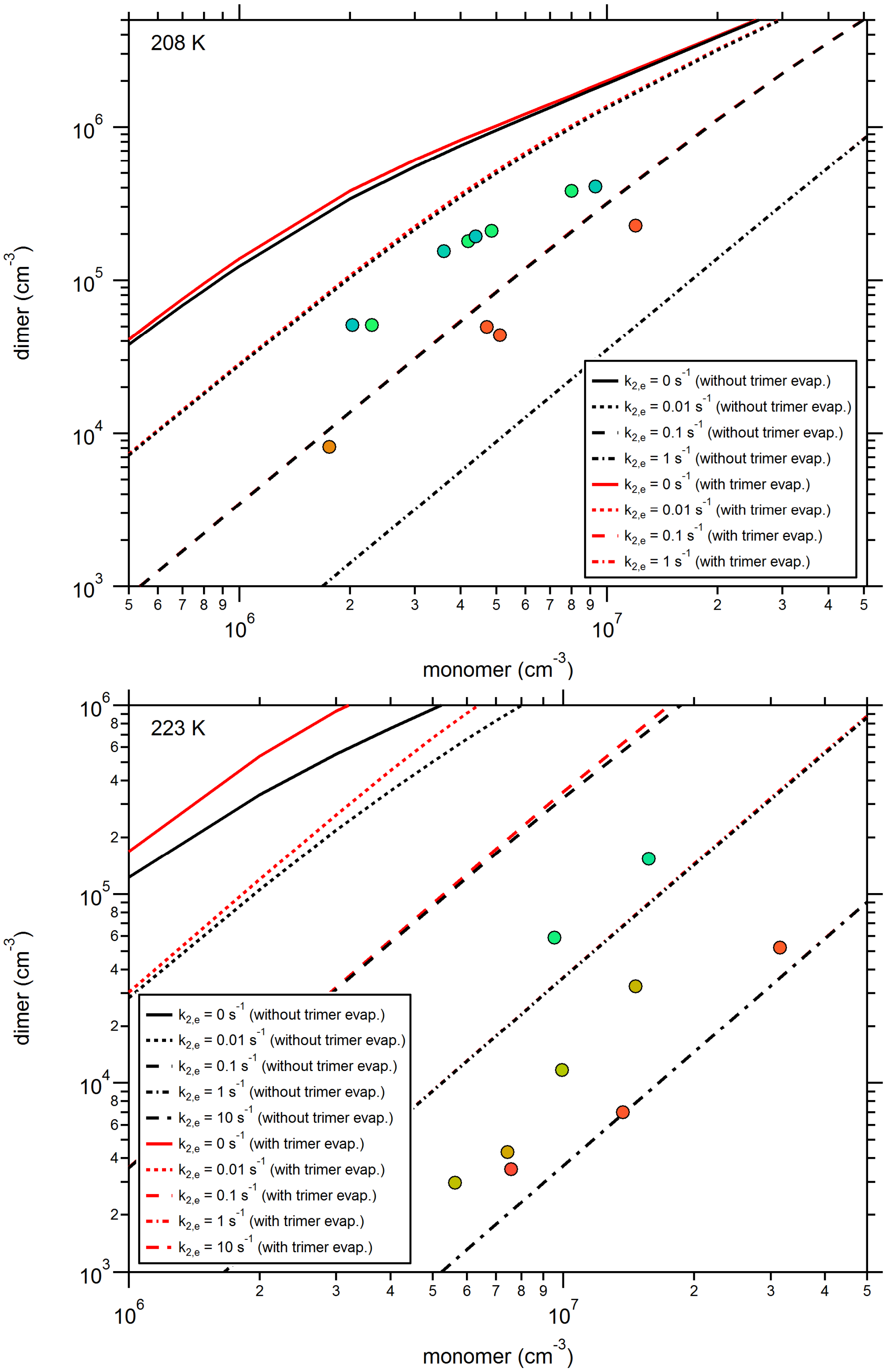


Figure. Sulfuric acid dimer concentration as function of the monomer. Similar to Fig. 4 and 5 of the manuscript but the SAWNUC calculations were once made using the assumption that the trimer does not evaporate (black lines) and once using trimer evaporation rates from Hanson and Lovejoy (2006) (red lines) for the respective temperatures ($k_{3,e} = 1.6\times10^{-3}$ s^{-1} (208 K), $k_{3,e} = 5.6\times10^{-2}$ s^{-1} (223 K)).

Page 13979, lines 17-18: "This is consistent with the assumption that cluster evaporation rates are negligible for the trimers and all larger clusters at this low temperature." One wonders would a model with also evaporation of larger clusters allowed reproduce the data equally well or even better? I don't think we can say anything about the evaporation rates of trimers and larger clusters based on the model–experimental data comparisons presented in this paper. Similarly page 13987, line 26-28: "the signals are consistent with the assumption that cluster growth is essentially kinetically controlled for all of the observed clusters above the dimer.", is misleading although the word conclude has not been used.

The referee is right; we cannot make any conclusions about the evaporation rates of the clusters based on the data from Figure 8 (previously Figure 7). However, the largest drop in concentrations occurs between the monomer and the dimer followed by a relatively mild decrease in cluster concentrations for the larger clusters (if one accepts that the trimer concentration is an outlier due to fragmentation). This slow decrease in concentrations is consistent with losses controlled by wall loss, dilution and coagulation and is qualitatively represented both by the model and the measured data. If very slow evaporation rates would be introduced in the model calculations for the clusters (trimer and larger) the shape of the modeled concentrations (black line) would not be affected much. However, since no big drop is observed in the cluster concentrations as a function of size (as seen between the monomer and the dimer) the cluster evaporation rates should in any case be significantly lower than the dimer evaporation rate.

The sentence on page 13979, line 17-18 has been reformulated:

"This suggests that cluster evaporation rates of the trimer and all larger clusters are not high enough to significantly affect their concentrations at this low temperature."

Regarding the statement on page 13987, line 26-28 "… the signals are consistent with the assumption that cluster growth is essentially kinetically controlled for all of the observed clusters above the dimer." we think this is a true statement because of the arguments outlined above. No big drop is seen in the concentrations for the clusters beyond the dimer. At a sulfuric acid monomer concentration of $1.7\text{x}10^{7}$ cm^{-3} the forward reaction rate (growth by monomers) is approximately $\sim 10^{-2}$ s^{-1}, whereas the dimer evaporation rate is $\sim 4\text{x}10^{-2}$ s^{-1}. This suggest rather low evaporation rates for the trimer and larger.

Page 13987, line 17: The model has been essentially fitted to the experimental data, so it is not fair to say that the model predict the dimer concentrations to a high accuracy. Page 13987, line 20: the thermo–chemical data is not based on solely experiments, but to a large extent on a model and its several strong assumptions.

We agree with the referee that these statements should be formulated more carefully.

The sentence (page 13987, line 17) "Using the proposed model, measured dimer concentrations in the ternary system can be predicted with a high accuracy." has been replaced by:

"Using the proposed model, measured dimer concentrations in the ternary system can be reproduced with a high accuracy for the conditions of this study."

And the sentence (page 13987, line 20) "With this observation, the model can be used to calculate nucleation rates in the ternary system, which completely relies on experimentally determined thermo-chemical data." has been replaced by:

"With this observation, the model can be used to calculate nucleation rates in the ternary system, which relies on experimentally determined thermo-chemical data and on the assumptions that ammonia containing trimers and tetramers have insignificant evaporation rates for the conditions of this study."

Major point 3: The effect of water on the clustering should be discussed in somewhat more detail. The formation enthalpy and entropy values in the binary case for the two sulphuric acid $(H_2SO_4)_2$ and in the ternary case for the one sulphuric acid-one ammonia $(H_2SO_4)(NH_3)$ clusters deduced from the experimental data represent averages over different water contents of these clusters, rather than those specific dry clusters. This should be stated clearly, especially pointing out that these values should not be compared directly to the quantum chemical results for the dry clusters as is done for in Table 1 and in a statement page 13984 lines 12-13.

For instance, for the level of theory used by Ortega et al. (2012), Henschel et al. (2014) have published quantum chemical values for the water-containing clusters relevant to this study. For different quantum chemical levels of theory, for example, Herb et al. (2011) and Temelso et al. (2012) have calculated values for hydrated clusters.

We agree with the referee that this should be discussed in more detail in the manuscript. After a careful literature research we think that the following publications should be included in the discussion:

- Ding et al. (2003): examined the effect of water on the sulfuric acid dimer formation
- Temelso et al. (2012): examined the sulfuric acid dimer hydration considering $(H_2SO_4)_2(H_2O)_{0-6}$ clusters
- Henschel et al. (2014): water content for $(SA)_{1-4}$ and up to $(SA)_{x=1-3}(NH_3)_{y<x}$; $(H_2SO_4)(NH_3)$ contains about 1 water at 20% RH and 298.15 K; dimers and trimers between 0 and 2 water.
- Nadykto and Yu (2007): thermodynamic data for $(H_2SO_4)(NH_3)(H_2O)_{0-3}$ clusters
- Herb et al. (2011): thermodynamic data for $(H_2SO_4)_3(NH_3)_1(H_2O)_{0,1}$ clusters

Regarding the binary system we have added the following to the end of Section 3.3 (page 13977, see also text on first page):

"However, our data agree within errors with results from quantum chemical calculations, taking into account the effect of water vapor (Ding et al., 2003). According to measurements by Hanson and Eisele (2000) and quantum chemical calculations (Temelso et al., 2012; Henschel et al. 2014) the sulfuric acid monomer and dimer can contain water molecules. Therefore, the data from Ding et al. (2003) taking into account the effect of water vapor are relevant for this study. Table 2 shows a comparison between different studies dealing with the sulfuric acid dimer formation. Regarding the effect of water vapor it should be noted that our experimentally determined evaporation rates represent an average for dimers containing different numbers of water molecules. The exact distribution of water associated with the dimers will be a function of relative humidity and temperature, which cannot be taken into account explicitly in this study."

Furthermore the data from Ding et al. (2003) were added to the new Table 1 (the previous Table 1 is now Table 4).

Concerning the ternary system (thermodynamics of the $H_2SO_4 \cdot NH_3$ cluster) the references to Nadykto and Yu (2007) and Herb et al. (2011) were added to the discussion. Furthermore, the Nadykto and Yu (2007) data were added to Table 4 (previously Table 1, see below). The discussion in Section 3.7 (previously Section 3.6) was replaced by the following (starting with line 24 on page 13983):

"Table 4 compares our d*H* and d*S* values as well as the corresponding evaporation rates for selected temperatures with other data obtained from quantum chemical calculations (Torpo et al., 2007; Nadykto and Yu, 2007; Ortega et al., 2012; Chon et al., 2014) and from one flow tube experiment (Jen et al., 2014). Overall, the agreement is good. However, it is difficult to take into account the effect the model assumptions have on the outcome of the values from our study. In addition, only a small number of data points have been taken into account in this study.

One also needs to keep in mind that the cluster formation was observed at ~25% RH (with respect to supercooled water) in this study, while most of the theoretical studies did not take into account the effect of water except the one by Nadykto and Yu (2007). Their data suggest that the evaporation rate of $H_2SO_4\bullet NH_3\bullet(H_2O)_x$ increases when the number of associated water molecules increase. The study by Henschel et al. (2014) indicates that about one water molecule is attached for the RH relevant of this study. However, Henschel et al. (2014) reported their results only for a temperature of 298 K, whereas the temperature of this study is 248 K and lower. Whether the evaporation rate is increasing with increasing RH cannot be concluded from our data, however, one needs to keep in mind that similar to the dimer in the binary system, the reported evaporation rates and thermodynamic data for the $H_2SO_4\bullet NH_3$ represent average values that can include clusters with attached water molecules.

The comparison in Table 4 also lists the experimental study by Jen et al. (2014) who determined the evaporation rate of $H_2SO_4\bullet NH_3$ at ~300 K from a transient version of their second scheme (formation of dimers only via AB, see above). The extrapolated value from the present study is, however, in relatively good agreement with their value. The somewhat lower evaporation rate of Jen et al. (2014) could be explained by the fact that they did not consider the formation of dimers by self-coagulation of A. Furthermore, they assumed that the trimer has an evaporation rate of 0.4 s^{-1}. Both these assumptions require a slower evaporation rate for AB than our study suggests to explain the measured dimer concentrations at a given monomer and base concentration.

Overall, our measurements in the ternary system yield values of the thermodynamic properties of the $H_2SO_4\bullet NH_3$ cluster that are in rather good agreement with the results from quantum chemical calculations. However, since the number of data points is limited, the uncertainty is rather high.”

Study	dH	dS	k_e at 210 K	k_e at 248 K	k_e at 300 K
	(kcal mol^{-1})	(cal mol^{-1} K^{-1})	(s^{-1})	(s^{-1})	(s^{-1})
this study[a]	-16.1±0.6	-26.4±2.6	0.11	36	9.8×10^3
Torpo et al. (2007)[b]	-15.81	-28.57	0.63	200	4.7×10^4
Nadykto and Yu (2007)[b]	-16.72	-30.01	0.15	64	2.1×10^4
Nadykto and Yu (2007), $H_2SO_4(H_2O) + NH_3$	-15.91	-30.23	1.1	370	9.2×10^4
Nadykto and Yu (2007), $H_2SO_4(H_2O)_2 + NH_3$	-15.27	-30.49	6.0	1.5×10^3	3.1×10^5
Nadykto and Yu (2007), $H_2SO_4(H_2O)_3 + NH_3$	-15.44	-32.30	10	2.7×10^3	5.8×10^5
Ortega et al. (2012)[b]	-16.00	-28.14	0.32	107	2.8×10^4
Chon et al. (2014)[b]	-15.43	-29.63	2.7	720	1.5×10^5
Jen et al. (2014)[c]	-	-	-	-	400 to 2500

Table 4. Thermodynamic properties (dH and dS) and evaporation rates of the $H_2SO_4\bullet NH_3$ cluster from this study and from the literature. [a]Experiments conducted at ~25% RH (with respect to supercooled water). [b]No effect of water vapor considered. [c]Experiment conducted at ~30% RH.

Additional comments:

(1) Page 13961, lines 6-7: expression "Similarly, the monomer of sulfuric acid may contain water or ammonia." should be replaced by something like "The term monomer refers to clusters with one suphuric acid, irrespective of whether the cluster contains also ammonia and/or water molecules or not."

The sentence has been replaced as suggested by the referee.

(2) Page 13961, lines 19-24: I would say that the uncertainties in the experiments are too large for narrowing down the theoretical uncertainties, as they are of the same order of magnitude. Comparison of experiments and theory rather provides a sanity check in both directions.

Lines 21 to 24 on page 13961 were replaced by

"In order to model NPF for the ternary system involving ammonia it is essential to better understand the thermodynamics of the clusters involved in the nucleation process. Cluster properties derived from measurements can be used for a comparison with the theoretical studies. Such a comparison provides a consistency check for both the models and the measurements."

(3) Page 13964, equations (1a) and (1b) and page 13965, line 1, sentence concerning the calibration constant. What is the uncertainty of the sulphuric acid monomer (and dimer) concentration? In some other CLOUD-related publications a factor of 2 uncertainty has been reported. How does such an uncertainty affect the results of this paper?

It is true that in previous publications we were reporting an uncertainty of a factor of 2 for the sulfuric acid monomer measurements (Kirkby et al., 2011; Almeida et al., 2013). These older publications were reporting our first sulfuric acid measurements and therefore, compared to our present knowledge, we provided a conservative estimate of the uncertainty. Our latest publication on the sulfuric acid measurements reported a factor of 1.5 uncertainty (Kürten et al., 2014). The reduction in the uncertainty is due to repeated calibrations using a dedicated calibration system for the H_2SO_4 CIMS measurements described by Kürten et al. (2012) where a systematic error of ~30% is reported.

The uncertainty for this study is mentioned in the beginning of section 3.8 (previously section 3.7, page 13984, line 18-23). To make clear that this uncertainty is mainly due to the calibration constant we have modified the sentence as follows:

"The error bars shown in Fig. 4 and 5 include the standard variation of the individual data points and a 30% (50%) systematic uncertainty in the monomer (dimer) concentration. The two error components are added together in quadrature. The systematic errors are estimated based on the uncertainties in the calibration coefficient *C* for the monomer. Due to the higher uncertainty of the sampling losses for the dimer, and the uncertainty of the transmission correction factor (Section 2.3) a somewhat higher uncertainty has been chosen in comparison to the monomer. The error bars in Fig. 7 are obtained when using Gaussian error propagation on equation (5) for the monomer and the dimer concentration."

(4) Page 13965, lines 10-11: "It was assumed that the diffusivity of the dimer equals 0.06 $cm^2\ s^{-1}$ at 298 K, and varies with temperature as $(298\ K/T)^{1.75}$". Are this value and temperature dependence derived for a pure dimer $(H_2SO_4)_2$? How reliable are they if there are some number of water and/or ammonia molecules attached to the dimer, and if the number of the attached molecules is temperature dependent?

The value of 0.06 $cm^2\ s^{-1}$ for the diffusion coefficient of a sulfuric acid is an estimate. The temperature dependence has been taken from Hanson and Eisele (2000). Hydration of the dimers certainly affects their diffusivity. The relative humidity in the CLOUD experiments is close to 30%. At this RH Henschel et al. (2014) report that the dimer contains on average between 2 (result from quantum chemical data) and 4 (result from E-AIM) water molecules. Therefore the molecular weight of a "dimer" is not 198 g mol^{-1} but rather 234 or 270 g mol^{-1}. This affects the diffusivity of the dimer to a similar extent as the monomer is affected when going from dry conditions to 30% RH (~15 % reduction in the diffusivity, see Hanson and Eisele, 2000). We therefore estimate the error of the dimer diffusivity to be (0.06±0.01) $cm^2 s^{-1}$. A variation of the diffusivity by 0.01 $cm^2 s^{-1}$ results in a variation of the calculated penetration L_{dimer} by less than 20%. Therefore, we estimate this to be a minor effect on the uncertainty of the dimer concentration.

The effect has been covered in the previous comment (comment (3)) by assuming a somewhat higher uncertainty for the reported dimer concentrations.

"It was assumed that the diffusivity of the hydrated dimer (see Henschel et al., 2012) equals 0.06±0.01 $cm^2 s^{-1}$ at 298 K, and varies with temperature as $(298K/T)^{1.75}$."

(5) Page 13965, line 15: dimer dissociation affect also the measured monomer concentration, not only that of the dimers. Has this been taken into account?

The contribution from dissociated dimers from monomers should be a minor effect. The data from Fig. 4 (208 K) shows that the maximum dimer concentration is $4x10^5$ cm^{-3} for a monomer concentration of $8x10^6$ cm^{-3}, i.e., 5% of the dimer. It should also be noted that the dimers can contribute only one monomer (i.e., one HSO_4^- ion) to the CIMS monomer channel (*m*/*z* 97). At the same time the bond enthalpy of a dimer is very strong (41.8 kcal/mol, Curtius, Froyd, Lovejoy, J Phys Chem A, 2001). Therefore, it seems unlikely that they are strongly affected by dissociation.

(6) Page 13967, lines 5-8: "Since low temperature conditions (208 and 223 K for the binary system) are considered in this study the assumption is made that only the smallest clusters (dimer and trimer) have appreciable evaporation rates (Hanson and Eisele, 2006)." Some theoretical evaporation rate values, or other such information, would strengthen the justification of this assumption.

Hanson and Lovejoy (2006) provide an upper estimate for the tetramer formation ($dG < -12$ kcal mol^{-1}) at 242 K. This corresponds to an upper limit of the tetramer evaporation rate of 0.09 s^{-1} (using a forward reaction rate $2x10^{-10}$ $cm^3 s^{-1}$ from Hanson and Lovejoy (2006)). The dimer and trimer evaporation rates at this temperature are 83 and 0.5 s^{-1}. For the lower temperatures of this study (208 and 223 K) all evaporation rates are considerably slower. The theoretical evaporation rates are substantially higher, e.g., Schobesberger et al. (2015) report a tetramer evaporation rate of 117 s^{-1} at 248 K. However, the theoretical evaporation rate is not taking into account the effect of water; therefore, we doubt that it is representative for the conditions of this study.

(7) Page 13967, lines 10-11: it should be stated clearly which specific evaporation rate $k_{i,e}$ is: the evaporation of acid, ammonia, or some combined effective evaporation rate? What is the effect of grouping clusters with equal amount of acid molecules to representative cluster sizes, without considering that there can exist clusters with similar acid content but different number of ammonia (and/or water) molecules?

In this study clusters are grouped regarding their amount of sulfuric acid molecules (the index *i* indicates the number of sulfuric acid molecules). The evaporation rate $k_{i,e}$ refers to the evaporation of one acid molecule from a cluster containing *i* sulfuric acid molecules. In this respect the evaporation rate represents a weighted average over different clusters containing different amounts of water and/or ammonia for a given number of acid. The most relevant clusters for this study are the dimer of sulfuric acid in the binary system $((H_2SO_4)_2(H_2O)_x)$ and the $(H_2SO_4)(NH_3)(H_2O)_y$ cluster in the ternary system with ammonia. For the dimer we derive the evaporation rate for different relative humidities and therefore account for the effect of water. For the cluster of sulfuric acid and ammonia no RH dependence of the evaporation rate is provided since the experiments were conducted in a rather narrow range of relative humidities. Therefore, an evaporation rate for the conditions of this study is provided. The fact that the cluster/particle concentrations N_i in equations (3) and (4) actually follow distributions with different amounts of water associated with the clusters is most likely small. As outlined in Section 2.4 (and also in the reply to major point 2) the dimer evaporation rate can be approximated by equation (5). In this equation different amounts of water will affect the collision rate between two monomers slightly. However, as discussed in the context of the first major comment, the actual value of the collision rate will not affect the thermochemical data for the dimer formation. Therefore, we think that the effect of different amounts of water/ammonia associated with the sulfuric acid clusters is not significant for the outcome of this paper.

In Section 2.4 we have replaced the part of the sentence explaining the evaporation rate $k_{i,e}$ by the following sentence (page 13967, line 10/11):

"The evaporation rate $k_{i,e}$ refers to the evaporation of one sulfuric acid molecule from a cluster containing *i* sulfuric acid molecules."

(8) Page 13968 equation (5): this represents the equilibrium cluster distribution, which should be stated clearly, and the authors should comment why is it is justified (or is it?) to use an equilibrium cluster distribution in a nucleating/particle forming vapour. Also related to this is the statement on Page 13971, lines 4-5 that the dimer is assumed to be in equilibrium initially. It seems that this assumption is used throughout the modeled period through equation (5).

It is true that steady-state concentrations are being used for the data analysis in equation (5). For a nucleating vapor conditions never reach a true steady-state for all particle sizes because the particles keep growing all the time and the cluster concentration is controlled by a balance between production and losses. However, for the smallest clusters (including the monomer and dimer) the losses are controlled almost entirely by wall loss, dilution and coagulation with the smallest clusters. Therefore, generally after tens of minutes, conditions are close to steady-state. This can e.g. be seen in an earlier publication showing measured cluster concentrations at the CLOUD chamber (Kürten et al., 2014).

The following has been added after equation (5), page 13968, line 22:

"The concentrations used in equation (5) are averages over periods where conditions are close to steady-state. These periods are defined by conditions where the production and loss rates for the dimer and the monomer are almost identical and the concentrations are not subject to significant changes anymore."

The statement on page 13971 (line 5) refers to the entrance region of the sampling line. This means that conditions in the CLOUD chamber are at steady-state. The dimer to monomer ratio is therefore only allowed to change within the CIMS sampling line. The change in the monomer and dimer concentration is taken into account by differential equations and therefore the steady-state assumption is not used within the domain of the CIMS sampling line (see reply to comment (13)).

(9) Page 13969, lines 10-13: "Cluster growth is treated explicitly by a step-by-step addition of sulfuric acid molecules while equilibrium with water molecules is assumed due to the relatively high concentration of H_2O compared to $[H_2SO_4]$." The text should be revised to state that the cluster growth is treated explicitly only concerning the addition of sulphuric acid, while water is assumed to be in equilibrium, and that the equilibrium assumption also requires a much higher evaporation rate for water than for sulphuric acid, not only a much higher concentration (collision rate) of water.

The text has been revised as suggested by the referee:

"Cluster growth is treated explicitly by a step-by-step addition of sulfuric acid molecules while equilibrium with water molecules is assumed due to the relatively high concentration and evaporation rate of H_2O compared to H_2SO_4."

(10) Page 13969, lines 15-16: the cluster thermodynamics reported by of Lovejoy and Curtius (2001) and Froyd and Lovejoy (2003) are only partly experimental, they are partly based on quantum chemical calculations. This should be stated.

The sentence on page 13969 (line 14-16) has been revised as follows:

"In SAWNUC, evaporation rates of small, negatively-charged clusters are based on measured thermodynamics and partly on quantum chemical calculations (Lovejoy and Curtius, 2001; Froyd and Lovejoy, 2003)."

(11) Page 13969 line 27. The authors should explain in some detail how the Kürten et al. (2014) model has been adapted to a binary system, since to my knowledge it has so far been only used for a one-component system, and the extension to more components is not necessarily trivial.

Since the results from the adjusted model by Kürten et al. (2014) are not presented in the paper we decided to remove the statement. The detailed description of the adjusted model will be subject of a forthcoming paper.

(12) Page 13970, line 1: How do the two independent models differ? Are the same net collision rate coefficients and evaporation coefficient used in both models?

Yes, the functions for calculating the collision rates and the van der Waals enhancement factors are identical. However, SAWNUC treats the presence of water in the clusters differently. The collision rate is obtained from a weighted average after calculating the collision rates of clusters containing different amounts of water individually, whereas the adjusted Kürten et al. (2014) model first determines the average amount of water and then calculates the collision rate just for this cluster. In this respect, SAWNUC should be more accurate, but the effect seems to be insignificant. Since we decided to remove the statement regarding the Kürten et al. (2014) model (see previous reply to comment (11), no change has been made to the text regarding this comment.

(13) Page 13970, lines 21-23: Much more detail is needed concerning the modelling resulting in the data shown in Figure 1, so that the readers would, even in principle, be able to reproduce the modeling

The following text has been added to Section 2.6:

"To estimate the evaporation effect, a finite difference method was used to calculate the temperature profile, as well as the dimer concentration across the sampling line over its full length. The differential equations for the monomer (i = 0) and dimer (i = 1) concentrations c_i were solved as a function of the radial and axial coordinates r and z (Kürten et al., 2012):

$$\frac{\partial c_i}{\partial t} = D_i \cdot \left(\frac{1}{r} \cdot \frac{\partial c_i}{\partial t} + \frac{\partial^2 c_i}{\partial r^2} + \frac{\partial^2 c_i}{\partial z^2}\right) - \frac{2Q}{\pi R^2} \cdot \left(1 - \frac{r^2}{R^2}\right) \cdot \frac{\partial c_i}{\partial z} + s_i, \qquad (6)$$

where D_i is the diffusivity, Q is the flow rate and R is the radius of the tube. A parabolic flow profile was assumed and the geometry was divided into small areas in order to solve the differential equations by a finite difference method. The source terms s_i include evaporation and production of dimers and loss and production of monomers due to self-coagulation and evaporation of dimers. Further reactions (coagulation with larger clusters/particles) were not taken into account since the time is rather short (< 1s for Q =7.5 slm, R = 0.005 m, and L = 1 m) and the other loss terms are dominant. A similar differential equation is used to determine the temperature inside the tube before the concentrations are calculated.

This temperature is used to calculate the evaporation of dimers in each of the small areas. The time-dependent equations (time *t*) are repeatedly solved until a reasonable degree of convergence is reached.”

(14) Page 13971, line 7: can the dimers grow if no larger clusters are taken into account?

The considered loss processes for the dimers are wall loss and evaporation. The loss rate due to diffusion in a tube can be approximated by (Hanson and Eisele, 2000):

$$k_{loss,dimer} = \frac{3.65 \cdot D}{r^2} = \frac{3.65 \cdot 0.06\ cm^2\ s^{-1}}{(0.5\ cm)^2} = 0.88\ s^{-1}$$

This loss rate is much higher than what can be expected for loss due to coagulation (< 0.01 s^{-1}), therefore, loss by diffusion to the walls dominates by far over the first 80 cm of the tube. Later, when temperatures increase loss by evaporation can overcome the wall loss rate. However, in all cases growth of dimers (or coagulation) can be neglected.

(15) Page 13972, section 3.2: the description of the ion-induced experiments could be shorted quite a bit, as most of that material has been presented in the Rondo et al (2014) paper, and they are not essential for the story of this paper.

We have deleted part of the summary of the Rondo et al. (2014) findings (page 13972, line 18 to 26). However, we feel that further shortening of this section would make it harder for the reader to understand the ion effect if he/she is not familiar with Rondo et al. (2014).

(16) Page 13972, line 8: does the statement “While the monomer concentration is not affected by the GCRs, . . .” imply that the ionization does not consume monomers, or at least not significantly? Or do the authors mean that the ions do not affect the apparent measured monomer concentration?

The monomer is not affected significantly as the small ion concentration is generally below 5x10^{-3} cm^{-3} (Kirkby et al., 2011; Franchin et al. 2015) and the HSO_4^- ions are not efficiently being detected by the CIMS (Rondo et al., 2014). This information has been added to the revised version. The sentence on page 13972 (line 8) has been reformulated as follows:

“While the monomer concentration is not affected significantly by the GCRs because the small ion concentration is generally only on the order of a couple of thousand (Franchin et al. 2015) and the HSO_4^- ions are not efficiently being detected by the CIMS (Rondo et al., 2014), the dimer concentration is.”

(17) Page 13973 26-27: “the dimer signal shows almost no enhancement during ion-induced experiments when ammonia is present in the chamber.” Could this be reformulated by saying that the dimer signal comes mainly from the neutral clusters?

Yes, the sentence has been reformulated and now reads

“Another interesting observation is that the dimer signal comes mainly from the neutral clusters when ammonia is present in the chamber.”

(18) Page 13974, line 24 and Figure 3 caption: It would be more illustrative to use the verb “sum” rather than “integrate” here, as the authors are probably talking about summing up the concentrations of clusters of different (discrete) sizes.

We agree, the word "integrate" was replaced by the verb "sum".

(19) Page 13974, lines 27-28: I don't think the curve in Fig 3 has leveled off at the right hand edge of the figure to the extent that one can safely conclude that factor 3 is an upper bound for the contribution of fragmentation of larger clusters to dimer concentration.

We agree that the curve has not reached a plateau yet but on the other hand one needs to take into account that a cluster containing 20 sulfuric acid molecules is quite heavy; its mass is at least 2000 amu (if associated water molecules are taken into account). Generally, the transmission of mass spectrometers falls of steeply at an upper mass limit much smaller (see e.g. Zhao et al., 2010). We therefore think that it is a safe assumption to exclude contribution of the very heavy clusters. Furthermore, fragmentation does not need to be complete and survival of heavier fragments could occur which would lower the values shown in Fig. 3.

The following text has been added to the end of Section 3.2:

"Another argument why the data from Fig. 3 provide an upper estimate is due to the reduction in transmission efficiency for the components of the mass spectrometer that is generally observed with increasing mass."

(20) Page 13977, lines 16-17: How do the values for dH and dS compare to theoretical (quantum chemical values)? The comparison could be added to Table 1. Values for the cluster formation enthalpies dH are expected to be temperature dependent: the authors should comment of this when giving singles value for the temperature ranges 208-223K (binary system) and 210-248K (ternary system).

The updated values from this study for the sulfuric acid dimer formation at 20% RH are d*H* = -20.1 kcal mol^{-1} and d*S* = -46.7 cal mol^{-1} K^{-1}. These agree well with the values reported by Ding et al. (2003) (see also Hanson and Lovejoy (2006)) where the values of Ding et al. were reported for the conditions of 20% RH). A new table (new Table 2) has been included (see comments in the beginning of this document on page 1 and 2).

The dependence of the enthalpy d*H* with temperature is generally small (see e.g. Temelso et al., 2012). However, we have added a sentence to the text in order to caution the reader that the assumption of a constant d*H* was made.

The following sentence was added to Section 3.3 (page 13977, line 17):

"We caution that in this study the assumption is made that d*H* does not vary with temperature; generally this variation should, however, be small."

(21) Page 13977, line 18, lines 22-23: Is there a physical justification for the RHp dependence? A plot of the evaporation rates as a function of relative humidity would help to assess how well the assumed RH-dependence fits the data. It should also be noted that since RH is connected to temperature through the temperature dependency of the saturation vapor pressure, data measured at same RH but different temperatures cannot be used to assess solely the effect of temperature because the absolute water vapor concentration may also vary (Figure 6).

We do not have a physical explanation for the power-dependence of the dimer evaporation rate regarding RH. As mentioned in the beginning, in the originally submitted manuscript the error was made that the RH over ice was used instead of the RH over (supercooled liquid) water. When updating the RH the plot shown in the beginning (new Figure 6) shows the dimer evaporation rates as a function of the RH for two temperatures (208 and 223 K) including power law fit curves. These fits indicate slopes of p = -1.6 for the 223 K data and p = -1 for the 208 K data.

(22) Pages 13978-13980, section 3.4: The CI-APi-TOF results presented in this section seem fairly unconnected from all the other material in the manuscript. Could this material be left out, and if not, can it be tied more to other parts of the work?

We would very much like to keep Section 3.4 in the paper. It is true that no quantitative conclusions can be drawn from the data in Figure 8 (previously Figure 7) can be drawn but the data are the first neutral cluster measurements made for the binary system at atmospherically relevant concentrations. This indicates that atmospheric binary nucleation should, in principle, be directly observable at low temperatures, e.g. during aircraft measurements. This is an important finding since a previous measurement was made only at relatively high sulfuric acid concentrations (~1×10^9 cm^{-3}, Eisele and Hanson, 2000).

We have added the following text to Section 3.4 (page 13978, line 16):

"However, their measurements were conducted at much higher sulfuric acid concentrations (~10^9 cm^{-3}) whereas in this study the conditions were atmospherically more relevant (sulfuric acid monomer concentration ~$1.7x10^7$ cm^{-3}). Therefore, the data presented in the following indicates that atmospheric binary nucleation should be directly observable at low temperature, e.g., during aircraft measurements."

(23) Page 13980, lines11-14: "In the presence of NH_3, a fraction of the sulfuric acid will be bound to ammonia. However, we assume that the sulfuric acid monomers and dimers will still be ionized by the nitrate primary ions at the same rate as the pure compounds." It seems inconsistent that while using different net collision rates between for sulphuric acid-bisulphate ion collision and sulphuric acid nitrate ion collision (major point 1), these ionization rates are taken to be the same.

This comment relates to the major comment #2. The maximum fraction of [H_2SO_4•NH_3] to [H_2SO_4] is ~1/3 for the lowest temperature of 210 K; at higher temperature this fraction decreases rapidly. A study by Kupiainen-Määttä et al. (2013) has estimated that binding of (H_2SO_4) with NH_3 can enhance the collision rate with the nitrate primary ions by a factor of 1.4. Assuming for the moment that the factor of 1.4 is appropriate, a ~13% overestimation of the monomer would result if 1/3 of the total sulfuric acid monomer is present as H_2SO_4•NH_3. On the other hand an earlier study by Kurtén et al. (2011) suggested that sulfuric acid monomers clustered with a base (ammonia or dimethylamine) could lower the detection efficiency of nitrate chemical ionization, which is the opposite effect that Kupiainen-Määttä et al. (2013) predicted. In the meantime experiments were carried out at CLOUD where the detection efficiency of sulfuric acid monomers by CIMS was investigated with and without the presence of dimethylamine while sulfuric acid was produced at a constant rate. These experiments are summarized in a submitted manuscript (Rondo et al., 2015) and suggest that there is no measurable effect on the CIMS detection efficiency although dimethylamine very likely bonds much more strongly to sulfuric acid than ammonia. For this reason we assume that the sulfuric acid measurement should not be affected significantly in this study through this effect.

However, to point the reader to this effect we have added the following discussion Section 3.5:

"It has been suggested that the sensitivity of a nitrate CIMS regarding the sulfuric acid measurements could be affected by the presence of ammonia (or other bases like dimethylamine), which cluster with sulfuric acid (Kurtén et al., 2011; Kupiainen-Määttä et al., 2013). However, recent measurements at the CLOUD chamber indicate that this is very likely a minor affect (Rondo et al. 2015)."

(24) Page 13981, lines 27-28: Again, a much more simple approach is used here than in treating the collisions between different ions and molecules differently (major point 1). How is this justified, as the

ammonia content of the cluster affects its collision cross section both through effective radius and the magnitude of the London van der Waals correction, which depends on the dipole moment of the cluster?

The comment relates to neutral clusters (tetramers and larger) which have not been measured with the CIMS and therefore no statements is made about the charging efficiency of such clusters. The reviewer is however correct that the ammonia content of the neutral clusters could affect their collision rates. Regarding the van der Waals enhancement it seems that there is not much difference between sulfuric acid-water particles and ammonium-sulfate aerosol (e.g. van Dingenen and Raes, 1990; Brockmann, McMurry, and Liu, 1982). Although the clusters/aerosols in this study are somewhat different than in the cited studies the chemical systems are related. Furthermore, the neutral-neutral collision rates for the larger clusters used in the model determine the loss rate of such clusters and the formation rate of the larger clusters. Therefore, their concentration has only a small effect on the sulfuric acid monomer/dimer and the H_2SO_4•NH_3 cluster.

(25) Page 13981 line 28-Page 13892, line 1: The author should provide justification for assumption “We further assume that the clusters cannot contain more bases than acids”

The study by Schobesberger et al. (2015) provides evaporation rates of $(H_2SO_4)_n(NH_3)_{n+1}$ clusters. Compared to $(H_2SO_4)_n(NH_3)_n$ the clusters with the higher basicity show a much faster evaporation rate concerning the base molecule. Since the base concentrations in this study are rather low (below 1×10^9 cm^{-3}) the evaporation of ammonia is much faster than the gain through collisions.

We have modified the sentence on page 13982 (line 1) as follows:

“We further assume that the clusters cannot contain more bases than acids, so reactions like AB + B are not considered as the extra base is expected to evaporate much more rapidly than it can be gained through collisions at the relatively low base concentrations (Schobesberger et al., 2015).”

(26) Page 13981, line 19: A reference also to the Almeida et al (2013) paper would be in order, as the same system is treated there using another model, and also a short description of the differences between these two models (that of the current manuscript and the model used in Almeida et al) should be added

The model used in Almeida et al. (2013) was the ACDC model using evaporation rates for the system of sulfuric acid and dimethylamine obtained from quantum chemical calculations. The other studies mentioned used different approaches to model acid-base nucleation and our simple heuristic model was motivated by those previous publications. In order to express this we have modified the sentence (page 13981, lines 16 to 19):

“In order to better understand what influences the dimer concentration in the ternary system, we have developed a simple model (Fig. 10). This heuristic model is motivated by recent studies which have simulated acid-base nucleation of sulfuric acid, ammonia, and amines with similar methods, i.e., without simulating every possible cluster configuration explicitly (Chen et al., 2012; Paasonen et al., 2012; Jen et al., 2014).”

(27) Figure 9: it would be interesting to know what are the contributions of different routes to the cluster growth.

Fig. 9 has been updated according to the referee’s suggestion; it now shows simulated concentrations for an example calculation at 248 K. The monomer concentration has been assumed as 1×10^7 cm^{-3} and the ammonia concentration is 2×10^8 cm^{-3}. These data indicate that the main path of dimer formation is via the H_2SO_4•NH_3 cluster. Some more discussion regarding this comment is also provided in our reply to the second major comment.

(28) Page 13982, lines 22-23: in addition to the Chen et al value for the evaporation rate of the base-containing dimer, theoretical (quantum chemical) value(s) should also be given for comparison

The following is partly a repetition of one of the replies to the second major comment.

Based on the referee's comment we have evaluated evaporation rates from quantum chemical data for the relevant clusters (containing 3 sulfuric acid molecules A and between 1 and 3 base (ammonia) molecules B). The data was taken from Ortega et al. (2012) and is listed in the following:

A evaporation from $SA_3.B_1$: 1034 s^{-1} (at 300 K) and 0.70 s^{-1} (at 248 K)
B evaporation from $SA_3.B_1$: $5.83x10^{-5}$ s^{-1} (at 300 K) and $1.49x10^{-9}$ s^{-1} (at 248 K)

A evaporation from $SA_3.B_2$: 0.047 s^{-1} (at 300 K) and $3.11x10^{-6}$ s^{-1} (at 248 K)
B evaporation from $SA_3.B_2$: 0.065 s^{-1} (at 300 K) and $7.33x10^{-6}$ s^{-1} (at 248 K)

A evaporation from $SA_3.B_3$: $4.23x10^{-8}$ s^{-1} (at 300 K) and $3.73x10^{-4}$ s^{-1} (at 248 K)
B evaporation from $SA_3.B_3$: 2.74 s^{-1} (at 300 K) and $7.24x10^{-14}$ s^{-1} (at 248 K)

These data indicate that the trimer containing two bases has the overall slowest evaporation rate since both the acid (A) and the base (B) evaporate rather slowly. The other cluster configurations (with only one base or with three bases) have either a fast evaporation rate regarding an acid or regarding a base molecule. However, if a base evaporates from the $SA_3.B_3$ cluster it results in a $SA_3.B_2$ cluster, which has an overall very slow evaporation rate. Therefore, the quantum chemistry data suggest that only the $SA_3.B$ cluster can be regarded as relatively unstable because an acid molecule can evaporate rapidly.

Furthermore, for the $(H_2SO_4)_{x\geq2}(NH_3)_{y\geq1}(H_2O)_{z\geq1}$ cluster data from Herb et al. (2011) is available.

A evaporation from $A_3B_1W_1$: $2.93x10^4$ s^{-1} (at 300 K) and 50 s^{-1} (at 248 K)
A evaporation from A_3B_1: $1.1x10^6$ s^{-1} (at 300 K) and $4.1x10^3$ s^{-1} (at 248 K)

For the cluster containing no water, the evaporation rate from Herb et al. (2011) is significantly higher than for the Ortega et al. (2012) data. However, Herb et al. (2011) simulated also the effect of water vapor and this lowers the evaporation rate by about 2 orders of magnitude.

In summary we have added the following after line 24 on page 13982:

"The quantum chemistry data from Ortega et al. (2012) support the assumption that a trimer containing at least two bases is relatively stable (evaporation rate below 0.1 s^{-1} at 300 K). However, it predicts that the trimer containing only one ammonia molecule has a high evaporation rate regarding an acid molecule (~1000 s^{-1} at 300 K); additional ammonia in the trimer will lower the evaporation rates. For this reason the trimer concentration will strongly depend on the ammonia concentration, which controls the cluster distribution. Therefore, the Chen et al. (2012) value can be regarded as a best estimate for the overall trimer evaporation rate for their experimental conditions. Herb et al. (2011) also simulated the effect that one water molecule has on the acid evaporation rate from $(H_2SO_4)_3(NH_3)_1(H_2O)_{0,1}$ clusters. While the water molecule lowers the evaporation rate the absolute evaporation rate is higher ($2.9x10^4$ s^{-1} at 300 K) than for the Ortega et al. (2012) data."

(29) Page 13983, lines 22-23: "Our calculated dimer concentration agrees with their measured concentration within better than a factor of two." A plot illustrating this would be good to see.

This statement refers to one experiment for which data was reported by Hanson and Eisele (2002). They reported a measured dimer concentration of $1.1x10^7$ cm^{-3} when the total sulfuric acid monomer was $1.9x10^9$ cm^{-3} and ammonia was at $3.8x10^9$ cm^{-3} (at 265 K and 10% RH). With our model using an evaporation rate of the $H_2SO_4•NH_3$ cluster for 265 K, we calculate a total dimer concentration of $7x10^6$

cm^{-3} (36% deviation from the reported measured concentration). This is an independent cross check of our model and the assumptions that went into the model but since just one data point is discussed it does not deserve a dedicated figure. However, in the meantime we have further compared the concentrations also for the larger clusters. The result is listed in the table below, which has been added to the manuscript (as the new Table 3). Furthermore the following text now replaces the sentence on page 13983 (line 22/23):

"Our calculated dimer concentration agrees with their measured concentration within about 40%. Table 3 shows a comparison with the cluster concentrations (dimer to pentamer) measured by Hanson and Eisele (2002) and the ones from this study using the acid-base model described above."

cluster	Hanson and Eisele (2002)	acid-base model, this study
N_2 (total dimer)	1.1x10^7 cm^{-3}	7.0x10^6 cm^{-3} (-36 %)
N_3 (total trimer)	6.5x10^6 cm^{-3}	5.6x10^6 cm^{-3} (-14 %)
N_4 (total tetramer)	6.6x10^6 cm^{-3}	4.7x10^6 cm^{-3} (-29 %)
N_5 (total pentamer)	~4x10^6 cm^{-3}	4.1x10^6 cm^{-3}

Table 3. Comparison between measured cluster concentrations by Hanson and Eisele (2002) and simulated cluster concentrations using the acid-base model described in Section 3.6.

(30) Page 13985, lines 12-18: What is the reason for considering theoretical evaporation rates of dry A_3B_1 and A_4B_1 clusters instead of clusters containing more ammonia molecules? Also hydration is likely to affect net evaporation rates. On the other hand, beyond the critical size the evaporation rate is lower than the collision frequency, so it would be useful to give the collision frequency with acid and ammonia molecules in the experimental conditions of Hanson and Eisele (2002) so the reader could more easily see what conclusions the authors wish to draw from this comparison.

The first part of the comment has been discussed in detail in the replies to other previous comments (e.g. comment (28)). The quantum chemical data indicate that the trimer and tetramer with only one base have the fastest evaporation rate towards sulfuric acid. Therefore, if the reported cluster evaporation rates are representative the mentioned clusters would be a bottleneck for further growth or cluster stabilization by additional base molecules.

We have added the following to page 13985 (line 13):

"However, the presence of further ammonia molecules in the trimer and tetramer can lower the evaporation rates and water should have a similar effect (Ortega et al., 2012; Herb et al., 2011)."

The collision frequency can be calculated from the reported concentrations by Hanson and Eisele (2002). At 265 K the collisions frequency due to sulfuric acid monomers is approximately 1 s^{-1} and for ammonia 2 s^{-1}. This indicates that the acid evaporation rate of the sulfuric acid trimer cannot be higher than ~1 s^{-1}. Since the temperatures of this study are substantially lower (248 K and colder) the expected upper limit for the trimer evaporation rate should be correspondingly slower. However, only an upper limit can be determined from this estimation and the actual trimer evaporation rate can be even lower and the replies to previous comments indicate that this could be the case. Since many of the previous comments aimed in a similar direction and we have answered these in detail no further additions are made to the manuscript in the context of the present comment.

References

Almeida, J., Schobesberger, S., Kürten, A., Ortega, I. K., Kupiainen-Määttä, O., Praplan, A. P., Adamov, A., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Donahue, N. M., Downard, A., Dunne, E. M., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Guida, R., Hakala, J., Hansel, A., Heinritzi, M., Henschel, H., Jokinen, T., Junninen, H., Kajos, M., Kangasluoma, J., Keskinen, H., Kupc, A., Kurtén, T., Kvashin, A. N., Laaksonen, A., Lehtipalo, K., Leiminger, M., Leppä, J., Loukonen, V., Makhmutov, V., Mathot, S., McGrath, M. J., Nieminen, T., Olenius, T., Onnela, A., Petäjä, T., Riccobono, F., Riipinen, I., Rissanen, M., Rondo, L., Ruuskanen, T., Santos, F. D., Sarnela, N., Schallhart, S., Schnitzhofer, R., Seinfeld, J. H., Simon, M., Sipilä, M., Stozhkov, Y., Stratmann, F., Tomé, A., Tröstl, J., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Virtanen, A., Vrtala, A., Wagner, P. E., Weingartner, E., Wex, H., Williamson, C., Wimmer, D., Ye, P., Yli-Juuti, T., Carslaw, K. S., Kulmala, M., Curtius, J., Baltensperger, U., Worsnop, D. R., Vehkamäki, H., and Kirkby, J.: Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere, Nature, 502, 359–363, 2013.

Brockmann, J. E., McMurry, P. H., and Liu, B. Y. H.: Experimental study of deposition and coagulation of free molecule aerosols in turbulent pipe flow, J. Colloid Interface Sci., 88, 522–529, 1982.

Chan, T. W., and Mozurkewich, M.: Measurement of the coagulation rate constant for sulfuric acid particles as a function of particle size using tandem differential mobility analysis, J. Aerosol Sci., 32, 321–339, 2001.

Chen, M., Titcombe, M., Jiang, J., Jen, C., Kuang, C., Fischer, M. L., Eisele, F. L., Siepmann, J. I., Hanson, D. R., Zhao, J., and McMurry, P. H.: Acid–base chemical reaction model for nucleation rates in the polluted atmospheric boundary layer, P. Natl. Acad. Sci. USA, 109, 18713–18718, doi: 10.1073/pnas.1210285109, 2012.

Chon, N. L., Lee, S.-H., and Lin, H.: A theoretical study of temperature dependence of cluster formation from sulfuric acid and ammonia, Chem. Phys., 433, 60–66, 2014.

Curtius, J., Froyd, K. D., and Lovejoy, E. R.: Cluster Ion Thermal Decomposition (I): Experimental Kinetics Study and ab Initio Calculations for $HSO_4^-(H_2SO_4)_x(HNO_3)_y$, J. Phys. Chem. A, 105, 10867–10873, 2001.

Ding, C.-G., Laasonen, K., and Laaksonen, A.: Two sulfuric acids in small water clusters, J. Phys. Chem. A, 107, 8648–8658, 2003.

Franchin, A., Ehrhart, S., Leppä, J., Nieminen, T., Gagné, S., Schobesberger, S., Wimmer, D., Duplissy, J., Riccobono, F., Dunne, E. M., Rondo, L., Downard, A., Bianchi, F., Kupc, A., Tsagkogeorgas, G., Lehtipalo, K., Manninen, H. E., Almeida, J., Amorim, A., Wagner, P. E., Hansel, A., Kirkby, J., Kürten, A., Donahue, N. M., Makhmutov, V., Mathot, S., Metzger, A., Petäjä, T., Schnitzhofer, R., Sipilä, M., Stozhkov, Y., Tomé, A., Kerminen, V.-M., Carslaw, K., Curtius, J., Baltensperger, U., and Kulmala, M.: Experimental investigation of ion–ion recombination under atmospheric conditions, Atmos. Chem. Phys., 15, 7203–7216, 2015.

Froyd, K. D., and Lovejoy, E. R.: Experimental thermodynamics of cluster ions composed of H_2SO_4 and H_2O. 2. Measurements and ab initio structures of negative ions, J. Phys. Chem. A, 107, 9812–9824, 2003.

Hanson, D. R., and Eisele, F.: Diffusion of H_2SO_4 in humidified nitrogen: hydrated H_2SO_4, J. Phys. Chem. A, 104, 1715–1719, 2000.

Hanson, D. R., and Eisele, F. L.: Measurement of prenucleation molecular clusters in the NH_3, H_2SO_4, H_2O system, J. Geophys. Res., 107, D12, 4158, 10.1029/2001JD001100, 2002.

Hanson, D. R., and Lovejoy, E. R.: Measurement of the thermodynamics of the hydrated dimer and trimer of sulfuric acid, J. Phys. Chem. A, 110, 9525–9528, 2006.

Henschel, H., Navarro, J. C. A., Yli-Juuti, T., Kupiainen-Määttä, O., Olenius, T., Ortega, I. K., Clegg, S. L., Kurtén, T., Riipinen, I., and Hanna Vehkamäki: Hydration of Atmospherically Relevant Molecular Clusters: Computational Chemistry and Classical Thermodynamics, J. Phys. Chem. A, 118, 2599–2611, 2014.

Herb, J., Nadykto, A. B., and Yu, F.: Large ternary hydrogen-bonded pre-nucleation clusters in the Earth's atmosphere, Chem. Phys. Lett., 518, 7–14, 2011.

Jen, C., McMurry, P. H., and Hanson, D. R.: Stabilization of sulfuric acid dimers by ammonia, methylamine, dimethylamine, and trimethylamine, J. Geophys. Res. Atmos., 119, 7502–7514, doi: 10.1002/2014JD021592, 2014.

Kangasluoma, J., Junninen, H., Lehtipalo, K., Mikkilä, J., Vanhanen, J., Attoui, M., Sipilä, M., Worsnop, D., Kulmala, M., and Petäjä, T.: Remarks on Ion Generation for CPC Detection Efficiency Studies in Sub-3-nm Size Range, Aerosol Sci. Technol., 47, 556–563, 2013.

Kirkby, J., Curtius, J., Almeida, J., Dunne, E., Duplissy, J., Ehrhart, S., Franchin, A., Gagné, S., Ickes, L., Kürten, A., Kupc, A., Metzger, A., Riccobono, F., Rondo, L., Schobesberger, S., Tsagkogeorgas, G., Wimmer, D., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Downard, A., Ehn, M., Flagan, R.C., Haider, S., Hansel, A., Hauser, D., Jud, W., Junninen, H., Kreissl, F., Kvashin, A., Laaksonen, A., Lehtipalo, K., Lima, J., Lovejoy, E. R., Makhmutov, V., Mathot, S., Mikkilä, J., Minginette, P., Mogo, S., Nieminen, T., Onnela, A., Pereira, P., Petäjä, T., Schnitzhofer, R., Seinfeld, J. H., Sipilä, M., Stozhkov, Y., Stratmann, F., Tomé, A., Vanhanen, J., Viisanen, Y., Vrtala, A., Wagner, P. E., Walther, H., Weingartner, E., Wex, H., Winkler, P. M., Carslaw, K. S., Worsnop, D. R., Baltensperger, U., and Kulmala, M.: Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation, Nature, 476, 429–435, 2011.

Kupiainen-Määttä, O., Olenius, T., Kurtén, T., and Vehkamäki, H.: CIMS sulfuric acid detection efficiency enhanced by amines due to higher dipole moments: a computational study, J. Phys. Chem. A, 117, 14109–14119, 2013.

Kürten, A., Rondo, L., Ehrhart, S., and Curtius, J.: Calibration of a chemical ionization mass spectrometer for the measurement of gaseous sulfuric acid, J. Phys. Chem. A, 116, 6375–6386, dx.doi.org/10.1021/jp212123n, 2012.

Kürten, A., Jokinen, T., Simon, M., Sipilä, M., Sarnela, N., Junninen, H., Adamov, A., Almeida, J., Amorim, A., Bianchi, F., Breitenlechner, M., Dommen, J., Donahue, N. M., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Hakala, J., Hansel, A., Heinritzi, M., Hutterli, M., Kangasluoma, J., Kirkby, J., Laaksonen, A., Lehtipalo, K., Leiminger, M., Makhmutov, V., Mathot, S., Onnela, A., Petäjä, T., Praplan, A. P., Riccobono, F., Rissanen, M. P., Rondo, L., Schobesberger, S., Seinfeld, J. H., Steiner, G., Tomé, A., Tröstl, J., Winkler, P. M., Williamson, C., Wimmer, D., Ye, P., Baltensperger, U., Carslaw, K. S., Kulmala, M., Worsnop, D. R., and Curtius, J.: Neutral molecular cluster formation of sulfuric acid-dimethylamine observed in real-time under atmospheric conditions, P. Natl. Acad. Sci. USA, 111, 15019–15024, doi: 10.1073/pnas.1404853111, 2014.

Kurtén, T., Petäjä, T., Smith, J., Ortega, I. K., Sipilä, M., Junninen, H., Ehn, M., Vehkamäki, H., Mauldin, L., Worsnop, D. R., and Kulmala, M.: The effect of H_2SO_4-amine clustering on chemical ionization mass spectrometry (CIMS) measurements of gas-phase sulfuric acid, Atmos. Chem. Phys., 11, 3007–3019, 2011.

Lovejoy, E. R., and Curtius, J.: Cluster ion thermal decomposition (II): Master equation modeling in the low-pressure limit and fall-off regions. Bond energies for $HSO_4^-(H_2SO_4)_x(HNO_3)_y$, J. Phys. Chem. A, 105, 10874–10883, 2001.

Marlow, W. H.: Lifshitz–van der Waals forces in aerosol particle collisions. I. Introduction: Water droplets, J. Chem. Phys., 73, 6288–6295, 1980.

McMurry, P. H.: Photochemical aerosol formation from SO_2: A theoretical analysis of smog chamber data, J. Colloid Interf. Sci., 78, 513–527, 1980.

Nadykto, A. B., and Yu, F.: Strong hydrogen bonding between atmospheric nucleation precursors and common organics, Chem. Phys. Lett., 435, 14–18, 2007.

Ortega, I. K., Kupiainen, O., Kurtén, T., Olenius, T., Wilkman, O., McGrath, M. J., Loukonen, V., and Vehkamäki, H.: From quantum chemical formation free energies to evaporation rates, Atmos. Chem. Phys., 12, 225–235, 2012.

Paasonen, P. , Olenius, T., Kupiainen, O., Kurtén, T., Petäjä, T., Birmili, W., Hamed, A., Hu, M., Huey, L. G., Plass-Duelmer, C., Smith, J. N., Wiedensohler, A., Loukonen, V., McGrath, M. J., Ortega, I. K., Laaksonen, A., Vehkamäki, H., Kerminen, V.-M., and Kulmala, M.: On the formation of sulphuric acid – amine clusters in varying atmospheric conditions and its influence on atmospheric new particle formation, Atmos. Chem. Phys., 12, 9113–9133, 2012.

Rondo, L., Kürten, A., Ehrhart, S., Schobesberger, S., Franchin, A., Junninen, H., Petäjä, T., Sipilä, M., Worsnop, D. R., and Curtius, J.: Effect of ions on the measurement of sulphuric acid in the CLOUD experiment at CERN, Atmos. Meas. Tech., 7, 3849–3859, 2014.

Rondo, L., Ehrhart, S., Kürten, A., Adamov, A., Bianchi, F., Breitenlechner, M., Duplissy, J., Franchin, A., Dommen, J., Donahue, N. M., Dunne, E. M., Flagan, R. C., Hakala, J., Hansel, A., Keskinen, H., Kim, J., Jokinen, T., Lehtipalo, K., Leiminger, M., Praplan, A., Riccobono, F., Rissanen, M. P., Sarnela, N., Schobesberger, S., Simon, M., Sipilä, M., Smith, J. N., Tomé, A., Tröstl, J., Tsagkogeorgas, G., Vaattovaara, P., Winkler, P. M., Williamson, C., Baltensperger, U., Kirkby, J., Kulmala, M., Worsnop, D. R., and Curtius, J.: Effect of dimethylamine on the gas phase sulfuric acid concentration measured by Chemical Ionization Mass Spectrometry (CIMS), submitted to J. Geophys. Res., 2015.

Schobesberger, S., Franchin, A., Bianchi, F., Rondo, L., Duplissy, J., Kürten, A., Ortega, I. K., Metzger, A., Schnitzhofer, R., Almeida, J., Amorim, A., Dommen, J., Dunne, E. M., Ehn, M., Gagné, S., Ickes, L., Junninen, H., Hansel, A., Kerminen, V.-M., Kirkby, J., Kupc, A., Laaksonen, A., Lehtipalo, K., Mathot, S., Onnela, A., Petäjä, T., Riccobono, F., Santos, F. D., Sipilä, M., Tomé, A., Tsagkogeorgas, G., Viisanen, Y., Wagner, P. E., Wimmer, D., Curtius, J., Donahue, N. M., Baltensperger, U., Kulmala, M., and Worsnop, D. R.: On the composition of ammonia-sulfuric acid clusters during aerosol particle formation, Atmos. Chem. Phys., 15, 55–78, 2015.

Temelso, B., Phan, T. N., and Shields, G. C.: Computational Study of the Hydration of Sulfuric Acid Dimers: Implications for Acid Dissociation and Aerosol Formation, J. Phys. Chem. A, 116, 9745–9758, 2012.

Torpo, L., Kurtén, T., Vehkamäki, H., Laasonen, K., Sundberg, M. R., and Kulmala, M.: Significance of ammonia in growth of atmospheric nanoclusters, J. Phys. Chem. A, 111, 10671–10674, 2007.

van Dingenen, R., and Raes, F.: Coagulation enhancement of H_2O-H_2SO_4 aerosols: Experiments and model calculations in the transition regime, J. Aerosol Sci., 21 (Suppl. 1), S237–S240, 1990.

Viggiano, A. A., Dale, F., and Paulson, J. F.: Measurements of some stratospheric ion-molecule association rates: Implications for ion chemistry and derived HNO_3 concentrations in the stratosphere, J. Geophys. Res., 90, D5, 7977–7984, 1985.

Zhao, J., Eisele, F. L., Titcombe, M., Kuang, C., and McMurry, P. H.: Chemical ionization mass spectrometric measurements of atmospheric neutral clusters using the cluster-CIMS, J. Geophys. Res., 115, D08205, doi: 10.1029/2009JD012606, 2010.

We thank the reviewer for carefully reading our manuscript and for providing constructive comments, which have improved the quality and clarity of our manuscript. The reviewers' comments are repeated in full below, with our replies indicated after each comment in blue font. Text which has been added to the manuscript is shown in red font.

Before we give our detailed replies to all comments we want to indicate one major change that has been implemented.

After the manuscript was published we realized that the relative humidity (RH) which was used in the data analysis was taken as the RH over ice instead of supercooled water (note that the reported experiments include only conditions where the temperature was 248 K or colder). Since Hanson and Lovejoy (2006) used the RH over supercooled water it is necessary to refer the data from this study also to water, which shifts the relative humidities to lower values.

As requested by the referee (comment (21)) we have added a new figure to the manuscript (new Figure 6, see page 3 in this document), which shows the dependence of the sulfuric acid dimer evaporation rate as a function of the RH for two temperatures (208 and 223 K). Figure 6 also shows power law fit curves for each of the two data sets, indicating that the evaporation rates decrease with a power of $p = -1$ at 208 K and with $p = -1.6$ at 223 K. Because the new RH values do not correspond to 20% RH the evaporation rates cannot be directly compared to the data by Hanson and Lovejoy (2006). Therefore, the data points from Figure 6 that are closest to 20% RH were interpolated to 20% and these data are then used in Figure 7 (previously Figure 6) to obtain the fit parameters dH and dS. Using the updated data the fit parameters are now dH = -20.1±1.2 kcal mol^{-1} and dS = -46.7±5.2 cal mol^{-1} K^{-1}. The new values are somewhat different from the data by Hanson and Lovejoy (2006) who reported dH = -18.3±1.8 kcal mol^{-1} and dS = -39.5±7.8 cal mol^{-1} K^{-1} but still agree within errors. On the other hand the new data agree very well with quantum chemical calculations taking into account the effect of water on the formation of sulfuric acid dimers (Ding et al., 2003). Ding et al. (2003) report dH = -21.1 kcal mol^{-1} and dS = -51.7 cal mol^{-1} K^{-1} for the reaction of $(H_2SO_4)(H_2O)_2 + (H_2SO_4)(H_2O)$. Comparison between the data by Ding et al. (2003) and from this study is now included and the data (from quantum chemistry and measurements) are now shown in a new Table 2 (the previous Table 1 is now Table 4).

Additional small changes:

- The colors of the symbols in Figure 4 and Figure 5 have changed because the RH now represents the relative humidity over supercooled water.
- RH has also been updated in the context of Figure 10 (previously Figure 9 but since the new Figure 6 has been inserted the number has been adjusted). Because the pure sulfuric acid dimer evaporation rates are now changed slightly (due to the new fit parameters discussed above), the evaporation rates for the H_2SO_4•NH_3 cluster are somewhat different. This results also in updated values for dH and dS. These are now dH = -16.1±0.6 kcal mol^{-1} and dS = -26.4±2.6 cal mol^{-1} K^{-1}. The previously reported values were dH = -16.1 kcal mol^{-1} and dS = -26.2 cal mol^{-1} K^{-1}; therefore the change is relatively small.
- The dashed black line has been removed from Figure 7 (previously Figure 6)
- A new Table (Table 2) has been added; this table compares thermodynamic data of the formation of sulfuric acid dimers in the binary system; the previous Table 1 is now labeled Table 4 (see later comments).

Besides the addition of Figure 6 and the updated thermodynamic data, parts of the text have been modified. Section 3.3 now includes discussion of the new Figure 6. This discussion replaces the last part of Section 3.3 (starting with line 8 on page 13977):

"We converted equilibrium constants reported by Hanson and Lovejoy (2006) to evaporation rates using equation (8). Hanson and Lovejoy (2006) determined evaporation rates at 20% RH; while our measurements were made at different RHs. Because RH has a significant influence on the dimer evaporation further analysis is necessary to make the two data sets comparable.

Figure 6 shows the evaluated dimer evaporation rates as a function of the relative humidity (with respect to supercooled water) for two different temperatures (208 and 223 K). The rates from this study are based on the data shown in Figures 4 and 5 and equation (5). The data were fitted by simple power law fits and the slopes of p = -1 (at 208 K) and p = -1.6 (at 223 K) indicate that the evaporation rates decrease significantly with increasing RH. Qualitatively this is in agreement with a previous experiment (Hanson and Lovejoy, 2006) and quantum chemical calculations (Ding et al., 2003). However, Hanson and Lovejoy (2006) reported p = -0.5, where the exponent p has an uncertainty of ±100%. Our data indicate a somewhat stronger influence of RH on the evaporation rates, which also seems to be dependent on temperature.

The evaporation rates from Figure 6 with RH between 10 and 30% were normalized to 20% RH using the reported slopes. Figure 7 shows the data from this study and from Hanson and Lovejoy (2006). Fitting the combined data set for 20% RH gives the following formulation for the equilibrium constant

$$K_{eq} = \frac{1}{\mathrm{Pa}} \cdot exp\left(\frac{(10109 \pm 609)\ K}{T} - (35.03 \pm 2.61)\right). \quad (9)$$

The black line in Fig. 7 shows the dimer evaporation rates derived from equation (9). The uncertainties in equation (9) are based on 95% confidence intervals. Overall, the two data sets are, within errors, consistent with one another, and yield dH = -20.1±1.2 kcal mol^{-1} and dS = -46.7±5.2 cal mol^{-1} K^{-1}. We caution that in this study the assumption is made that dH does not vary with temperature; generally this variation should, however, be small. These data are slightly different than what has been reported by Hanson and Lovejoy (2006). However, our data agree within errors with results from quantum chemical calculations, taking into account the effect of water vapor (Ding et al., 2003). According to measurements by Hanson and Eisele (2000) and quantum chemical calculations (Temelso et al., 2012; Henschel et al. 2014) the sulfuric acid monomer and dimer can contain water molecules. Therefore, the data from Ding et al. (2003) taking into account the effect of water vapor are relevant for this study. Table 2 shows a comparison between different studies dealing with the sulfuric acid dimer formation. Regarding the effect of water vapor it should be noted that our experimentally determined evaporation rates represent an average for dimers containing different numbers of water molecules. The exact distribution of water associated with the dimers will be a function of relative humidity and temperature, which cannot be taken into account explicitly in this study."

Study	dH (kcal mol^{-1})	dS (cal mol^{-1} K^{-1})	$k_{2,e}$ at 208 K (s^{-1})	$k_{2,e}$ at 223 K (s^{-1})
this study (20% RH)	-20.1±1.2	-46.7±5.2	0.15	3.9
Hanson and Lovejoy (20% RH)	-18.3±1.8	-39.5±7.8	0.32	6.0
$(H_2SO_4)(H_2O) + (H_2SO_4)(H_2O)$[a]	-17.8	-48.3	89.3	1550
$(H_2SO_4)(H_2O)_2 + (H_2SO_4)(H_2O)$[a]	-21.1	-51.7	0.17	5.0
$(H_2SO_4)(H_2O)_2 + (H_2SO_4)(H_2O)_2$[a]	-25.6	-55.7	2.4×10^{-5}	1.5×10^{-3}

Table 2. Thermodynamic properties (dH and dS) and evaporation rates of the sulfuric acid dimer from this study and from the literature. [a]Literature data from Ding et al. (2003).

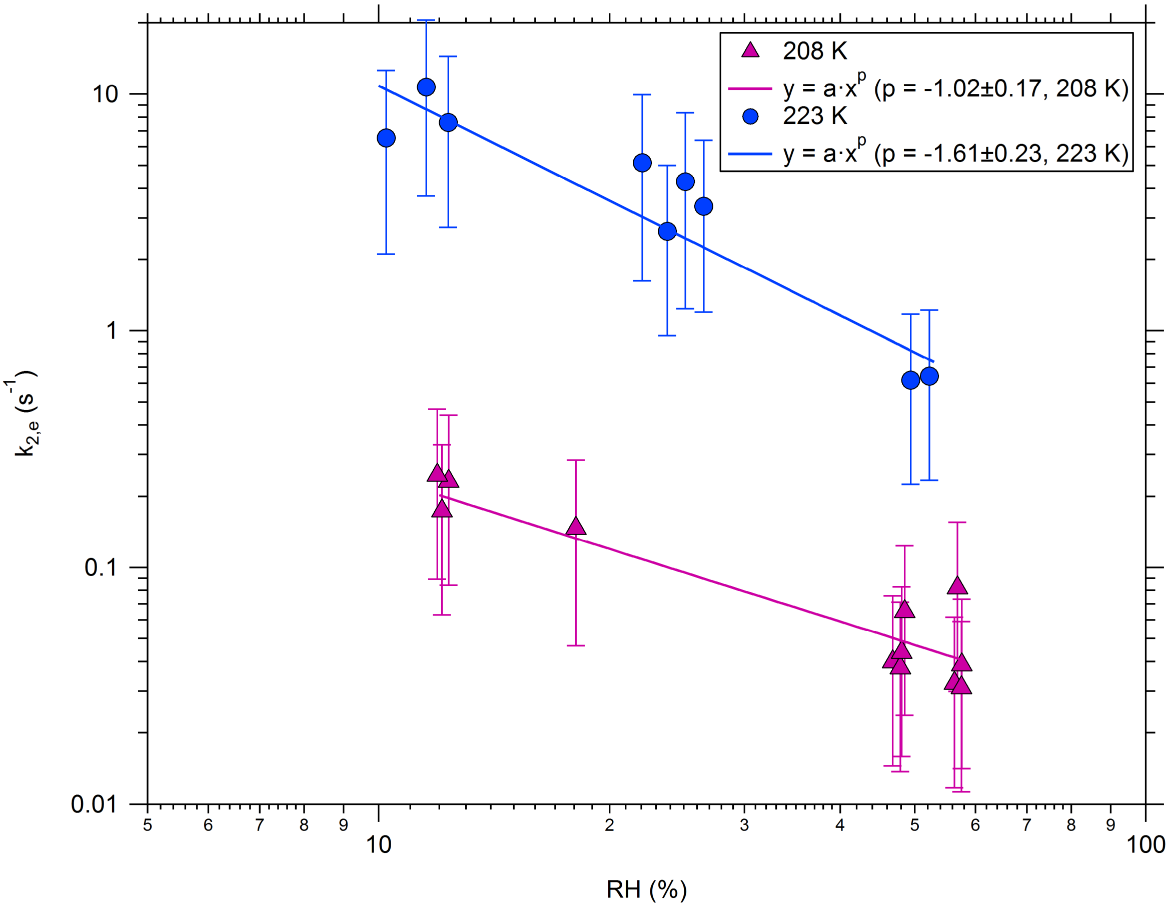


Fig. 6. Dimer evaporation rate as a function of the RH for two different temperatures (208 and 223 K). Power law fit curves are shown and the slopes *p* are indicated in the figure legend.

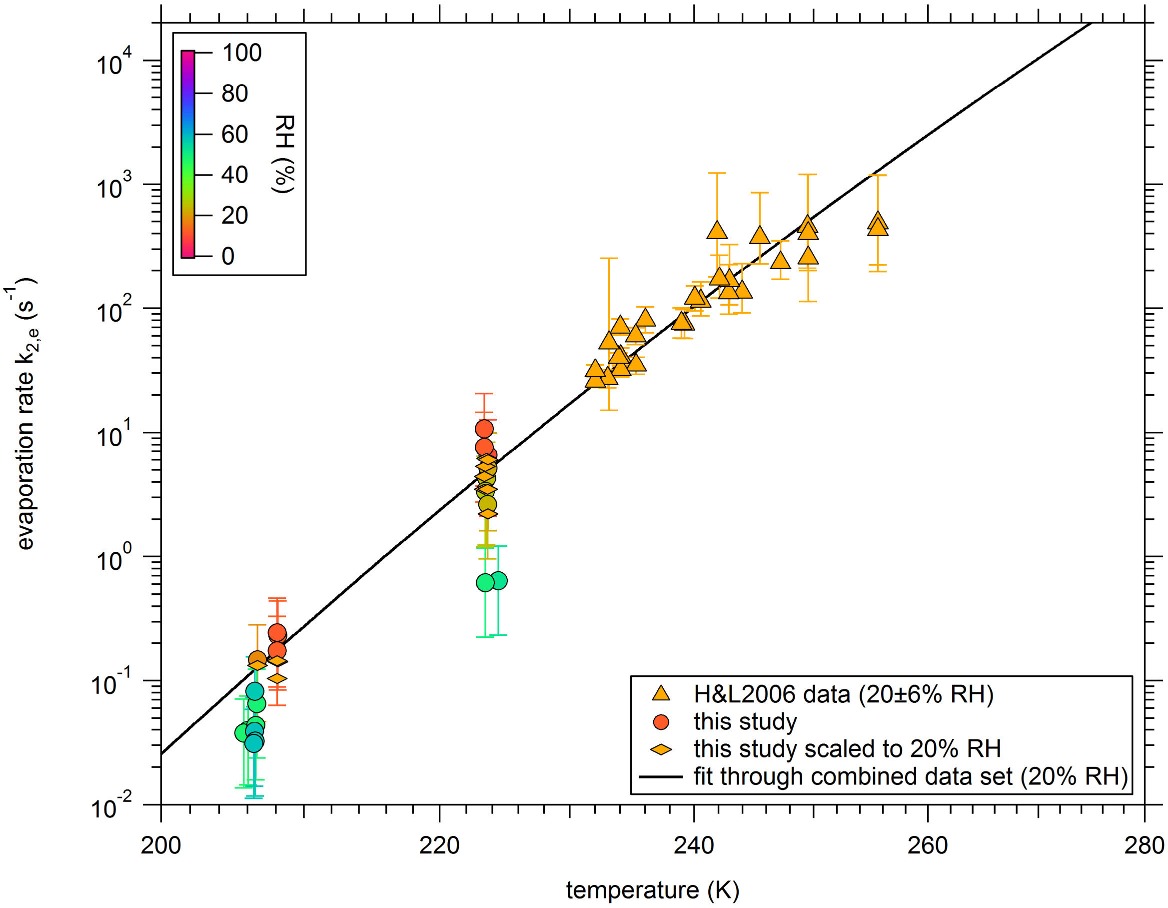


Fig. 7. Comparison of the sulfuric acid dimer evaporation rates from this study (circles) and from the literature (triangles, see Hanson and Lovejoy, 2006) as a function of temperature. The color code indicates the relative humidity during the experiments. Diamond symbols represent the data from this study scaled to 20% RH. The solid line shows a best fit through the data with the thermodynamic properties dH = -20.1±1.2 kcal mol^{-1} and dS = -46.7±5.2 cal mol^{-1} K^{-1} at 20% RH.

Referee #2:

This paper present a comprehensive and detailed analysis of a experiments, performed at the CERN CLOUD chamber, to determine the thermodynamic properties of the dimer formation in the systems listed in the title. In practice this means experimentally determining the evaporation rate of the dimer, calculating the equilibrium constant for dimer formation, and fitting to observations to determine the change in enthalpy dH and entropy dS for the dimer formation. These values are determined for the first time at temperatures <232K, which are relevant for the upper troposphere where new particle formation is known to occur and play an important role in both stratospheric and tropospheric processes. In addition these measurements, first estimates of the thermodynamics of the H_2SO_4-NH_3 cluster formation are also calculated. The paper is very thorough and well-written, and covers an important topic in atmospheric chemistry and physics. I recommend it for publication with minor modifications. There are two relatively substantive changes I'd like to see; the other changes are technical.

1) There are several combinations of projects (CLOUD5 and CLOUD7), instruments (CIMS, API-TOF-MS, CI-API-TOF-MS), and conditions (with and without natural GCR produced ions). It's very difficult for someone not intimately familiar with the CLOUD projects to understand which instruments contribute to which measurements and findings. Might it be possible to construct a text-based table which lists the various combinations of instruments and conditions that contribute to each finding? The rows might be the findings (e.g., evaporation rate of the dimer, thermodynamics of the ternary cluster) and the columns the various experiments (e.g., CLOUD5-charged; CLOUD7-neutral), and the content of each cell would be the instruments that were used. I simply lost track and spent much time flipping back and forth in the manuscript trying to make sense of the various combinations of measurements and analyses.

Thank you for this comment. We have added the following table (new Table 1) to the manuscript and refer to it at the end of Section 2.1.

campaign	instruments	binary system	ternary system	main findings
CLOUD5	CIMS, APi-TOF	investigated at 208 and 223 K, RH ~10 to 60%	investigated at 210, 223, and 248 K, ammonia between ~0.5 and 8 pptv	a) binary system: ion effect on apparent CIMS dimer measurements (Section 3.1) b) binary system: thermodynamics of sulfuric acid dimers (Section 3.3) c) ternary system: thermodynamics of H_2SO_4•NH_3 cluster (Sections 3.5 and 3.7)
CLOUD7	CIMS, CI-APi-TOF	investigated at 206 K	not investigated at low temperatures	observation of neutral clusters containing up to 10 sulfuric acid molecules (Section 3.4)

Table 1. Overview over the different conditions, instruments and main findings relevant to this study from the CLOUD5 and CLOUD7 campaigns.

2) It should be possible to estimate the uncertainty in dH and dS determined from the H_2SO_4-NH_3 measurements. Without uncertainties the suggestion that the experimental measurements "agree" with quantum chemical calculations is pointless. Errors may be estimated as follows: experimental uncertainties are shown in Fig. 8. If the evaporation rates for H_2SO_4-NH_3 are adjusted to span the range of the observed uncertainty (rather than the arbitrary factor of 5 and 0.2 shown), you should be able to calculate a range of dH and dS that are consistent with the stated experimental uncertainties, even if these uncertainties are "high". This would be more scientifically useful than an estimate without uncertainties, which is essentially meaningless.

In the revised version of the manuscript we now provide errors for dH and dS of the H_2SO_4•NH_3 cluster formation. These errors originate from the uncertainty in the fitted data and the updated values are dH = -16.1+0.6 kcal mol^{-1} and dS = -26.4-2.6 cal mol^{-1} K^{-1}.

In order to reflect the uncertainties of dH and dS we have chosen the following method to calculate the error bars in Figure 9 (previously Fig. 8) for the calculated dimer concentrations: To calculate the minimum dimer concentration (error bars in the lower direction) dH = -16.1+0.6 kcal mol^{-1} and d*S* = -26.4-2.6 cal mol^{-1} K^{-1} were used. The error in the positive direction (maximum dimer concentration) is calculated with dH = -16.1-0.6 kcal mol^{-1} and dS = -26.4+2.6 cal mol^{-1} K^{-1}. This method should provide an idea about the uncertainty in predicting dimer concentrations with the acid-base model for this study.

Besides updating Fig. 9 (previously Fig. 8) the following text was added to Section 3.7 (previously Section 3.6):

"The error bars reflect a variation of the evaporation rate for H_2SO_4•NH_3 according to the uncertainties of the dH and dS values. The lowest dimer concentrations result if the error of dH is implemented in the positive direction and the error of dS in the negative direction. The highest dimer concentrations result by reversing the signs in the error calculation."

Technical corrections:

a) p. 13962, line 18-19, please use Kelvin here as in the rest of the manuscript.

Done.

b) Page 13963, and elsewhere. The instrument acronym definitions are repeatedly defined here, in the Abstract, and in Section 1. Just once, please. Same on p. 13965, line 17.

The definitions have been removed as suggested.

c) p. 13970, line 18. Was the tubing length not measured? Why is an estimate necessary?

The distance has been measured and is closer to 15 cm than to 20 cm but to be conservative we provided the range. This information has been added and the sentence now reads:

"The CIMS ion drift tube was connected to the tip of the copper jacketed sampling line by means of a short tube that was not temperature-controlled, exposing the last 15 to 20 cm (the measured length is closer to 15 cm but to be conservative we took into account a somewhat longer distance) of the sampling line to warmer temperatures."

d) p. 13975, line 16. "data are", not "data is". Check elsewhere in manuscript for consistency with this plural noun.

Done.

e) p. 13977, line 22. It might be helpful to plot the dimer evaporation rate at 220K as a function of RH to see the RH dependence and the validity of the exponent assumed.

The information of $k_{2,e}$ vs. RH has been implemented (see comments on the first pages) in the form of the new Fig. 6 and some discussion in Section 3.3.

f) p. 13987, line 14. The precision of the thermodynamic parameters given is excessive given the measurement uncertainties and the lack of error analysis.

The thermodynamic parameters were adjusted and errors are provided (see also reply to major comment 2).

g) Figure 7. Would it be possible to add error bars to Fig. 7b? I don't know whether the variations in the trend in signal with cluster size is significant or not.

We have added error bars to the red symbols in Fig. 8b (previously Fig. 7b). These are rather small (a maximum of ~7%) since they are based on the statistical variation of the data from Fig. 8a, which is quite small. The error of the mean is determined from the standard deviation divided by the square root of the number of data points used to calculate the average values.

Thank you for writing an interesting and well-written manuscript.

Thank you for commenting and for the positive review.

Thermodynamics of the formation of sulfuric acid dimers in the binary (H_2SO_4-H_2O) and ternary (H_2SO_4-H_2O-NH_3) system

A. Kürten[1], S. Münch[1], L. Rondo[1], F. Bianchi[2,a], J. Duplissy[3,b], T. Jokinen[4], H. Junninen[4], N. Sarnela[4], S. Schobesberger[4,c], M. Simon[1], M. Sipilä[4], J. Almeida[3], A. Amorim[5], J. Dommen[2], N. M. Donahue[6], E. M. Dunne[7,d], R.C. Flagan[8], A. Franchin[4], J. Kirkby[1,3], A. Kupc[9], V. Makhmutov[10], T. Petäjä[4], A. P. Praplan[2,4,e], F. Riccobono[2,f], G. Steiner[4,11,g], A. Tomé[5], G. Tsagkogeorgas[12], P. E. Wagner[9], D. Wimmer[1,b], U. Baltensperger[2], M. Kulmala[4], D. R. Worsnop[4,13], and J. Curtius[1]

[1]Institute for Atmospheric and Environmental Sciences, Goethe-University Frankfurt am Main, Frankfurt am Main, Germany.
[2]Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, Villigen, Switzerland.
[3]CERN (European Organization for Nuclear Research), Geneva, Switzerland.
[4]Department of Physics, University of Helsinki, Helsinki, Finland.
[5]Laboratory for Systems, Instrumentation, and Modeling in Science and Technology for Space and the Environment (SIM), University of Lisbon and University of Beira Interior, Lisbon, Portugal.
[6]Center for Atmospheric Particle Studies, Carnegie Mellon University, Pittsburgh, USA.
[7]School of Earth and Environment, University of Leeds, Leeds, UK.
[8]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, USA.
[9]Aerosol Physics and Environmental Physics, University of Vienna, Vienna, Austria.
[10]Solar and Cosmic Ray Research Laboratory, Lebedev Physical Institute, Moscow, Russia.
[11]Ion Physics and Applied Physics, University of Innsbruck, Innsbruck, Austria.
[12]Leibniz Institute for Tropospheric Research, Leipzig, Germany.
[13]Aerodyne Research Incorporated, Billerica, MA, USA.

[a]Now at: Institute for Atmospheric and Climate Science, ETH Zurich, Zurich, Switzerland.
[b]Now at: Department of Physics, University of Helsinki, Helsinki, Finland.
[c]Now at: Department of Atmospheric Sciences, University of Washington, Seattle, USA.
[d]Now at: Finnish Meteorological Institute, Kuopio, Finland.
[e]Now at: Finnish Meteorological Institute, Helsinki, Finland.
[f]Now at: Joint Research Centre, European Commission, Ispra, Italy.
[g]Now at: Faculty of Physics, University of Vienna, Vienna, Austria.

Correspondence to: Andreas Kürten (kuerten@iau.uni-frankfurt.de)

Feldfunktion geändert

KEYWORDS: Chemical Ionization Mass Spectrometry, Chemical Ionization-Atmospheric Pressure interface-Time Of Flight Mass Spectrometry, CLOUD experiment, nucleation, new particle formation, clusters

ABSTRACT

Sulfuric acid is an important gas influencing atmospheric new particle formation (NPF). Both the binary (H_2SO_4-H_2O) system, and the ternary system involving ammonia (H_2SO_4-H_2O-NH_3) may be important in the free troposphere. An essential step in the nucleation of aerosol particles from gas-phase precursors is the formation of a dimer, so an understanding of the thermodynamics of dimer formation over a wide range of atmospheric conditions is essential to describe NPF. We have used the CLOUD chamber to conduct nucleation experiments for these systems at temperatures from 208 to 248 K. Neutral monomer and dimer concentrations of sulfuric acid were measured using a Chemical Ionization Mass Spectrometer (CIMS). From these measurements dimer evaporation rates in the binary system were derived for temperatures of 208 and 223 K. We compare these results to literature data from a previous study that was conducted at higher temperatures but is in good agreement with the present study. For the ternary system the formation of $H_2SO_4 \bullet NH_3$ is very likely an essential step in the formation of sulfuric acid dimers, which were measured at 210, 223, and 248 K. We estimate the thermodynamic properties (d*H* and d*S*) of the $H_2SO_4 \bullet NH_3$ cluster using a simple heuristic model and the measured data. Furthermore, we report the first measurements of large neutral sulfuric acid clusters containing as many as 10 sulfuric acid molecules for the binary system using Chemical Ionization-Atmospheric Pressure interface-Time Of Flight (CI-APi-TOF) mass spectrometry.

1. INTRODUCTION

The formation of new particles from the gas phase is a frequent and important process in the atmosphere. Substantial progress has been made in recent years describing the chemical systems and the mechanisms that could potentially be relevant to atmospheric new particle formation (NPF). Observed atmospheric boundary-layer nucleation rates typically correlate with the concentration of gaseous sulfuric acid (Kulmala et al., 2004; Kuang et al., 2008). Moreover, it is generally accepted that the presence of water vapor enhances nucleation in the binary (H_2SO_4-H_2O) system. However, nucleation under typical ground-level conditions cannot be explained by the binary nucleation of sulfuric acid and water vapor (Kulmala et al., 2004; Kerminen et al., 2010), even if the enhancing effect due to ions is taken into account (Kirkby et al., 2011). Therefore, assuming that sulfuric acid is required for nucleation, at least one additional compound is necessary to stabilize the nucleating clusters (Zhang et al., 2012). Ammonia, amines and highly-oxidized organic compounds have been identified in ambient samples or tested in laboratory experiments (Ball et al., 1999; Hanson and Eisele, 2002; Chen et al., 2012; Kulmala et al., 2013). Recent chamber experiments showed that the observed atmospheric boundary layer nucleation rates can, in principle, be explained by sulfuric acid acting in combination with either amines or the oxidation products from α-pinene (Almeida et al., 2013; Schobesberger et al., 2013; Riccobono et al., 2014).

Nucleation has also frequently been observed in the free troposphere, where the temperature and gas mixture differ from those at the surface (Brock et al., 1995; Weber et al., 1995; Clarke et al., 1999; Lee et al., 2003). An important source for stratospheric particles is the tropical tropopause region where nucleation mode particles have been observed. Additionally, new particle formation has also been observed in the free troposphere (Brock et al., 1995; Clarke et al., 1999; Borrmann et al., 2010; Weigel et al., 2011). Due to the volatility and the identification of sulfur in collected particles it was concluded that binary nucleation contributes to (or dominates) the formation of these particles (Brock et al., 1995). Binary homogenous nucleation also seems to play an important role in forming the mid-stratospheric condensation nuclei layer, although ion-induced binary nucleation cannot be ruled-out (Campbell and Deshler, 2014). Several studies provide evidence that ion-induced nucleation may be an important process in the free troposphere (Lee et al., 2003; Lovejoy et al., 2004; Kanawade and Tripathi, 2006; Weigel et al., 2011). These studies suggest that binary nucleation is important on a global scale – especially in regions where very low temperatures prevail, and where the concentrations of stabilizing substances involved in ternary nucleation are low.

Nucleation in the binary system starts with the collision of two hydrated sulfuric acid monomers, which form a dimer (Petäjä et al., 2011). In this study, the notation “dimer” refers to a cluster that contains two sulfuric acid molecules plus an unknown amount of water and, in the ternary system, ammonia. The term monomer refers to clusters with one sulfuric acid, irrespective of whether the cluster contains also ammonia and/or water molecules or not.~~Similarly, the monomer of sulfuric acid~~

~~may contain water or ammonia.~~ Unless stated otherwise the terms "monomer" and "dimer" describe the neutral, i.e., uncharged molecules and clusters. The probability that a dimer will or will not grow larger depends on its evaporation rate as well as its collision rate with monomers and larger clusters. Therefore, it is crucial to know the evaporation rate (or the equilibrium constant) of the sulfuric acid dimer in order to understand and model binary nucleation. Hanson and Lovejoy (2006) measured the dimer equilibrium constant over a temperature range of 232 to 255 K. However, no direct measurements have been performed for lower temperatures. Moreover, evidence exists that ammonia is an important trace gas influencing new particle formation in some regions of the atmosphere (Weber et al., 1998; Chen et al., 2012). Numerous studies using quantum chemical calculations have been conducted to study the cluster thermodynamics for the sulfuric acid-ammonia system (Kurtén et al., 2007; Nadykto and Yu, 2007; Torpo et al., 2007; Ortega et al., 2012; Chon et al., 2014). To our knowledge, however, only very few studies have yet reported experimentally determined dimer concentrations for this system (Hanson and Eisele, 2002; Jen et al., 2014). In order to model NPF for the ternary system involving ammonia it is essential to better understand the thermodynamics of the clusters involved in the nucleation process. Cluster properties derived from measurements can be used for a comparison with the theoretical studies. Such a comparison provides a consistency check for both the models and the measurements.~~In order to model NPF for the ternary system involving ammonia it is essential to better understand the thermodynamics of the clusters involved in the nucleation process from experiments in order to narrow down the uncertainties from the theoretical studies.~~

Here we present experimentally derived dimer evaporation rates for the binary system (H_2SO_4-H_2O) at temperatures of 208 and 223 K. The measurements of the sulfuric acid monomer and dimer were made with a Chemical Ionization Mass Spectrometer (CIMS) at the Cosmics Leaving OUtdoor Droplets (CLOUD) chamber. The data are discussed and compared to previously published dimer evaporation rates for the binary system (Hanson and Lovejoy, 2006). Dimer measurements are also available for the ternary system (H_2SO_4-H_2O-NH_3) at 210, 223, and 248 K and some ammonia mixing ratios (< ~10 pptv). The thermodynamics (dH and dS) of the $H_2SO_4 \bullet NH_3$ cluster were retrieved from comparison of the measured monomer and dimer concentrations with those predicted using a simple model. Furthermore, neutral cluster measurements using Chemical Ionization-Atmospheric Pressure interface-Time Of Flight (CI-APi-TOF) mass spectrometry are presented for the binary system at 206 K for clusters containing up to 10 sulfuric acid molecules.

2. METHODS

2.1 CLOUD chamber

CIMS monomer and dimer measurements were conducted primarily during the CLOUD5 campaign in October and November 2011. Additional CI-APi-TOF measurements were made during one experiment in November 2012 (CLOUD7). The CLOUD chamber has been described in previous publications (Kirkby et al., 2011; Almeida et al. 2013; Riccobono et al., 2014). The 26.1 m^3 electropolished stainless-steel chamber provides an ultra-clean environment for studying new particle formation and growth. A well-insulated thermal housing and temperature control allow measurements down to ~~-80 °C~~193 K with a stability of a few hundredth of a degree. For cleaning purposes the chamber can be heated up to ~~100 °C~~373 K and flushed with ultra-clean air at a high ozone concentration. Pure neutral nucleation was studied by applying a high voltage (±30 kV) to upper and lower transparent field cage electrodes (termed clearing field high voltage or CFHV in the following). Sampling ports are located around the mid-plane of the cylindrical chamber, where the clearing field is at 0 V. Grounding the electrodes allows measurements of ion-induced nucleation. In the absence of a clearing field galactic cosmic rays produce ion pairs at a rate of ~2 cm^{-3} s^{-1}). Much higher ion pair production rates can be achieved by illuminating a section of the chamber (approximately 1.5 m times 1.5 m) using a defocused pion beam from CERN’s proton synchrotron (Duplissy et al., 2010). Ultra-clean gas is provided to the chamber by mixing nitrogen and oxygen from cryogenic liquids at a ratio of 79:21. Different relative humidities (RH) can be achieved by passing a portion of the dry air through a nafion humidification system. The temperature and the dew/frost point inside the chamber are monitored continuously; the RH is calculated using the equations given by Murphy and Koop (2005). A fibre optic system (Kupc et al., 2011) feeds UV light into the chamber, which initiates the photolytic production of sulfuric acid when H_2O, O_2, O_3, and SO_2 are present. Two mixing fans continuously stir the air inside the chamber assuring its homogeneity (Voigtländer et al., 2011).

The CLOUD5 campaign was dedicated to experiments investigating new particle formation at low temperatures (down to ~208 K) for the binary (H_2SO_4-H_2O) and the ternary (H_2SO_4-H_2O-NH_3) systems. The particle formation rates at low temperature will be reported in forthcoming papers; this publication focuses on measurements of the sulfuric acid monomer and the sulfuric acid dimer. One future paper will also focus on the determination of the ammonia mixing ratios at the low temperatures. These were evaluated from a careful characterization of the CLOUD gas system, which delivers ammonia diluted in ultra-clean nitrogen and air to the CLOUD chamber. The gas system was characterized by measurements with a LOng Path Absorption Photometer (LOPAP, Bianchi et al., 2012), an Ion Chromatograph (IC, Praplan et al., 2012) and a Proton Transfer Reaction-Mass Spectrometer (PTR-MS, Norman et al., 2007).

Table 1 gives an overview over the main findings relevant to this study obtained from the two different campaigns.

2.2 Chemical Ionization Mass Spectrometer (CIMS) and Chemical Ionization-Atmospheric Pressure interface-Time Of Flight (CI-APi-TOF) mass spectrometer

During CLOUD5 a ~~Chemical Ionization Mass Spectrometer (~~CIMS~~)~~ was used for the measurement of sulfuric acid monomers and dimers (Kürten et al., 2011). Using nitrate ions $NO_3^-(HNO_3)_{x=0\text{-}2}$, sulfuric acid can be selectively ionized; detection limits below 10^5 cm^{-3} (referring to the monomer of sulfuric acid) can be reached for short integration times, thereby enabling high time resolution (Eisele and Tanner, 1993; Mauldin et al., 1999; Berresheim et al., 2000). The instrument was calibrated before and after the campaign using a system that produces a known concentration of sulfuric acid (Kürten et al., 2012). In this way, the recorded ion signals – for the primary ions and the reactant ions – can be converted into a concentration of sulfuric acid.

HSO_4^- (the product ion from the sulfuric acid monomer) and $HSO_4^-(H_2SO_4)$ (the product ion from the sulfuric acid dimer) are formed by reactions such as

$$NO_3^-(HNO_3)_x + (H_2SO_4)_{1\text{-}2}\cdot X \rightarrow HSO_4^-(H_2SO_4)_{0\text{-}1}(HNO_3)_y + (x-y+1)\cdot(HNO_3) + X. \qquad \text{(R1)}$$

The compound X is, in most cases, water, but in the case of the ternary system, both experiments and quantum chemical calculations suggest that dimers could also be bound to ammonia (Hanson and Eisele, 2002; Kurtén et al., 2007). Ammonia (or X) is expected to evaporate rapidly after the ionization (Ortega et al., 2014). It should be noted here that even if X did not evaporate after the ionization it would probably be removed in the CIMS collision dissociation chamber (CDC). In the CDC any remaining water molecules are stripped off from the core ions and the $NO_3^-(HNO_3)_{0\text{-}2}$ ions yield mostly NO_3^- due to the declustering. Therefore, the monomer and dimer sulfuric acid concentrations are estimated to be:

$$[\mathrm{H_2SO_4}] = \frac{C}{L_{monomer}} \cdot ln\left(1 + \frac{CR_{97}}{CR_{62}}\right), \qquad (1a)$$

$$[(H_2SO_4)_2] = \frac{C}{L_{dimer}} \cdot ln\left(1 + \frac{CR_{195}}{CR_{62}}\right). \qquad (1b)$$

Here, *CR* denotes the count rate for the primary ions (CR_{62} at *m*/*z* 62 for NO_3^-), the HSO_4^- ions (CR_{97} at *m*/*z* 97), and the $HSO_4^-(H_2SO_4)$ ions (CR_{195} at *m*/*z* 195), respectively. The constant *C* is derived from a calibration and has been evaluated as 1.1×10^{10} cm^{-3} with a typical uncertainty of ~30% (Kürten et al., 2012). The same calibration constant is used for the monomer and the dimer because it is not possible to calibrate the dimer signal. Since both H_2SO_4 and $(H_2SO_4)_2$ are thought to react with the nitrate ions at the collision limit this assumption is well justified. The factors $L_{monomer}$ and L_{dimer} take into account the penetration through the sampling line from the CLOUD chamber to the CIMS ion source. A sample flow rate of 7.6 standard liters per minute (slm) and a sampling line length of 100 cm were used to calculate the transmission. The diffusion coefficient has been calculated for the respective temperature and RH for the monomer from the data given by Hanson and Eisele (2000). It was assumed that the diffusivity of the hydrated dimer (see Henschel et al., 2012) equals 0.06±0.01 cm^2 s^{-1} at 298 K, and varies with temperature as $(298K/T)^{1.75}$.

Some dimer dissociation in the CIMS CDC section cannot be ruled out, although the $HSO_4^-(H_2SO_4)$ ion has a very high bond energy (Curtius et al. 2001). However, as described in the next section, this effect is very likely minor, and, to the extent that it occurs, it is taken into account in the characterization of the dimer detection efficiency.

During the CLOUD7 campaign sulfuric acid and its clusters were measured with two ~~Chemical Ionization Atmospheric Pressure interface Time Of Flight (~~CI-APi-TOF~~)~~ mass spectrometers (Jokinen et al., 2012; Kürten et al., 2014); the H_2SO_4 monomer was also measured by the CIMS. However, during CLOUD7 it was not possible to measure the dimers with the CIMS due to instrumental problems. The CI-APi-TOF has an almost identical chemical ionization source as the CIMS but it uses a time of flight mass spectrometer with high mass resolution (around 4500 Th/Th) and mass accuracy (better than 10 ppm). These features as well as the wide mass range (up to around 2000 Th) enable detection and unambiguous identification of the elemental composition of clusters. As will be shown in Section 3.4 neutral clusters containing as many as 10 sulfuric acid molecules were detected during a binary experiment at 206 K.

2.3 Quantification of sulfuric acid dimer concentration

As it is not possible to calibrate the CIMS or the CI-APi-TOF with a known concentration of sulfuric acid dimers, a different method was chosen to allow the quantification of the dimer concentration. To estimate the relative sensitivity towards the dimers (*m/z* 195) in comparison to the monomer (*m/z* 97) ion-induced clustering (IIC) during calibration can be evaluated. If the sulfuric acid monomer concentration is large enough efficient formation of $HSO_4^-(H_2SO_4)$ can occur due to clustering of HSO_4^- and H_2SO_4 within the CIMS ion drift tube (Hanson and Eisele, 2002). The estimated dimer count rate through this process is (Zhao et al., 2010; Chen et al., 2012)

$$CR_{195,\mathrm{IIC}} = \frac{1}{2} \cdot k_{21} \cdot t_{react} \cdot CR_{97} \cdot C \cdot ln\left(1 + \frac{CR_{97}}{CR_{62}}\right). \qquad (2)$$

The reaction time t_{react} is approximately 50 ms in our case (Kürten et al., 2012). A value of 8×10^{-10} cm^3 s^{-1} was used for k_{21}, the rate constant for reaction between HSO_4^- and H_2SO_4 (Zhao et al., 2010). The measured count rate CR_{195} was compared to the expected count rate during a calibration in which a high concentration of sulfuric acid monomers was presented to the CIMS. From this comparison, we concluded that the dimer signal is suppressed by a factor of 1.2 relative to the monomer signal. The discrepancy can either be due to mass discrimination or due to some fragmentation in the CIMS CDC. In any case, it means that the measured dimer signal needs to be multiplied by a factor of 1.2 (with an estimated statistical uncertainty of less than 10%) when its concentration is evaluated.

The background signal, e.g., from electronic noise, is always subtracted before the dimer concentration is evaluated according to equation (1b). The background was obtained by averaging over a certain period just before the experiment started, i.e., before the UV lights were turned on and the H_2SO_4 was produced. In addition to the background, the contribution from IIC is subtracted from the dimer signal (Chen et al., 2012). This effect becomes relevant at about 1x10^{7} cm^{-3} for the sulfuric acid monomer under the conditions of this study.

2.4 Sulfuric acid dimer evaporation rate

The goal of this study is to determine sulfuric acid dimer evaporation rates from data obtained by monomer and dimer measurements. In order to derive a formula for the evaporation rate it is useful to start with the basic equations governing the loss and the production of the clusters. Since low temperature conditions (208 and 223 K for the binary system) are considered in this study the assumption is made that only the smallest clusters (dimer and trimer) have appreciable evaporation rates (Hanson and Eisele, 2006). The balance equation for the dimer concentration in this case is

$$\frac{dN_2}{dt} = 0.5 \cdot G_{1,1} \cdot K_{1,1} \cdot N_1^2 + k_{3,e} \cdot N_3 - \left(k_{2,w} + k_{dil} + \sum_{i=1}^{n} G_{2,i} \cdot K_{2,i} \cdot N_i + k_{2,e}\right) \cdot N_2 \qquad (3)$$

where N_i is the concentration of the cluster containing i sulfuric acid molecules~~,~~. The evaporation rate $k_{i,e}$ refers to the evaporation of one sulfuric acid molecule from a cluster containing i sulfuric acid molecules.~~and $k_{i,e}$ is its evaporation rate.~~ In a chamber experiment such as CLOUD, three loss processes are relevant for neutral particles; these include the wall loss rate $k_{i,w}$, the dilution rate k_{dil} through the replenishment of the chamber air (independent of particle size), and coagulation with the coefficient $K_{i,j}$ describing collisions between the clusters i and j. The factor $G_{i,j}$ represents an enhancement in the collision rates due to London-van der Waals forces (McMurry, 1980; Chan and Mozurkevich, 2001). In order to derive an expression for the dimer evaporation rate, we assume steady-state ($dN_2/dt = 0$). Equation (3) can then be written as

$$k_{2,e} = \frac{0.5 \cdot G_{1,1} \cdot K_{1,1} \cdot N_1^2}{N_2} + \frac{k_{3,e} \cdot N_3}{N_2} - \left(k_{2,w} + k_{dil} + \sum_{i=1}^{n} G_{2,i} \cdot K_{2,i} \cdot N_i\right). \qquad (4)$$

It is useful to estimate the relative importance of the three terms on the right-hand side of equation (4). The numerator in the first term describes the production rate of dimers from monomers. The collision constant for two monomers is approximately ~~4x10~~2.8x10^{-10} cm^{3} s^{-1} at 208 K. If the enhancement factor G due to London-van der Waals forces is included, this value is ~6.9~~1~~x10^{-}~~^{9}~~$^{-10}$ cm^{3} s^{-1} (McMurry, 1980; Chan and Mozurkevich, 2001). As an example, at 208 K under binary conditions, the smallest monomer concentration evaluated is 2x10^{6} cm^{-3}, at which point the dimer was evaluated as 1x10^{4} cm^{-3} (Section 3.3). These values yield 0.2 s^{-1} for the first term. The second term is significantly smaller than the first term, so it can be neglected ~~in the following discussion~~due to the reasons listed in the following. The trimer concentration (although it was not measured) should be smaller than the dimer concentration because the trimer is produced from the dimer. Moreover, the trimer evaporation rate is expected to be lower than the dimer evaporation rate (e.g., 1.6x10^{-3} s^{-1} for the trimer, and 0.3 s^{-1} for the dimer at 208 K and 20% RH, see Hanson and Lovejoy, 2006). The third term includes losses due to walls, dilution, and coagulation. The wall loss rate for a dimer is approximately 1.5x10^{-3} s^{-1}, while loss due to dilution is ~1x10^{-4} s^{-1} (Kürten et al., 2014). The loss due to coagulation depends on the particle size distribution, and can be important when the dimer evaporation rate is small. Loss of dimers due to collisions with monomers (i.e., growth to form trimers) then dominates the coagulation term, which is usually on the order of 10^{-2} s^{-1} (e.g. N_1 = $1\text{x}10^7$ cm^{-3} and $G_{1,1}$•$K_{1,1}$ = ~~1x10~~6.9x10^{-}~~^{9}~~$^{-10}$ cm^3 s^{-1}). All elements of the third term are, thus, small compared with the first term, and so these can also be neglected. For the conditions of this study, consistent with the extrapolated data by Hanson and Lovejoy (2006), the evaporation rates are however larger than 10^{-2} s^{-1}. This means that evaporation dominates over the other losses; therefore, $k_{2,e}$ can be approximated by

$$k_{2,e} = \frac{0.5 \cdot G_{1,1} \cdot K_{1,1} \cdot N_1^2}{N_2}. \qquad (5)$$

The concentrations used in equation (5) are averages over periods where conditions are close to steady-state. These periods are defined by conditions where the production and loss rates for the dimer and the monomer are almost identical and the concentrations are not subject to significant changes anymore. If losses by processes other than evaporation were not negligible, retrieval of evaporation rates would require use of a numeric model that also includes larger clusters since coagulation loss depends on concentrations of all other clusters. Nevertheless, model calculations simulating cluster and particle concentrations are needed to evaluate other effects relevant to this study, as will be discussed in the next sections.

Comparison of the rate constants used for the reactions between HSO_4^- and H_2SO_4 (Section 2.3) and between H_2SO_4 and H_2SO_4 yields that the neutral-neutral collision rate is ~~slightly faster than~~about the same as the charged-neutral collision rate. This is due to the relatively large enhancement factor from London-van der Waals forces for the neutral-neutral rates (McMurry, 1980; Chan and Mozurkevich, 2001) and the observation that the reaction between the bisulfate ion and sulfuric acid seems not to proceed at the collisional rate (Zhao et al., 2010). Further discussion about the consequences this has on the present study is provided in Section 3.8.

2.5 SAWNUC model

The Sulfuric Acid Water NUCleation model (SAWNUC) of Lovejoy et al. (2004) simulates ion-induced nucleation in the binary system. Cluster growth is treated explicitly by a step-by-step addition of sulfuric acid molecules while equilibrium with water molecules is assumed due to the relatively high concentration and evaporation rate of H_2O compared to H_2SO_4. SAWNUC takes into account sulfuric acid condensation and evaporation, coagulation, and losses due to walls and dilution (Ehrhart and Curtius, 2013). In SAWNUC, evaporation rates of small, negatively-charged clusters are based on measured thermodynamics and partly on quantum chemical calculations (Lovejoy and Curtius, 2001; Froyd and Lovejoy, 2003). More detailed information on SAWNUC can be found in Lovejoy et al. (2004), Kazil and Lovejoy (2007), and Ehrhart and Curtius (2013).

As this study focuses on neutral binary nucleation, we neglect the charged-cluster channel, and only simulate the neutral channel. Coagulation coefficients have been calculated according to Chan and Mozurkewich (2001). They quantified London-van der Waals forces for particles in the binary system based on the theory by Sceats (1989). Within this study of nucleation at low temperatures, only dimer (and sometimes trimer) evaporation has been taken into account. The exact input parameters are specified in the following sections.

~~All model calculations have also been repeated using a numeric model recently presented by Kürten et al. (2014), which has been adapted to the binary system. The results of the two independent models agree very well, which strengthens our confidence in the calculations that are presented below.~~

2.6 Dimer transmission through the sampling line

Previous dimer evaporation rates were evaluated with the CIMS ionization source integrated within a temperature-controlled flow tube (Hanson and Lovejoy, 2006). This set-up ensured that the temperature did not change between the times when the dimers were formed, and when they were ionized. In the present study, the dimers formed inside the CLOUD chamber, which is very precisely temperature-controlled. However, the monomers and dimers had to be transported from the chamber to the CIMS through a 100 cm long sampling line. The first ~80 cm of this line were held at the same temperature as the chamber because it protruded through the thermal housing and into the chamber. Moreover, the sampling line was enclosed by an insulated copper tube. Since a large part of the copper volume was placed inside the thermal housing, the cold temperature was maintained over the full length of the copper tube due to efficient heat conduction even for a short section of the tube that was located outside the chamber, while the insulation minimized heat transfer to the surrounding air. The CIMS ion drift tube was connected to the tip of the copper jacketed sampling line by means of a short tube that was not temperature-controlled, exposing the last 15 to 20 cm (the measured length is closer to 15 cm but to be conservative we took into account a somewhat longer distance) of the sampling line to warmer temperatures. In this region the dimers could in principle have suffered from evaporation.

To estimate the evaporation effect, a finite difference method was used to calculate the temperature profile, as well as the dimer concentration across the sampling line over its full length. The differential equations for the monomer ($i = 0$) and dimer ($i = 1$) concentrations c_i were solved as a function of the radial and axial coordinates r and z (Kürten et al., 2012):

$$\frac{\partial c_i}{\partial t} = D_i \cdot \left(\frac{1}{r} \cdot \frac{\partial c_i}{\partial t} + \frac{\partial^2 c_i}{\partial r^2} + \frac{\partial^2 c_i}{\partial z^2}\right) - \frac{2Q}{\pi R^2} \cdot \left(1 - \frac{r^2}{R^2}\right) \cdot \frac{\partial c_i}{\partial z} + s_i, \qquad (6)$$

where D_i is the diffusivity, Q is the flow rate and R is the radius of the tube. A parabolic flow profile was assumed and the geometry was divided into small areas in order to solve the differential equations by a finite difference method. The source terms s_i include evaporation and production of dimers and loss and production of monomers due to self-coagulation and evaporation of dimers. Further reactions (coagulation with larger clusters/particles) were not taken into account since the time is rather short (<

1s for Q =7.5 slm, R = 0.005 m, and L = 1 m) and the other loss terms are dominant. A similar differential equation is used to determine the temperature inside the tube before the concentrations are calculated. This temperature is used to calculate the evaporation of dimers in each of the small areas. The time-dependent equations (time t) are repeatedly solved until a reasonable degree of convergence is reached.

Figure 1 shows the results for a chamber temperature of 223 K. The walls of the first 80 cm of the sampling line were held at 223 K, while the last 20 cm were held at 293 K (which was a typical maximum day-time temperature in the experimental hall during the CLOUD5 campaign). It should be noted that this is an extreme case because, in reality, the temperature would slowly approach 293 K over the last 20 cm due to heat conduction along the walls of the sampling line. However, the calculations performed here are used to obtain an upper-bound estimate of the error due to evaporation. The temperature of the walls is indicated by the black color (223 K) and the grey color (293 K). Figure 1 shows the normalized concentration of dimers after initializing the monomer concentration to 1x10^7 cm^{-3}; the dimer was assumed to be at equilibrium initially. It was further assumed that both monomers and dimers are lost to the walls due to diffusion, and that at the same time dimers are formed due to collisions of monomers, but can also evaporate. Larger clusters or particles were not taken into account. The dimer evaporation rate as a function of temperature was taken from the literature at this stage (Hanson and Lovejoy, 2006).

The profile shown in Fig. 1 indicates that, during the first 80 cm, dimers are lost primarily via diffusion because, in this section, they are essentially in equilibrium regarding formation and evaporation; only over the last 20 cm does evaporation have an appreciable effect on the dimer concentration. However, only the region close to the walls of the sampling line shows a rise in the gas temperature; the center of the sample flow is essentially unaffected. The estimated overall transmission efficiency for dimers is 0.228 at a flow rate of 7.6 slm in the half-inch tube (inner diameter ~10 mm). If the temperature were held constant at 223 K over the entire tube length, the transmission would increase to 0.475 because only wall losses would take place. Since the dimer concentration is corrected for the effect of diffusion loss (see equation (1b)), the additional loss factor due to evaporation would be (1/0.228)/(1/0.475) = 2.08. However, this is an upper bound estimate of the error introduced through evaporation since the temperature is, in reality, gradually changing over the last 20 cm instead of increasing as a step function as simulated. For the lower temperature of 208 K, the effect is even smaller. From the estimations presented in this section it can, therefore be concluded that, while the sampling conditions are not ideal, the maximum error introduced is very likely smaller than a factor of 2 (see also error discussion in Section 3.~~7~~8).

3. RESULTS AND DISCUSSION

3.1 Neutral vs. ion-induced experiments

Figure 2 (upper panel) shows the measured monomer and dimer concentrations from a binary experiment at 208 K. The experiment is started when the UV lights are turned on (at 14:16 UTC). The first stage is conducted in a neutral environment with the CFHV enabled. At 16:00 UTC (marked by the dashed vertical line) the electrodes are grounded and galactic cosmic rays (GCRs) lead to a build-up of ions in the chamber. While the monomer concentration is not affected significantly by the GCRs because the small ion concentration is generally only on the order of a couple of thousand (Franchin et al. 2015) and the HSO_4^- ions are not efficiently being detected by the CIMS (Rondo et al., 2014), the dimer concentration is.~~While the monomer concentration is not affected by the GCRs, the dimer concentration is.~~ For the neutral conditions the dimer signal above background is due to neutral $(H_2SO_4)_2$. During the GCR stage of the experiment, the dimer signal gradually increases. This could be due either to neutral dimers being charged in the CIMS or charged dimer ions forming within the CLOUD chamber.

Unfortunately, there was no ion filter installed in the CIMS sampling line during CLOUD5 to eliminate the ion contribution to the CIMS signal. However, evidence exists that the additional signal during GCR conditions is caused by a buildup of chamber ions rather than formation of additional neutral dimers during the ion-induced experiments. Recently, it was reported that HSO_4^- ions clustered to large oxidized organic molecules (OxOrg) can be efficiently detected by the CIMS (Rondo et al., 2014). ~~Those experiments were conducted for the ternary system of sulfuric acid, water and pinanediol oxidation products at CLOUD. The most likely explanation for the signal enhancement seen by the CIMS is reduced sampling line loss of the clusters compared to HSO_4^-. This enhances the signal of HSO_4^- (which is not formed by ionization of neutral sulfuric acid in the CIMS drift tube). Upon reaching the CIMS CDC, the HSO_4^-•OxOrg clusters break apart, and the bisulfate ions are subsequently detected. This example shows that the CIMS can, in some cases, also be sensitive to ions and not just towards neutral molecules.~~

When both ions and sufficient H_2SO_4 are present in the chamber, $HSO_4^-(H_2SO_4)_n$ with $n \geq 1$ will be formed (Eisele et al., 2006); these ions are apparently being detected by the CIMS as dimers to some extent. The light HSO_4^- ions will be rapidly lost to the walls of the CIMS sampling line, whereas the larger $HSO_4^-(H_2SO_4)_{n\geq1}$ ions will have a lower loss rate. Therefore, the larger ions tend to have a higher chance to survive the transport to the CIMS where they can be eventually detected as artifact dimers. If this were the case, some of the observed dimer signal from the GCR stage in Fig. 2 might not be related to the neutral dimers, and should be discarded.

The Atmospheric Pressure interface-Time Of Flight (APi-TOF, Junninen et al., 2010) mass spectrometer measured the ion composition during the first part of the CLOUD5 campaign. Figure 2 (lower panel) shows the $HSO_4^-(H_2SO_4)_n$ (n = 0 to 8) cluster ion signals during a binary beam experiment at 223 K. In addition, the apparent CIMS dimer concentration is displayed. The dimer signal is well correlated with the $HSO_4^-(H_2SO_4)_n$ signal for $n \geq 5$ (e.g. Pearson's correlation coefficient between the dimer and the $HSO_4^-(H_2SO_4)_5$ signal is 0.93), indicating that the dimer signal due to ions arises mostly from larger cluster ions (hexamer and larger) which, at least partly, fragment to $HSO_4^-(H_2SO_4)$ before they reach the mass spectrometer. It is, however, not clear whether only the relatively large charged clusters fragment, or if only these large clusters reach the mass spectrometer due to an enhanced transmission. The study by Rondo et al. (2014) indicates that ions need to be relatively heavy (or have a low enough electrical mobility) in order to reach the CIMS ion drift region. It is, therefore, also possible that ions that are smaller than the hexamer could, in principle, contribute to the CIMS dimer channel, but since they are not efficiently reaching the CIMS, their contribution is negligible. Either possibility would lead to the large charged clusters contributing to the dimer signal (Fig. 2).

Another interesting observation is that the dimer signal comes mainly from the neutral clusters when ammonia is present in the chamber.~~shows almost no enhancement during ion-induced experiments when ammonia is present in the chamber.~~ Recent publications on the ternary ammonia system investigated at CLOUD showed that the APi-TOF detects $HSO_4^-(H_2SO_4)_n(NH_3)_m$ with $m \geq 1$ when $n \geq 3$ (Kirkby et al., 2011; Schobesberger et al., 2015). Our findings support the observation that the mixed sulfuric acid ammonia ion clusters are more stable than pure sulfuric acid clusters because they do not seem to fragment to the same extent. As a consequence of the observations discussed in this section, only neutral experiments were considered for the evaluation of the dimer evaporation rates in the binary system.

3.2 Effect of fragmentation during neutral experiments

In the binary system, large cluster ions can fragment and contribute to the measured dimer signal. In this section the maximum error due to the observed fragmentation described in Section 3.1 is estimated. For neutral cluster measurements, this process is, however, different from that described in the previous section. Under ion-induced conditions the ions are directly sampled from the CLOUD chamber. Therefore, a relatively low concentration of cluster ions can contribute significantly to the dimer signal because the ionization process in the CIMS drift tube is not needed for their detection.

In a worst-case scenario all cluster ions larger than the dimer (originating from neutral clusters after ionization) would fragment and yield one $HSO_4^-(H_2SO_4)$ thereby increasing the apparent dimer concentration. It is important to note that even a very large charged cluster could only yield one $HSO_4^-(H_2SO_4)$ because the clusters carry only one negative charge. The cluster concentrations (dimer and larger) can be calculated using the SAWNUC model. In any case, the cluster concentrations decrease with increasing size, so the potential contribution decreases with increasing cluster size. Figure 3 provides an upper bound estimate of the magnitude of this effect. In an example calculation for a temperature of 223 K, a sulfuric acid monomer concentration of $2\text{x}10^7$ cm^{-3}, and dimer and trimer evaporation rates from the literature (Hanson and Lovejoy, 2006) are used, while all other evaporation rates are set to zero. The model yields concentrations for the neutral dimer and all larger clusters. ~~Integrating~~ Summing the concentrations from the dimer up to a certain cluster size, and normalizing the sum with the dimer concentration, yields the results shown in Fig. 3 which indicate that the contribution of the larger clusters to the dimer is, at most, a factor of 3 larger than that of the dimers, even as one considers the contributions from very large clusters. Again, in this estimation it is considered that even a large fragmented cluster can contribute only one $HSO_4^-(H_2SO_4)$ because all clusters are singly charged. For this reason the cluster number concentrations are ~~integrated~~ summed and not the number of neutral dimers in a cluster.

The estimated factor in this section is an upper limit. It is unlikely that all clusters will fragment, or that they always yield $HSO_4^-(H_2SO_4)$ as the product. Instead, HSO_4^- might result from the fragmentation, because, not being an equilibrium process, fragmentation would not always yield the most stable cluster configuration. Moreover, since evaporation cools the cluster, evaporation of neutral sulfuric acid molecules from the largest clusters may be incomplete. Another argument why the data from Fig. 3 provide an upper estimate is due to the reduction in transmission efficiency for the components of the mass spectrometer that is generally observed with increasing mass. In summary, the maximum effect of fragmentation is very likely on the order of a factor of 2, or lower (see also error discussion in Section 3.~~7~~8).

3.3 Binary (H_2SO_4-H_2O) dimer concentrations and evaporation rates

Figure 4 shows the steady-state dimer concentrations as a function of the monomer concentrations at a temperature of 208 K. The data are~~is~~ segregated into binary neutral (solid circles) and ion-induced (open triangles). The color code indicates the relative humidity (RH) over ~~ice~~supercooled water. The black lines show the results from the SAWNUC model assuming four different dimer evaporation rates between 0 and 1 s^{-1} (indicated in the legend of the figure). Comparison between the modeled curves and the experimental data gives an indication of the magnitude of the dimer evaporation rates, but the actual values are calculated with equation (5) and will be discussed in the context of Fig. ~~6~~7. While the model curves for 0.1 and 1 s^{-1} are straight lines with a slope of two on a log-log-plot, the lines for 0 and 0.01 s^{-1} show a pronounced curvature with a slope that approaches a value of one for the high monomer and dimer concentrations. This curvature indicates that a full model calculation would be required in order to derive even smaller evaporation rates than those observed in this study. If the evaporation rate is comparable to the other loss rates, these mechanisms need to be taken into account when estimating $k_{2,e}$. Only when the evaporation rate dominates dimer loss over the full range of [H_2SO_4] can other mechanisms be neglected. The neutral binary data in Fig. 4 indicate that the dimer evaporation rate varies between 0.2 s^{-1} for ~12 % RH and 0.04 s^{-1} for 58 % RH at 208 K. Therefore, relative humidity has a relatively strong effect, one that is more strongly pronounced than the higher temperature (232 to 255 K) data of Hanson and Lovejoy (2006) suggest (see discussion below). Our signal-to-noise ratio was, however, not high enough to quantify the dimer at temperatures above 223 K for direct comparison. Figure 4 also gives an idea of the magnitude of the ion effect on the CIMS dimer measurements (open triangles). As discussed in Section 3.1, the ion-induced binary experiments show systematically higher apparent dimer concentrations than do the neutral experiments. For this reason they are discarded when deriving dimer evaporation rates.

Figure 5 shows the monomer and dimer data for a temperature of 223 K. Again, the data show a pronounced influence of relative humidity. The dimer evaporation rate is approximately 8 s^{-1} at 12 % RH and 0.6 s^{-1} at 50 % RH. The ion enhancement effect can be divided into two regimes, one in which it seems to be limited by the availability of sulfuric acid, and a second one in which it is limited by the availability of ions and reaches a plateau where the dimer signal ceases to increase with the sulfuric acid monomer concentration (open triangles).

The evaporation rates derived herein can be compared with the rates reported by Hanson and Lovejoy (2006) after some unit conversions. The equilibrium constant K_{eq} for sulfuric acid dimer formation from monomers in the presence of water has been reported as (Hanson and Lovejoy, 2006)

$$K_{eq} = \frac{p_2}{(p_1)^2} = \frac{1}{\text{Pa}} \cdot exp\left(\frac{A}{T} - B\right)$$ (~~6~~7)

with A = (9210±930) K, and B = 31.4±3.9 for the temperature, 232 ≤ T ≤ 255 K, and a relative humidity of 20% over supercooled water. Given the reported values for A and B the thermodynamic properties are estimated to be dH = -18.3±1.8 kcal mol^{-1} and dS = -39.5±7.8 cal mol^{-1} K^{-1} (Hanson and Lovejoy, 2006). Equation (~~6~~7) provides the equilibrium constant in units of Pa^{-1} since the partial pressures p of the monomers and dimers are used. In order to calculate evaporation rates it is necessary to convert the equilibrium constant to units of cm^3, and to further apply the relationship between equilibrium constant, evaporation rate, and collision constant for the dimers (Ortega et al., 2012), leading to:

$$k_e = 0.5 \cdot \frac{G_{1,1} \cdot K_{1,1}}{k_B \cdot T \cdot 10^6 \cdot K_{eq}},$$ (~~7~~8)

where k_B is the Boltzmann constant. We converted equilibrium constants reported by Hanson and Lovejoy (2006) to evaporation rates using equation (8). Hanson and Lovejoy (2006) determined evaporation rates at 20% RH; while our measurements were made at different RHs. Because RH has a significant influence on the dimer evaporation further analysis is necessary to make the two data sets comparable.

Figure 6 shows the evaluated dimer evaporation rates as a function of the relative humidity (with respect to supercooled water) for two different temperatures (208 and 223 K). The rates from this study are based on the data shown in Figures 4 and 5 and equation (5). The data were fitted by simple power law fits and the slopes of p = -1 (at 208 K) and p = -1.6 (at 223 K) indicate that the evaporation rates decrease significantly with increasing RH. Qualitatively this is in agreement with a previous experiment (Hanson and Lovejoy, 2006) and quantum chemical calculations (Ding et al., 2003).

However, Hanson and Lovejoy (2006) reported p = -0.5, where the exponent p has an uncertainty of ±100%. Our data indicate a somewhat stronger influence of RH on the evaporation rates, which also seems to be dependent on temperature.

The evaporation rates from Figure 6 with RH between 10 and 30% were normalized to 20% RH using the reported slopes. Figure 7 shows the data from this study and from Hanson and Lovejoy (2006). Fitting the combined data set for 20% RH gives the following formulation for the equilibrium constant

$$K_{eq} = \frac{1}{\mathrm{Pa}} \cdot exp\left(\frac{(10109 \pm 609)\ K}{T} - (35.03 \pm 2.61)\right). \qquad (9)$$

The black line in Fig. 7 shows the dimer evaporation rates derived from equation (9). The uncertainties in equation (9) are based on 95% confidence intervals. Overall, the two data sets are, within errors, consistent with one another, and yield dH = -20.1±1.2 kcal mol^{-1} and dS = -46.7±5.2 cal mol^{-1} K^{-1}. We caution that in this study the assumption is made that dH does not vary with temperature; generally this variation should, however, be small. These data are slightly different than what has been reported by Hanson and Lovejoy (2006). However, our data agree within errors with results from quantum chemical calculations, taking into account the effect of water vapor (Ding et al., 2003). According to measurements by Hanson and Eisele (2000) and quantum chemical calculations (Temelso et al., 2012; Henschel et al. 2014) the sulfuric acid monomer and dimer can contain water molecules. Therefore, the data from Ding et al. (2003) taking into account the effect of water vapor are relevant for this study. Table 2 shows a comparison between different studies dealing with the sulfuric acid dimer formation. Regarding the effect of water vapor it should be noted that our experimentally determined evaporation rates represent an average for dimers containing different numbers of water molecules. The exact distribution of water associated with the dimers will be a function of relative humidity and temperature, which cannot be taken into account explicitly in this study.~~We converted equilibrium constants reported by Hanson and Lovejoy (2006) to evaporation rates using equation (7), while the rates from this study are based on the data shown in Figures 4 and 5 and equation (5). Figure 6 shows both data sets (triangles and circles). Fitting the combined data set for 20% RH gives the following formulation for the equilibrium constant~~

~~$K_{eq} = \frac{1}{\mathrm{Pa}} \cdot exp\left(\frac{(9371 \pm 649)\ K}{T} - (32.00 \pm 2.76)\right). \qquad (8)$~~

~~The solid black line in Fig. 6 shows the dimer evaporation rates derived from equation (8). The uncertainties in equation (8) are based on 95% confidence intervals. Overall, the two data sets are consistent with one another, and yield dH = -18.6±1.3 kcal mol^{-1} and dS = -40.7±5.5 cal mol^{-1} K^{-1}. Hanson and Lovejoy (2006) reported that dimer evaporation rates decrease with increasing RH according to RH^p with p = 0.5, where the exponent p has an uncertainty of ±100%. Our data indicate a rather strong influence of RH on the evaporation rates, so we assumed an exponent of 1. The resulting dimer evaporation rates at 100% RH are shown with a dashed line in Fig. 6. The high RH data at 208 K can very well be explained with the assumed dependency on the relative humidity.~~

3.4 Neutral cluster measurement with CI-APi-TOF in the binary system

During the CLOUD7 campaign, experiments were conducted at ~206 K under binary conditions. In addition to the CIMS two CI-APi-TOFs were deployed (Jokinen et al., 2012; Kürten et al., 2014). The two instruments are labeled CI-APi-TOF-UFRA (instrument from the University of Frankfurt) and CI-APi-TOF-UHEL (instrument from the University of Helsinki). In contrast to the CIMS used during CLOUD5, the sampling lines of the CI-APi-TOFs were not temperature-controlled. Therefore, dimer evaporation was likely more pronounced. For this reason, we did not attempt to quantify the dimer evaporation rate, although the dimer signals are quantitatively consistent with the data shown in Fig. 3. However, the CI-APi-TOFs have a much wider mass range than the CIMS, i.e., a maximum of approximately 2000 Th. This increased mass range allowed larger clusters to be measured; indeed, neutral sulfuric acid clusters containing up to 10 sulfuric acid molecules, i.e., $HSO_4^-(H_2SO_4)_n$ (*n* from 0 to 9) were detected (Fig. ~~7~~8). Eisele and Hanson (2000) previously reported detection of neutral clusters containing up to eight sulfuric acid molecules in a flow-tube experiment using a quadrupole mass spectrometer. However, their measurements were conducted at much higher sulfuric acid concentrations (~10^9 cm^{-3}) whereas in this study the conditions were atmospherically more relevant (sulfuric acid monomer concentration ~1.7x10^7 cm^{-3}). Therefore, the data presented in the following indicates that atmospheric binary nucleation should be directly observable at low temperature, e.g., during aircraft measurements. Water molecules associated with the clusters were not detected with the CI-APi-TOFs; these were most likely evaporated during ion transfer into the high vacuum section of the instruments. No ammonia was detected in any of the clusters either, even though ammonia can, in principle, be observed with a similar instrument that measures charged clusters (Kirkby et al., 2011), so it can be concluded that the experiment was, indeed, under pure binary conditions.

The upper panel of Fig. ~~7~~ 8 shows the time-resolved signals from one of the CI-APi-TOFs ranging from the monomer (HSO_4^-, i.e., S1) up to the decamer ($HSO_4^-(H_2SO_4)_9$, i.e., S10); all of these signals clearly increase following the start of the experiment at 10:02 UTC. From the time-resolved data, the steady-state signals for the different clusters were obtained for both instruments (red and blue ~~circles~~ symbols in Fig. ~~7~~8, lower panel). It was not attempted to derive concentrations from the count-rate signals due to the unknown influence of cluster evaporation within the sampling line and transmission within the mass spectrometers. However, the CIMS, which was operated in parallel to the CI-APi-TOFs with its own dedicated sampling line, yielded a monomer concentration of 1.7x10^7 cm^{-3}.

For this experiment we calculated the extent to which ion-induced clustering (IIC) could contribute to the signals. The equations provided by Chen et al. (2012) were used to estimate the maximum contribution from IIC (Fig. ~~7~~8, lower panel). The dashed red line indicates what cluster signals would be expected if all neutral cluster concentrations (dimer and larger) were zero, and the only cluster ions were formed by addition of H_2SO_4 monomers to the HSO_4^- ions within the CIMS drift tube. The large discrepancy between the observations (red ~~circles~~diamonds) and the dashed red line (it falls off very steeply with increasing cluster size) shows that the contribution from IIC is negligible. Using SAWNUC together with the dimer and trimer evaporation rates (from this study and from Hanson and Lovejoy (2006), respectively) allows us to predict all cluster concentrations and then calculate the expected signals (black curve). While the expected signals from the model calculation are substantially higher than the measured ones from the CI-APi-TOF-UFRA, the shape of the black (modeled) and the red (measured) curve is very similar. This suggests that cluster evaporation rates of the trimer and all larger clusters are not high enough to significantly affect their concentrations at this low temperature.~~This is consistent with the assumption that cluster evaporation rates are negligible for the trimers and all larger clusters at this low temperature.~~ The slightly steeper slope of the measurements could be due to a decrease in the detection efficiency as a function of mass of the CI-APi-TOF-UFRA. In this context it is also important to note that the CI-APi-TOF-UFRA was tuned differently than in a previous study (Kürten et al., 2014) in which a relatively steep drop in the sensitivity as a function of mass was observed. The tuning in this study might have led to a more constant detection efficiency as a function of mass. The fact that the measured trimer signal is lower than the tetramer signal is thought to result from fragmentation of the trimers. Similarly, the hexamer appears to suffer some fragmentation. The CI-APi-TOF-UHEL was tuned to maximize the signals in the mass range up to the pentamer. Consequently, in comparison to the other CI-APi-TOF, this led to substantially higher signals in the mass region up to the pentamer, with a pronounced local maximum around the tetramer (blue curve in Fig. ~~7~~8). However, for the larger masses the signal drops, reaching levels that are comparable to those from the CI-APi-TOF-UFRA.

Because so many questions remain regarding fragmentation, cluster quantification, and the effect of evaporation in the sampling line, the CI-APi-TOF signals are only discussed qualitatively in the present study.

3.5 Sulfuric acid dimer concentrations in the ternary (H_2SO_4-H_2O-NH_3) system

During CLOUD5, ternary nucleation experiments were conducted at temperatures of 210, 223, and 248 K. The addition of relatively small amounts of ammonia (mixing ratios below ~10 pptv) led to a significant increase in the sulfuric acid dimer concentrations compared to the binary system confirming the enhancing effect of ammonia on new particle formation (Ball et al., 1999; Kirkby et al., 2011; Zollner et al., 2012; Jen et al. 2014). In the presence of NH_3, a fraction of the sulfuric acid will be bound to ammonia. However, we assume that the sulfuric acid monomers and dimers will still be ionized by the nitrate primary ions at the same rate as the pure compounds. The ammonia will, however, evaporate very rapidly after the ionization (Hanson and Eisele, 2002). For this reason it is not possible to determine directly the fractions of either the sulfuric acid monomer or the dimer that contain ammonia. Therefore, in the following we assume that the measured monomer is the sum of the pure sulfuric acid monomer and the sulfuric acid monomer bound to ammonia; the same assumption is made for the dimer. It has been suggested that the sensitivity of a nitrate CIMS regarding the sulfuric acid measurements could be affected by the presence of ammonia (or other bases like dimethylamine), which cluster with sulfuric acid (Kurtén et al., 2011; Kupiainen-Määttä et al., 2013). However, recent measurements at the CLOUD chamber indicate that this is very likely a minor affect (Rondo et al. 2015).

Figure ~~8~~ 9 shows the measured sulfuric acid dimer concentration as a function of the sulfuric acid monomer concentration for three different temperatures (210, 223, and 248 K), and several ammonia mixing ratios (< ~10 pptv) under ternary conditions. Two limiting cases that bracket the possible dimer concentrations and the influence of ammonia are indicated by the solid black line and the dashed black line. The solid black line shows the case in which all evaporation rates are set to zero in the SAWNUC model (the kinetic limit); the dashed black line indicates the case for binary conditions at 40% RH. It can be seen that, at the lowest temperature (210 K), the dimer concentrations are close to the expected concentrations for kinetically limited cluster formation, as has been previously reported for the ternary sulfuric acid, water and dimethylamine system at 278 K (Kürten et al., 2014). The ammonia mixing ratio is ~6 pptv in this case (Fig. ~~8~~9, upper panel). At 223 K two different ammonia mixing ratios were investigated. It can clearly be seen that the dimer concentrations increase with increasing ammonia mixing ratio. Different ammonia mixing ratios (~2.5 to 8 pptv) were also studied at 248 K, but in this case the variation in the ammonia concentration was smaller than for 223 K; therefore, the dimer concentration variation is also less pronounced. In addition, the relative humidity changed from experiment to experiment (RH is indicated by the small numbers written next to the data points); it apparently influenced the dimer concentration, which is not surprising given the results described in Section 3.3, and those of Hanson and Lovejoy (2006). Our data show that very small ammonia mixing ratios (pptv range) can strongly enhance dimer formation under atmospherically relevant sulfuric acid concentrations and low temperatures.

3.6 ~~Thermodynamics of the H_2SO_4•NH_3 cluster~~Acid-base model

In order to better understand what influences the dimer concentration in the ternary system, we have developed a simple model (Fig. 10). This heuristic model is motivated by recent studies which have simulated acid-base nucleation of sulfuric acid, ammonia, and amines with similar methods, i.e., without simulating every possible cluster configuration explicitly (Chen et al., 2012; Paasonen et al., 2012; Jen et al., 2014).~~In order to better understand what influences the dimer concentration in the ternary system, we have developed a simple model (Fig. 9); this is motivated by recent studies of acid-base nucleation of sulfuric acid, ammonia, and amines (Chen et al., 2012; Paasonen et al., 2012; Jen et al., 2014).~~ Following the notation of Chen et al. (2012), a sulfuric acid molecule is termed A, while the base ammonia is termed B. Dimers (A_2 or A_2B) may form via two different routes: (a) two sulfuric acid molecules A can collide and form a pure sulfuric acid dimer (A_2), which can further collide with B and form A_2B, or (b) a sulfuric acid molecule can collide with an ammonia molecule and form an AB cluster, which can further collide with A (or another AB cluster) to form A_2B (or A_2B_2). The model further assumes that trimers can either contain solely sulfuric acid (A_3), or are associated with ammonia (A_3B_x).

For all larger clusters we make no distinction between pure sulfuric acid clusters and ammonia containing clusters. We further assume that the clusters cannot contain more bases than acids, so reactions like AB + B are not considered as the extra base is expected to evaporate much more~~very~~ rapidly than it can be gained through collisions at the relatively low base concentrations (Schobesberger et al., 2015).

The model differs somewhat from that used by Chen et al. (2012) and Jen et al. (2014). They considered two separate schemes; in their first scheme, they assumed that two different dimer versions exist – a volatile dimer, and a less volatile dimer that is formed through collision between the volatile dimer and a base molecule. The less volatile dimer can form a trimer or a tetramer (through self-coagulation), which are assumed to be stable. This scheme is similar to pathway (a) described above. Their second scheme assumes that the sulfuric acid monomer can form a cluster AB, which can be turned into a stable dimer. This dimer can then form a trimer that is allowed to evaporate at a rather slow rate (0.4 s^{-1} at 300 K). Once the size of the tetramer is reached the cluster is assumed to be stable. Except for the evaporation rate of the base-containing trimer this scheme is identical to route (b) described above. Our approach combines the two channels because it seems likely that dimers can be formed through the two different pathways at the same time (Fig. ~~9~~10), especially when the temperature is low and the evaporation of A_2 is relatively slow. In addition, we assume that the only base-containing cluster that can still evaporate at these low temperatures (248 K and colder) is AB. Quantum chemical calculations (Ortega et al., 2012), and the measurements of Hanson and Eisele (2002) support the assumption that the cluster containing two sulfuric acid molecules and one ammonia molecule is stable even at relatively high temperature (275 K in the Hanson and Eisele (2002) study). Furthermore, since the evaporation rate of the base-containing trimer reported by Chen et al. (2012) is quite small at 300 K (0.4 s^{-1}), we assume that, at the very low temperatures of this study, this evaporation rate becomes negligible.

The quantum chemistry data from Ortega et al. (2012) support the assumption that a trimer containing at least two bases is relatively stable (evaporation rate below 0.1 s^{-1} at 300 K). However, it predicts that the trimer containing only one ammonia molecule has a high evaporation rate regarding an acid molecule (~1000 s^{-1} at 300 K); additional ammonia in the trimer will lower the evaporation rates. For this reason the trimer concentration will strongly depend on the ammonia concentration, which controls the cluster distribution. Therefore, the Chen et al. (2012) value can be regarded as a best estimate for the overall trimer evaporation rate for their experimental conditions. Herb et al. (2011) also simulated the effect that one water molecule has on the acid evaporation rate from

$(H_2SO_4)_3(NH_3)_1(H_2O)_{0,1}$ clusters. While the water molecule lowers the evaporation rate the absolute evaporation rate is higher (2.9x10^4 s^{-1} at 300 K) than for the Ortega et al. (2012) data.

3.7 Thermodynamics of the H_2SO_4•NH_3 cluster

Under these assumptions, the model of Fig. ~~9~~ 10 was used to probe the kinetics using the measured sulfuric acid monomer, and ammonia concentrations, along with the dimer (A_2) and trimer (A_3) evaporation rates as a function of relative humidity and temperature from this study and from Hanson and Lovejoy (2006). The only free parameter in the model is then the evaporation rate of AB; we adjusted this until the modeled dimer concentration matched the measured one under steady-state conditions. From the evaporation rates at the different temperatures the thermodynamics (d*H* and d*S*) of the cluster AB were retrieved from a least-square linear fit (logarithm of the equilibrium constant vs. the inverse temperature) which yields d*H* = -16.1±0.6 kcal mol^{-1} and d*S* = -26.4±2.6 cal mol^{-1} K^{-1} for H_2SO_4•NH_3.

Unfortunately, the number of data points used to derive the d*H* and d*S* values is quite small. At 210 K the measured dimer concentrations are very close to the kinetic limit estimation, so the evaporation rates must be very low. This indicates that small variations in the monomer and dimer concentration can lead to a large variation in the evaporation rate of AB. These data points were, therefore, neglected. On the other hand, the effect of the relative humidity on the evaporation rates of ammonia containing clusters is not known, so only those experiments that were conducted at similar RH, i.e., ~~~36~~25%, were considered.

Figure ~~8~~ 9 also shows the calculated dimer concentrations using the model with the evaporation rate of AB inferred using the derived thermodynamics (open colored triangles). The error bars reflect a variation of the evaporation rate for H_2SO_4•NH_3 ~~by a factor of 5 and 0.2~~according to the uncertainties of the dH and dS values. The lowest dimer concentrations result if the error of dH is implemented in the positive direction and the error of dS in the negative direction. The highest dimer concentrations result by reversing the signs in the error calculation. The good agreement between measured and modeled values indicates that the model successfully ~~describes~~ reproduces the dimer concentrations over a wide range of conditions. Furthermore, we~~We~~ have also simulated the experiments of Hanson and Eisele (2002) for the ternary system involving ammonia, who used a sulfuric acid concentration of 1.9x10^9 cm^{-3} and an ammonia concentration of 3.8x10^9 cm^{-3} at a temperature of 265 K and an RH of ~10%. Our calculated dimer concentration agrees with their measured concentration within about 40%. Table 3 shows a comparison with the cluster concentrations (dimer to pentamer) measured by Hanson and Eisele (2002) and the ones from this study using the acid-base model described above.~~Our calculated dimer concentration agrees with their measured concentration within better than a factor of two.~~

Table 4 compares our d*H* and d*S* values as well as the corresponding evaporation rates for selected temperatures with other data obtained from quantum chemical calculations (Torpo et al., 2007; Nadykto and Yu, 2007; Ortega et al., 2012; Chon et al., 2014) and from one flow tube experiment (Jen et al., 2014). Overall, the agreement is good. However, it is difficult to take into account the effect the model assumptions have on the outcome of the values from our study. In addition, only a small number of data points have been taken into account in this study.

One also needs to keep in mind that the cluster formation was observed at ~25% RH (with respect to supercooled water) in this study, while most of the theoretical studies did not take into account the effect of water except the one by Nadykto and Yu (2007). Their data suggest that the evaporation rate of H_2SO_4•NH_3•$(H_2O)_x$ increases when the number of associated water molecules increase. The study by Henschel et al. (2014) indicates that about one water molecule is attached for the RH relevant of this study. However, Henschel et al. (2014) reported their results only for a temperature of 298 K, whereas the temperature of this study is 248 K and lower. Whether the evaporation rate is increasing with increasing RH cannot be concluded from our data, however, one needs to keep in mind that similar to the dimer in the binary system, the reported evaporation rates and thermodynamic data for the H_2SO_4•NH_3 represent average values that can include clusters with attached water molecules.

The comparison in Table 4 also lists the experimental study by Jen et al. (2014) who determined the evaporation rate of H_2SO_4•NH_3 at ~300 K from a transient version of their second scheme (formation of dimers only via AB, see above). The extrapolated value from the present study is, however, in relatively good agreement with their value. The somewhat lower evaporation rate of Jen et al. (2014) could be explained by the fact that they did not consider the formation of dimers by self-coagulation of A. Furthermore, they assumed that the trimer has an evaporation rate of 0.4 s^{-1}. Both these assumptions require a slower evaporation rate for AB than our study suggests to explain the measured dimer concentrations at a given monomer and base concentration.

Overall, our measurements in the ternary system yield values of the thermodynamic properties of the H_2SO_4•NH_3 cluster that are in rather good agreement with the results from quantum chemical calculations. However, since the number of data points is limited, the uncertainty is rather high.~~Table 1 compares our d*H* and d*S* values as well as the corresponding evaporation rates for selected temperatures with other data mainly obtained from quantum chemical calculations (Torpo et al., 2007; Ortega et al., 2012; Chon et al., 2014; Jen et al., 2014). Overall, the agreement is good, although the uncertainty of our values is quite high. However, it is difficult to derive an error estimate due to the small number of data points. One needs to keep in mind that the cluster formation was observed at ~36% RH in this study, while the theoretical studies did not take into account the effect of water. The comparison in Table 1 also lists the experimental study by Jen et al. (2014) who determined the evaporation rate of H_2SO_4•NH_3 at ~300 K from a transient version of their second scheme (formation of dimers only via AB, see above). The extrapolated value from the present study is, however, in relatively good agreement with their value. The somewhat lower evaporation rate of Jen et al. (2014)~~

~~could be explained by the fact that they did not consider the formation of dimers by self-coagulation of A. Furthermore, they assumed that the trimer has an evaporation rate of 0.4 s^{-1}. Both these assumptions require a slower evaporation rate for AB than our study suggests to explain the measured dimer concentrations at a given monomer and base concentration.~~

~~Overall, our measurements in the ternary system yield values of the thermodynamic properties of the H_2SO_4•NH_3 cluster that are in good agreement with the results from quantum chemical calculations. However, since the number of data points is limited, the uncertainty is rather high. Nevertheless, it seems that, within the accuracy of the measurements, the evaporation rates for H_2SO_4•NH_3 from both quantum chemistry and the present study are appropriate for use in nucleation models.~~

3.~~7~~ 8 Uncertainties

The error bars shown in Fig. 4 and 5 include the standard variation of the individual data points and a 30% (50%) systematic uncertainty in the monomer (dimer) concentration. The two error components are added together in quadrature. The systematic errors are estimated based on the uncertainties in the calibration coefficient *C* for the monomer~~and the sampling line transmission~~. Due to the higher uncertainty of the sampling losses for the dimer, and the uncertainty of the transmission correction factor (Section 2.3) a somewhat higher uncertainty has been chosen in comparison to the monomer. The error bars in Fig. ~~6~~ 7 are obtained when using Gaussian error propagation on equation (5) for the monomer and the dimer concentration.

In addition to these errors, the effects of evaporation of the dimer in the sampling line (Section 2.6) and fragmentation (Section 3.2) have been discussed above. Each of these effects is very likely on the order of a factor of two or smaller. These processes probably influence all of the dimer data to some extent. However, these errors work in opposite directions: evaporation will lead to a reduction of the dimer concentration, while fragmentation of larger clusters will tend to increase the apparent concentration. Therefore, the two effects partially compensate each other, so they were not taken into account in the calculation of the error bars.

One additional uncertainty is introduced by the assumption that the CIMS detection efficiency is independent of temperature. The study of Viggiano et al. (1997) indicates that the collision rate between nitrate primary ions and sulfuric acid is only a weak function of temperature between 200 and 300 K. Therefore, we expect that temperature only has a small effect on the sulfuric acid concentrations.

The exact values of dimer evaporation rates depend on the choice of $G_{1,1}\bullet K_{1,1}$, i.e., on the overall collision rate between two neutral dimers and is therefore subject to an additional uncertainty because this value is based on theoretical calculations. However, the thermodynamic data derived in this study does not depend on the value of $G_{1,1}\bullet K_{1,1}$ because both the data from this study and the one from

Hanson and Lovejoy (2006) in Fig. 7 were calculated using the same factors. Therefore, when deriving d*H* and d*S* the collision rate cancels out in the calculations (cf. equations (5) and (8)).

In contrast to the exact value of $G_{1,1} \bullet K_{1,1}$ the charged-neutral collision rate k_{21} between HSO_4^- and H_2SO_4 is important because its value scales the dimer concentrations and evaporation rates from this study while leaving the data from Hanson and Lovejoy (2006) unaffected. The reported value of 8×10^{-10} cm^3 s^{-1} for k_{21} from Zhao et al. (2010) suggests that this charged-neutral reaction is not proceeding at the collision limit (value of ~2×10^{-9} cm^3 s^{-1}). When using the faster reaction rate for the charged-neutral collision limit some of the dimer concentrations would exceed the kinetic limit (cf. Fig. 9, upper panel) because all dimer concentrations would need to be scaled up by a factor of 2.5; therefore the faster rate seems to be implausible. However, using the upper limit for the collision rate results in d*H* = -23.0±1.6 kcal mol^{-1} and d*S* = -58.5±6.9 cal mol^{-1} K^{-1}.

The estimates of the thermodynamic properties of the $H_2SO_4 \bullet NH_3$ cluster rely on the assumptions made in the model (Section 3.6). One of the important assumptions made is that the base-containing trimer and tetramer do not evaporate significantly. The data of Ortega et al. (2012) suggest that the evaporation rates of the A_3B_1 and the A_4B_1 clusters are not negligible, even at temperatures at and below 248 K. However, the presence of further ammonia molecules in the trimer and tetramer can lower the evaporation rates and water should have a similar effect (Ortega et al., 2012; Herb et al., 2011). In contrast, the base containing dimer (A_2B) has a very small evaporation rate. No experimental data have been found that support the relatively high evaporation rates of the base containing trimer and tetramer. Instead, the study by Hanson and Eisele (2002) concluded that the critical cluster in the H_2SO_4-H_2O-NH_3 system very likely contains two sulfuric acid molecules and one ammonia molecule at temperatures up to 275 K. In addition, an evaporation rate of 0.4 s^{-1} for the base-containing trimer could explain observed atmospheric nucleation rates at relatively warm temperatures of 300 K (Chen et al., 2012). This evaporation rate should decrease further at lower temperatures. Significant uncertainties remain regarding the evaporation rates of these clusters; further experiments will be needed to reduce these in the future.

4. SUMMARY AND CONCLUSIONS

A Chemical Ionization Mass Spectrometer (CIMS) was used to measure the concentrations of the neutral sulfuric acid monomer and dimer during nucleation experiments at the CLOUD chamber. These experiments were conducted at temperatures as low as 208 K, making them relevant to conditions in the free troposphere. Both, the binary (H_2SO_4-H_2O) system, and the ternary system involving ammonia (H_2SO_4-H_2O-NH_3) were investigated.

Comparison of neutral and ion-induced nucleation experiments indicate that the CIMS detected a significant number of fragmented ion clusters. This confirms the so called “ion-effect” on the CIMS measurements that was recently described by Rondo et al. (2014). However, while Rondo et al. (2014) observed that fragmented HSO_4^-•OxOrg clusters contributed to the CIMS sulfuric acid monomer measurement, we observed a similar effect for the CIMS sulfuric acid dimer measurement (m/z 195). Interestingly, the ion effect on the CIMS dimers was almost absent as soon as ammonia was present in the CLOUD chamber. This is consistent with the observation that ammonia stabilizes sulfuric acid clusters and, thereby, enhances nucleation (Kirkby et al., 2011; Schobesberger et al., 2015).

From the measured monomer and dimer signals dimer evaporation rates were derived and compared to previous flow tube measurements made by Hanson and Lovejoy (2006) for the binary system. Their measurements were performed over a temperature range of 232 to 255 K. The data from the present study were obtained at lower temperatures, 208 to 223 K. Together, the two data sets yield a ~~slightly~~ revised version of the Hanson and Lovejoy (2006) formulation for the dimer equilibrium constant at 20% RH with dH = -20.1±1.2 kcal $\mathrm{mol^{-1}}$ and dS = -46.7±5.2 cal $\mathrm{mol^{-1}\ K^{-1}}$. Due to the wide temperature range (208 to 255 K) covered by the two data sets, this new estimate provides a high degree of confidence when being used at the very low temperatures where binary nucleation can be efficient. Regarding the formation of dimers in the binary system Hanson and Lovejoy (2006) stated that an increase in the relative humidity leads to an increase in the dimer equilibrium constant ($K_p \sim RH^p$) with a power dependency of p between 0 and 1. The best estimate for the power dependency was reported to be 0.5 (Hanson and Lovejoy, 2006). Our data indicate that the exponent is ~~close to~~around 1 at 208 K and around 1.6 at 223 K, i.e., at the upper end of what has been previously assumed.

The ternary experiments involving ammonia (H_2SO_4-H_2O-NH_3) showed that the addition of very small amounts of ammonia (in the pptv range) strongly enhances the sulfuric acid dimer concentration. The dimer concentrations are systematically higher than those for the binary system at a given temperature and sulfuric acid monomer concentration. Furthermore, they increase with increasing ammonia mixing ratio. This confirms previous suggestions that ammonia acts as a stabilizing agent, even for the very small sulfuric acid clusters. In contrast to the previous experiments, the present results were obtained at atmospherically relevant concentrations of sulfuric acid and ammonia, and at low temperature. For the first time the thermodynamics of the H_2SO_4•NH_3 cluster was experimentally investigated from measurements of the monomer and the dimer. The measurements were made at temperatures of 210, 223, and 248 K, with ammonia mixing ratios below ~10 pptv. Using a revised version of a simple conceptual model first proposed by Chen et al. (2012) we were able to derive the thermodynamic properties of the H_2SO_4•NH_3 cluster. The obtained values of dH = -16.1±0.6 kcal $\mathrm{mol^{-1}}$ and dS = -26.4±2.6 cal $\mathrm{mol^{-1}\ K^{-1}}$ are in good agreement with results from quantum chemical calculations. Using the proposed model, measured dimer concentrations in the ternary system can be reproduced with a high accuracy for the conditions of this study.~~Using the proposed model, measured dimer concentrations in the ternary system can be predicted with a high accuracy.~~ A previous study suggested that the $(H_2SO_4)_2$•NH_3 cluster is thermodynamically stable (Hanson and Eisele, 2002). With this observation, the model can be used to calculate nucleation rates in the ternary system, which relies on experimentally determined thermo-chemical data and on the assumptions that ammonia containing trimers and tetramers have insignificant evaporation rates for the conditions of this study.~~With this observation, the model can be used to calculate nucleation rates in the ternary system, which completely relies on experimentally determined thermo-chemical data.~~

Finally, large neutral sulfuric acid clusters containing as many as 10 sulfuric acid molecules were observed for the binary system at 206 K. These clusters were measured with two Chemical Ionization-Atmospheric Pressure interface-Time Of Flight (CI-APi-TOF) mass spectrometers. Since these measurements were not made with a temperature-controlled sampling line the absolute determination of the cluster concentrations was not attempted. However, the signals are consistent with the assumption that cluster growth is essentially kinetically controlled for all of the observed clusters above the dimer. The observation of these large clusters at the upper end of atmospherically relevant sulfuric acid monomer concentration of ~1.7×10^7 cm^{-3} shows that observation of nucleating clusters in the atmosphere should be feasible. In the future, aircraft operation or measurements at high-altitude stations using CI-APi-TOF could provide insight into the importance of binary vs. ternary ammonia nucleation in the free troposphere.

Acknowledgements

We would like to thank CERN for supporting CLOUD with important technical and financial resources, and for providing a particle beam from the CERN Proton Synchrotron. This research was funded by the European Commission Seventh Framework Programme (Marie Curie Initial Training Network “CLOUD-ITN”, grant no. 215072), the German Federal Ministry of Education and Research (project nos. 01LK0902A and 01LK1222A), the European Research Council Advanced Grant “ATMNUCLE” (project no. 227463), the Academy of Finland (project nos. 1133872, 1118615, and 272041), the Swiss National Science Foundation (project nos. 200020_135307 and 206620_141278), the US National Science Foundation (grants AGS-1439551 and AGS-1447056), the Austrian Science Fund (project nos. P19546 and L593), and the Davidow foundation. We thank the tofTools team for providing tools for mass spectrometry analysis.

REFERENCES

Almeida, J., Schobesberger, S., Kürten, A., Ortega, I. K., Kupiainen-Määttä, O., Praplan, A. P., Adamov, A., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Donahue, N. M., Downard, A., Dunne, E. M., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Guida, R., Hakala, J., Hansel, A., Heinritzi, M., Henschel, H., Jokinen, T., Junninen, H., Kajos, M., Kangasluoma, J., Keskinen, H., Kupc, A., Kurtén, T., Kvashin, A. N., Laaksonen, A., Lehtipalo, K., Leiminger, M., Leppä, J., Loukonen, V., Makhmutov, V., Mathot, S., McGrath, M. J., Nieminen, T., Olenius, T., Onnela, A., Petäjä, T., Riccobono, F., Riipinen, I., Rissanen, M., Rondo, L., Ruuskanen, T., Santos, F. D., Sarnela, N., Schallhart, S., Schnitzhofer, R., Seinfeld, J. H., Simon, M., Sipilä, M., Stozhkov, Y., Stratmann, F., Tomé, A., Tröstl, J., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Virtanen, A., Vrtala, A., Wagner, P. E., Weingartner, E., Wex, H., Williamson, C., Wimmer, D., Ye, P., Yli-Juuti, T., Carslaw, K. S., Kulmala, M., Curtius, J., Baltensperger, U., Worsnop, D. R., Vehkamäki, H., and Kirkby, J.: Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere, Nature, 502, 359–363, 2013.

Ball, S. M., Hanson, D. R., Eisele, F. L., and McMurry, P. H.: Laboratory studies of particle nucleation: Initial results for H_2SO_4, H_2O, and NH_3 vapors, J. Geophys. Res., 104(D19), 23709–23718, doi: 10.1029/1999JD900411, 1999.

Berresheim, H., Elste, T., Plass-Dülmer, C., Eisele, F. L., and Tanner, D. J.: Chemical ionization mass spectrometer for long-term measurements of atmospheric OH and H_2SO_4, Int. J. Mass Spectrom., 202, 91–109, 2000.

Bianchi, F., Dommen, J., Mathot, S., and Baltensperger, U.: On-line determination of ammonia at low pptv mixing ratios in the CLOUD chamber, Atmos. Meas. Tech., 5, 1719–1725, 2012.

Borrmann, S., Kunkel, D., Weigel, R., Minikin, A., Deshler, T., Wilson, J. C., Curtius, J., Volk, C. M., Homan, C. D., Ulanovsky, A., Ravegnani, F., Viciani, S., Shur, G. N., Belyaev, G. V., Law, K. S., and Cairo, F.: Aerosols in the tropical and subtropical UT/LS: in-situ measurements of submicron particle abundance and volatility, Atmos. Chem. Phys., 10, 5573–5592, 2010.

Brock, C. A., Hamill, P., Wilson, J. C., Jonsson, H. H., and Chan, K. R.: Particle formation in the upper tropical troposphere: a source of nuclei for the stratospheric aerosol, Science, 270, 1650–1653, 1995.

Campbell, P., and Deshler, T.: Condensation nuclei measurements in the midlatitude (1982-2012) and Antarctic (1986-2010) stratosphere between 20 and 35 km, J. Geophys. Res., 119, 137–152, doi: 10.1002/2013JD019710, 2014.

Chan, T. W., and Mozurkewich, M.: Measurement of the coagulation rate constant for sulfuric acid particles as a function of particle size using tandem differential mobility analysis, J. Aerosol Sci., 32, 321–339, 2001.

Chen, M., Titcombe, M., Jiang, J., Jen, C., Kuang, C., Fischer, M. L., Eisele, F. L., Siepmann, J. I., Hanson, D. R., Zhao, J., and McMurry, P. H.: Acid–base chemical reaction model for nucleation rates in the polluted atmospheric boundary layer, P. Natl. Acad. Sci. USA, 109, 18713–18718, doi: 10.1073/pnas.1210285109, 2012.

Chon, N. L., Lee, S.-H., and Lin, H.: A theoretical study of temperature dependence of cluster formation from sulfuric acid and ammonia, Chem. Phys., 433, 60–66, 2014.

Clarke, A. D., Eisele, F., Kapustin, V. N., Moore, K., Tanner, D., Mauldin, L., Litchy, M., Lienert, B., Carroll, M. A., and Albercook, G.: Nucleation in the equatorial free troposphere: favorable environments during PEM-Tropics, J. Geophys. Res., 104, D5, 5735–5744, 1999.

Curtius, J., Froyd, K. D., and Lovejoy, E. R.: Cluster ion thermal decomposition (I): Experimental kinetics study and ab initio calculations for $HSO_4^-(H_2SO_4)_x(HNO_3)_y$, J. Phys. Chem. A, 105, 10867–10873, 2001.

Ding, C.-G., Laasonen, K., and Laaksonen, A.: Two sulfuric acids in small water clusters, J. Phys. Chem. A, 107, 8648–8658, 2003.

Duplissy, J., Enghoff, M. B., Aplin, K. L., Arnold, F., Aufmhoff, H., Avngaard, M., Baltensperger, U., Bondo, T., Bingham, R., Carslaw, K., Curtius, J., David, A., Fastrup, B., Gagné, S., Hahn, F., Harrison, R. G., Kellett, B., Kirkby, J., Kulmala, M., Laakso, L., Laaksonen, A., Lillestol, E., Lockwood, M., Mäkelä, J., Makhmutov, V., Marsh, N. D., Nieminen, T., Onnela, A., Pedersen, E., Pedersen, J. O. P., Polny, J., Reichl, U., Seinfeld, J. H., Sipilä, M., Stozhkov, Y., Stratmann, F., Svensmark, H., Svensmark, J., Veenhof, R., Verheggen, B., Viisanen, Y., Wagner, P. E., Wehrle, G., Weingartner, E., Wex, H., Wilhelmsson, M., and Winkler, P. M.: Results from the CERN pilot CLOUD experiment, Atmos. Chem. Phys., 10, 1635–1647, 2010.

Ehrhart, S., and Curtius, J.: Influence of aerosol lifetime on the interpretation of nucleation experiments with respect to the first nucleation theorem, Atmos. Chem. Phys., 13, 11465–11471, 2013.

Eisele, F. L., and Tanner, D. J.: Measurement of the gas phase concentration of H_2SO_4 and methane sulfonic acid and estimates of H_2SO_4 production and loss in the atmosphere, J. Geophys. Res., 98, D5, 9001–9010, 1993.

Eisele, F. L., and Hanson, D. R.: First measurement of prenucleation molecular clusters, J. Phys. Chem. A, 104, 830–836, 2000.

Eisele, F. L., Lovejoy, E. R., Kosciuch, E., Moore, K. F., Mauldin III, R. L., Smith, J. N., McMurry, P. H., and Iida, K.: Negative atmospheric ions and their potential role in ion-induced nucleation, J. Geophys. Res., 111, D04305, doi: 10.1029/2005JD006568, 2006.

Franchin, A., Ehrhart, S., Leppä, J., Nieminen, T., Gagné, S., Schobesberger, S., Wimmer, D., Duplissy, J., Riccobono, F., Dunne, E. M., Rondo, L., Downard, A., Bianchi, F., Kupc, A., Tsagkogeorgas, G., Lehtipalo, K., Manninen, H. E., Almeida, J., Amorim, A., Wagner, P. E., Hansel, A., Kirkby, J., Kürten, A., Donahue, N. M., Makhmutov, V., Mathot, S., Metzger, A., Petäjä, T., Schnitzhofer, R., Sipilä, M., Stozhkov, Y., Tomé, A., Kerminen, V.-M., Carslaw, K., Curtius, J., Baltensperger, U., and Kulmala, M.: Experimental investigation of ion–ion recombination under atmospheric conditions, Atmos. Chem. Phys., 15, 7203–7216, 2015.

Froyd, K. D., and Lovejoy, E. R.: Experimental thermodynamics of cluster ions composed of H_2SO_4 and H_2O. 2. Measurements and ab initio structures of negative ions, J. Phys. Chem. A, 107, 9812–9824, 2003.

Hanson, D. R., and Eisele, F.: Diffusion of H_2SO_4 in humidified nitrogen: hydrated H_2SO_4, J. Phys. Chem. A, 104, 1715–1719, 2000.

Hanson, D. R., and Eisele, F. L.: Measurement of prenucleation molecular clusters in the NH_3, H_2SO_4, H_2O system, J. Geophys. Res., 107, D12, 4158, 10.1029/2001JD001100, 2002.

Hanson, D. R., and Lovejoy, E. R.: Measurement of the thermodynamics of the hydrated dimer and trimer of sulfuric acid, J. Phys. Chem. A, 110, 9525–9528, 2006.

Henschel, H., Navarro, J. C. A., Yli-Juuti, T., Kupiainen-Määttä, O., Olenius, T., Ortega, I. K., Clegg, S. L., Kurtén, T., Riipinen, I., and Hanna Vehkamäki: Hydration of Atmospherically Relevant Molecular Clusters: Computational Chemistry and Classical Thermodynamics, J. Phys. Chem. A, 118, 2599–2611, 2014.

Herb, J., Nadykto, A. B., and Yu, F.: Large ternary hydrogen-bonded pre-nucleation clusters in the Earth's atmosphere, Chem. Phys. Lett., 518, 7–14, 2011.

Jen, C., McMurry, P. H., and Hanson, D. R.: Stabilization of sulfuric acid dimers by ammonia, methylamine, dimethylamine, and trimethylamine, J. Geophys. Res. Atmos., 119, 7502–7514, doi: 10.1002/2014JD021592, 2014.

Jokinen, T., Sipilä, M., Junninen, H., Ehn, M., Lönn, G., Hakala, J., Petäjä, T., Mauldin III, R. L., Kulmala, M., and Worsnop, D. R.: Atmospheric sulphuric acid and neutral cluster measurements using CI-APi-TOF, Atmos. Chem. Phys., 12, 4117–4125, 2012.

Junninen, H., Ehn, M., Petäjä, T., Luosujärvi, L., Kotiaho, T., Kostiainen, R., Rohner, U., Gonin, M., Fuhrer, K., Kulmala, M., and Worsnop, D. R.: A high-resolution mass spectrometer to measure atmospheric ion composition, Atmos. Meas. Tech., 3, 1039–1053, 2010.

Kanawade, V., and Tripathi, S. N.: Evidence for the role of ion-induced particle formation during an atmospheric nucleation event observed in Tropospheric Ozone Production about the Spring Equinox (TOPSE), J. Geophys. Res., 111, D02209, doi: 10.1029/2005JD006366, 2006.

Kazil, J., and Lovejoy, E. R.: A semi-analytical method for calculating rates of new sulfate aerosol formation from the gas phase, Atmos. Chem. Phys., 7, 3447–3459, 2007.

Kerminen, V.-M. , Petäjä, T., Manninen, H. E., Paasonen, P., Nieminen, T., Sipilä, M., Junninen, H., Ehn, M., Gagné, S., Laakso, L., Riipinen, I., Vehkamäki, H., Kurten, T., Ortega, I. K., Dal Maso, M., Brus, D., Hyvärinen, A., Lihavainen, H., Leppä, J., Lehtinen, K. E. J., Mirme, A., Mirme, S., Hõrrak, U., Berndt, T., Stratmann, F., Birmili, W., Wiedensohler, A., Metzger, A., Dommen, J., Baltensperger, U., Kiendler-Scharr, A., Mentel, T. F., Wildt, J., Winkler, P. M., Wagner, P. E., Petzold, A., Minikin, A., Plass-Dülmer, C., Pöschl, U., Laaksonen, A., and Kulmala, M.: Atmospheric nucleation: highlights of the EUCAARI project and future directions, Atmos. Chem. Phys., 10, 10829–10848, 2010.

Kirkby, J., Curtius, J., Almeida, J., Dunne, E., Duplissy, J., Ehrhart, S., Franchin, A., Gagné, S., Ickes, L., Kürten, A., Kupc, A., Metzger, A., Riccobono, F., Rondo, L., Schobesberger, S., Tsagkogeorgas, G., Wimmer, D., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Downard, A., Ehn, M., Flagan, R.C., Haider, S., Hansel, A., Hauser, D., Jud, W., Junninen, H., Kreissl, F., Kvashin, A., Laaksonen, A., Lehtipalo, K., Lima, J., Lovejoy, E. R., Makhmutov, V., Mathot, S., Mikkilä, J., Minginette, P., Mogo, S., Nieminen, T., Onnela, A., Pereira, P., Petäjä, T., Schnitzhofer, R., Seinfeld, J. H., Sipilä, M., Stozhkov, Y., Stratmann, F., Tomé, A., Vanhanen, J., Viisanen, Y., Vrtala, A., Wagner, P. E., Walther, H., Weingartner, E., Wex, H., Winkler, P. M., Carslaw, K. S., Worsnop, D. R., Baltensperger, U., and Kulmala, M.: Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation, Nature, 476, 429–435, 2011.

Kuang, C., McMurry, P. H., McCormick, A. V., and Eisele, F. L.: Dependence of nucleation rates on sulfuric acid vapor concentration in diverse atmospheric locations, J. Geophys. Res., 113, D10209, doi: 10.1029/2007JD009253, 2008.

Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W., and McMurry, P. H.: Formation and growth rates of ultrafine atmospheric particles: a review of observations, J. Aerosol Sci., 35, 143–176, 2004.

Kulmala, M., Kontkanen, J., Junninen, H., Lehtipalo, K., Manninen, H. E., Nieminen, T., Petäjä, T., Sipilä, M., Schobesberger, S., Rantala, P., Franchin, A., Jokinen, T., Järvinen, E., Äijälä, M., Kangasluoma, J., Hakala, J., Aalto, P. P., Paasonen, P., Mikkilä, J., Vanhanen, J., Aalto, J., Hakola, H., Makkonen, U., Ruuskanen, T., Mauldin III, R. L., Duplissy, J., Vehkamäki, H., Bäck, J., Kortelainen, A., Riipinen, I., Kurtén, T., Johnston, M. V., Smith, J. N., Ehn, M., Mentel, T. F., Lehtinen, K. E. J., Laaksonen, A., Kerminen, V.-M., and Worsnop, D. R.: Direct observations of atmospheric aerosol nucleation, Science, 339, 943–946, doi: 10.1126/science.1227385, 2013.

Kupc, A., Amorim, A., Curtius, J., Danielczok, A., Duplissy, J., Ehrhart, S., Walther, H., Ickes, L., Kirkby, J., Kürten, A., Lima, J. M., Mathot, S., Minginette, P., Onnela, A., Rondo, L., and Wagner, P. E.: A fibre-optic UV system for H_2SO_4 production in aerosol chambers causing minimal thermal effects, J. Aerosol Sci., 42, 532–543, 2011.

Kupiainen-Määttä, O., Olenius, T., Kurtén, T., and Vehkamäki, H.: CIMS sulfuric acid detection efficiency enhanced by amines due to higher dipole moments: a computational study, J. Phys. Chem. A, 117, 14109–14119, 2013.

Kürten, A., Rondo, L., Ehrhart, S., and Curtius, J.: Performance of a corona ion source for measurement of sulfuric acid by chemical ionization mass spectrometry, Atmos. Meas. Tech., 4, 437–443, 2011.

Kürten, A., Rondo, L., Ehrhart, S., and Curtius, J.: Calibration of a chemical ionization mass spectrometer for the measurement of gaseous sulfuric acid, J. Phys. Chem. A, 116, 6375–6386, dx.doi.org/10.1021/jp212123n, 2012.

Kürten, A., Jokinen, T., Simon, M., Sipilä, M., Sarnela, N., Junninen, H., Adamov, A., Almeida, J., Amorim, A., Bianchi, F., Breitenlechner, M., Dommen, J., Donahue, N. M., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Hakala, J., Hansel, A., Heinritzi, M., Hutterli, M., Kangasluoma, J., Kirkby, J., Laaksonen, A., Lehtipalo, K., Leiminger, M., Makhmutov, V., Mathot, S., Onnela, A., Petäjä, T., Praplan, A. P., Riccobono, F., Rissanen, M. P., Rondo, L., Schobesberger, S., Seinfeld, J. H., Steiner, G., Tomé, A., Tröstl, J., Winkler, P. M., Williamson, C., Wimmer, D., Ye, P., Baltensperger, U., Carslaw, K. S., Kulmala, M., Worsnop, D. R., and Curtius, J.: Neutral molecular cluster formation of sulfuric acid-dimethylamine observed in real-time under atmospheric conditions, P. Natl. Acad. Sci. USA, 111, 15019–15024, doi: 10.1073/pnas.1404853111, 2014.

Kurtén, T., Torpo, L., Ding, C.-G., Vehkamäki, H., Sundberg, M. R., Laasonen, K., and Kulmala, M.: A density functional study on water-sulfuric acid-ammonia clusters and implications for atmospheric cluster formation, J. Geophys. Res., 112, D04210, doi: 10.1029/2006JD007391, 2007.

Kurtén, T., Petäjä, T., Smith, J., Ortega, I. K., Sipilä, M., Junninen, H., Ehn, M., Vehkamäki, H., Mauldin, L., Worsnop, D. R., and Kulmala, M.: The effect of H_2SO_4-amine clustering on chemical ionization mass spectrometry (CIMS) measurements of gas-phase sulfuric acid, Atmos. Chem. Phys., 11, 3007–3019, 2011.

Lee, S.-H., Reeves, J. M., Wilson, J. C., Hunton, D. E., Viggiano, A. A., Miller, T. M., Ballenthin, J. O., and Lait, L. R.: Particle formation by ion nucleation in the upper troposphere and lower stratosphere, Science, 301, 1886–1889, doi: 10.1126/science.1087236, 2003.

Lovejoy, E. R., and Curtius, J.: Cluster ion thermal decomposition (II): Master equation modeling in the low-pressure limit and fall-off regions. Bond energies for $HSO_4^-(H_2SO_4)_x(HNO_3)_y$, J. Phys. Chem. A, 105, 10874–10883, 2001.

Lovejoy, E. R., Curtius, J., and Froyd, K. D.: Atmospheric ion-induced nucleation of sulfuric acid and water, J. Geophys. Res., 109, D08204, doi:10.1029/2003JD004460, 2004.

Mauldin, R. L., Tanner, D. J., Heath, J. A., Huebert, B. J., and Eisele, F. L.: Observations of H_2SO_4 and MSA during PEM-Tropics-A, J. Geophys. Res., 104, D5, 5801–5816, 1999.

McMurry, P. H.: Photochemical Aerosol Formation from SO_2: A theoretical analysis of smog chamber data, J. Colloid Interf. Sci., 78, 513–527, 1980.

Murphy, D. M., and Koop, T.: Review of the vapour pressures of ice and supercooled water for atmospheric applications, Q. J. R. Meteorol. Soc., 131, 1539–1565, 2005.

Nadykto, A. B., and Yu, F.: Strong hydrogen bonding between atmospheric nucleation precursors and common organics, Chem. Phys. Lett., 435, 14–18, 2007.

Norman, M., Hansel, A., and Wisthaler, A.: O_2^+ as reagent ion in the PTR-MS instrument: detection of gas-phase ammonia, Int. J. Mass Spectrom., 265, 382–387, 2007.

Ortega, I. K., Kupiainen, O., Kurtén, T., Olenius, T., Wilkman, O., McGrath, M. J., Loukonen, V., and Vehkamäki, H.: From quantum chemical formation free energies to evaporation rates, Atmos. Chem. Phys., 12, 225–235, 2012.

Ortega, I. K., Olenius, T., Kupiainen-Määttä, O., Loukonen, V., Kurtén, T., and Vehkamäki, H.: Electrical charging changes the composition of sulfuric acid–ammonia/dimethylamine clusters, Atmos. Chem. Phys., 14, 7995–8007, 2014.

Paasonen, P. , Olenius, T., Kupiainen, O., Kurtén, T., Petäjä, T., Birmili, W., Hamed, A., Hu, M., Huey, L. G., Plass-Duelmer, C., Smith, J. N., Wiedensohler, A., Loukonen, V., McGrath, M. J., Ortega, I. K., Laaksonen, A., Vehkamäki, H., Kerminen, V.-M., and Kulmala, M.: On the formation of sulphuric acid – amine clusters in varying atmospheric conditions and its influence on atmospheric new particle formation, Atmos. Chem. Phys., 12, 9113–9133, 2012.

Petäjä, T., Sipilä, M., Paasonen, P., Nieminen, T., Kurtén, T., Ortega, I. K., Stratmann, F., Vehkamäki, H., Berndt, T., and Kulmala, M.: Experimental observation of strongly bound dimers of sulfuric acid: application to nucleation in the atmosphere, Phys. Rev. Lett., 106, 228302-1–228302-4, 2011.

Praplan, A. P., Bianchi, F., Dommen, J., and Baltensperger, U.: Dimethylamine and ammonia measurements with ion chromatography during the CLOUD4 campaign, Atmos. Meas. Tech., 5, 2161–2167, 2012.

Riccobono, F., Schobesberger, S., Scott, C. E., Dommen, J., Ortega, I. K., Rondo, L., Almeida, J., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Downard, A., Dunne, E. M., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Hansel, A., Junninen, H., Kajos, M., Keskinen, H., Kupc, A., Kürten, A., Kvashin, A. N., Laaksonen, A., Lehtipalo, K., Makhmutov, V., Mathot, S., Nieminen, T., Onnela, A., Petäjä, T., Praplan, A. P., Santos, F. D., Schallhart, S., Seinfeld, J. H., Sipilä, M., Spracklen, D. V., Stozhkov, Y., Stratmann, F., Tomé, A., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Vrtala, A., Wagner, P. E., Weingartner, E., Wex, H., Wimmer, D., Carslaw, K. S., Curtius, J., Donahue, N. M., Kirkby, J., Kulmala, M., Worsnop, D. R., and Baltensperger, U.: Oxidation products of biogenic emissions contribute to nucleation of atmospheric particles, Science, 344, 717–721, 2014.

Rondo, L., Kürten, A., Ehrhart, S., Schobesberger, S., Franchin, A., Junninen, H., Petäjä, T., Sipilä, M., Worsnop, D. R., and Curtius, J.: Effect of ions on the measurement of sulphuric acid in the CLOUD experiment at CERN, Atmos. Meas. Tech., 7, 3849–3859, 2014.

Rondo, L., Ehrhart, S., Kürten, A., Adamov, A., Bianchi, F., Breitenlechner, M., Duplissy, J., Franchin, A., Dommen, J., Donahue, N. M., Dunne, E. M., Flagan, R. C., Hakala, J., Hansel, A., Keskinen, H., Kim, J., Jokinen, T., Lehtipalo, K., Leiminger, M., Praplan, A., Riccobono, F., Rissanen, M. P., Sarnela, N., Schobesberger, S., Simon, M., Sipilä, M., Smith, J. N., Tomé, A., Tröstl, J., Tsagkogeorgas, G., Vaattovaara, P., Winkler, P. M., Williamson, C., Baltensperger, U., Kirkby, J., Kulmala, M., Worsnop, D. R., and Curtius, J.: Effect of dimethylamine on the gas phase sulfuric acid concentration measured by Chemical Ionization Mass Spectrometry (CIMS), submitted to J. Geophys. Res., 2015.

Sceats, M. G.: Brownian coagulation in aerosols–The role of long range forces, J. Colloid Interf. Sci., 129, 105–112, 1989.

Schobesberger, S., Junninen, H., Bianchi, F., Lönn, G., Ehn, M., Lehtipalo, K., Dommen, J., Ehrhart, S., Ortega, I. K., Franchin, A., Nieminen, T., Riccobono, F., Hutterli, M., Duplissy, J., Almeida, J., Amorim, A., Breitenlechner, M., Downard, A. J., Dunne, E. M., Flagan, R. C., Kajos, M., Keskinen, H., Kirkby, J., Kupc, A., Kürten, A., Kurtén, T., Laaksonen, A., Mathot, S., Onnela, A., Praplan, A. P., Rondo, L., Santos, F. D., Schallhart, S., Schnitzhofer, R., Sipilä, M., Tomé, A., Tsagkogeorgas, G., Vehkamäki, H., Wimmer, D., Baltensperger, U., Carslaw, K. S., Curtius, J., Hansel, A., Petäjä, T., Kulmala, M., Donahue, N. M., and Worsnop, D. R.: Molecular understanding of atmospheric particle formation from sulfuric acid and large oxidized organic molecules, P. Natl. Acad. Sci. USA, 110, 17223–17228, doi:10.1073/pnas.1306973110, 2013.

Schobesberger, S., Franchin, A., Bianchi, F., Rondo, L., Duplissy, J., Kürten, A., Ortega, I. K., Metzger, A., Schnitzhofer, R., Almeida, J., Amorim, A., Dommen, J., Dunne, E. M., Ehn, M., Gagné, S., Ickes, L., Junninen, H., Hansel, A., Kerminen, V.-M., Kirkby, J., Kupc, A., Laaksonen, A., Lehtipalo, K., Mathot, S., Onnela, A., Petäjä, T., Riccobono, F., Santos, F. D., Sipilä, M., Tomé, A., Tsagkogeorgas, G., Viisanen, Y., Wagner, P. E., Wimmer, D., Curtius, J., Donahue, N. M., Baltensperger, U., Kulmala, M., and Worsnop, D. R.: On the composition of ammonia-sulfuric acid clusters during aerosol particle formation, Atmos. Chem. Phys., 15, 55–78, 2015.

Temelso, B., Phan, T. N., and Shields, G. C.: Computational Study of the Hydration of Sulfuric Acid Dimers: Implications for Acid Dissociation and Aerosol Formation, J. Phys. Chem. A, 116, 9745–9758, 2012.

Torpo, L., Kurtén, T., Vehkamäki, H., Laasonen, K., Sundberg, M. R., and Kulmala, M.: Significance of ammonia in growth of atmospheric nanoclusters, J. Phys. Chem. A, 111, 10671–10674, 2007.

Viggiano, A. A., Seeley, J. V., Mundis, P. L., Williamson, J. S., and Morris, R. A.: Rate constants for the reactions of $XO_3^-(H_2O)_n$ (X = C, HC, and N) and $NO_3^-(HNO_3)_n$ with H_2SO_4: implications for atmospheric detection of H_2SO_4, J. Phys. Chem. A, 101, 8275–8278, 1997.

Voigtländer, J., Duplissy, J., Rondo, L., Kürten, A., and Stratmann, F.: Numerical simulations of mixing conditions and aerosol dynamics in the CERN CLOUD chamber, Atmos. Chem. Phys., 12, 2205–2214, 2012.

Weber, R. J., McMurry, P. H., Eisele, F. L., and Tanner, D. J.: Measurement of expected nucleation precursor species and 3-500-nm diameter particles at Mauna Loa observatory, Hawaii, J. Atmos. Sci., 52, 2242–2257, 1995.

Weber, R., McMurry, P. H., Mauldin, L., Tanner, D. J., Eisele, F. L., Brechtel, F. J., Kreidenweis, S. M., Kok, G., Schillawski, R. D., and Baumgardner, D.: A study of new particle formation and growth involving biogenic and trace gas species measured during ACE 1, J. Geophys. Res., 103, D13, 16385–16396, 1998.

Weigel, R., Borrmann, S., Kazil, J., Minikin, A., Stohl, A:, Wilson, J. C., Reeves, J. M., Kunkel, D., de Reus, M., Frey, W., Lovejoy, E. R., Volk, C. M., Viciani, S., D'Amato, F., Schiller, C., Peter, T., Schlager, H., Cairo, F., Law, K. S., Shur, G. N., Belyaev, G. V., and Curtius, J.: In situ observations of new particle formation in the tropical upper troposphere: the role of clouds and the nucleation mechanism, Atmos. Chem. Phys., 11, 9983–10010, 2011.

Zhang, R., Khalizov, A., Wang, L., Hu, M., and Xu, W.: Nucleation and growth of nanoparticles in the atmosphere, Chem. Rev., 112, 1957–2011, 2012.

Zhao, J., Eisele, F. L., Titcombe, M., Kuang, C., and McMurry, P. H.: Chemical ionization mass spectrometric measurements of atmospheric neutral clusters using the cluster-CIMS, J. Geophys. Res., 115, D08205, doi: 10.1029/2009JD012606, 2010.

Zollner, J. H., Glasoe, W. A., Panta, B., Carlson, K. K., McMurry, P. H., and Hanson, D. R.: Sulfuric acid nucleation: power dependencies, variation with relative humidity, and effect of bases, Atmos. Chem. Phys., 12, 4399–4411, 2012.

TABLES

Campaign	Instruments	Binary system	Ternary system	Main findings
CLOUD5	CIMS, APi-TOF	investigated at 208 and 223 K, RH ~10 to 60%	investigated at 210, 223, and 248 K, ammonia between ~0.5 and 8 pptv	a) binary system: ion effect on apparent CIMS dimer measurements (Section 3.1) b) binary system: thermodynamics of sulfuric acid dimers (Section 3.3) c) ternary system: thermodynamics of H_2SO_4•NH_3 cluster (Sections 3.5 and 3.7)
CLOUD7	CIMS, CI-APi-TOF	investigated at 206 K	not investigated at low temperatures	observation of neutral clusters containing up to 10 sulfuric acid molecules (Section 3.4)

Table 1. Overview over the different conditions, instruments and main findings relevant to this study from the CLOUD5 and CLOUD7 campaigns.

Study	d*H* (kcal mol^{-1})	d*S* (cal mol^{-1} K^{-1})	$k_{2,e}$ at 208 K (s^{-1})	$k_{2,e}$ at 223 K (s^{-1})
this study (20% RH)	-20.1±1.2	-46.7±5.2	0.15	3.9
Hanson and Lovejoy (20% RH)	-18.3±1.8	-39.5±7.8	0.32	6.0
$(H_2SO_4)(H_2O) + (H_2SO_4)(H_2O)$[a]	-17.8	-48.3	89.3	1550
$(H_2SO_4)(H_2O)_2 + (H_2SO_4)(H_2O)$[a]	-21.1	-51.7	0.17	5.0
$(H_2SO_4)(H_2O)_2 + (H_2SO_4)(H_2O)_2$[a]	-25.6	-55.7	2.4×10^{-5}	1.5×10^{-3}

Table 2. Thermodynamic properties (d*H* and d*S*) and evaporation rates of the sulfuric acid dimer from this study and from the literature. [a]Literature data from Ding et al. (2003).

cluster	Hanson and Eisele (2002)	acid-base model, this study
N_2 (total dimer)	1.1x10^7 cm^{-3}	7.0x10^6 cm^{-3} (-36 %)
N_3 (total trimer)	6.5x10^6 cm^{-3}	5.6x10^6 cm^{-3} (-14 %)
N_4 (total tetramer)	6.6x10^6 cm^{-3}	4.7x10^6 cm^{-3} (-29 %)
N_5 (total pentamer)	~4x10^6 cm^{-3}	4.1x10^6 cm^{-3}

Table 3. Comparison between measured cluster concentrations by Hanson and Eisele (2002) and simulated cluster concentrations using the acid-base model described in Section 3.6.

Study	d*H* (kcal mol^{-1})	d*S* (cal mol^{-1} K^{-1})	k_e at 210 K (s^{-1})	k_e at 248 K (s^{-1})	k_e at 300 K (s^{-1})
this study[a]	-16.1±0.6	-26.4±2.6	0.11	36	9.8×10^3
Torpo et al. (2007)[b]	-15.81	-28.57	0.63	200	4.7×10^4
Nadykto and Yu (2007)[b]	-16.72	-30.01	0.15	64	2.1×10^4
Nadykto and Yu (2007), $H_2SO_4(H_2O) + NH_3$	-15.91	-30.23	1.1	370	9.2×10^4
Nadykto and Yu (2007), $H_2SO_4(H_2O)_2 + NH_3$	-15.27	-30.49	6.0	1.5×10^3	3.1×10^5
Nadykto and Yu (2007), $H_2SO_4(H_2O)_3 + NH_3$	-15.44	-32.30	10	2.7×10^3	5.8×10^5
Ortega et al. (2012)[b]	-16.00	-28.14	0.32	107	2.8×10^4
Chon et al. (2014)[b]	-15.43	-29.63	2.7	720	1.5×10^5
Jen et al. (2014)[c]	-	-	-	-	400 to 2500

Table 4. Thermodynamic properties (d*H* and d*S*) and evaporation rates of the H_2SO_4•NH_3 cluster from this study and from the literature. [a]Experiments conducted at ∼~~36~~25% RH (with respect to supercooled water). [b]No effect of water vapor considered. [c]Experiment conducted at ∼30% RH.

FIGURES

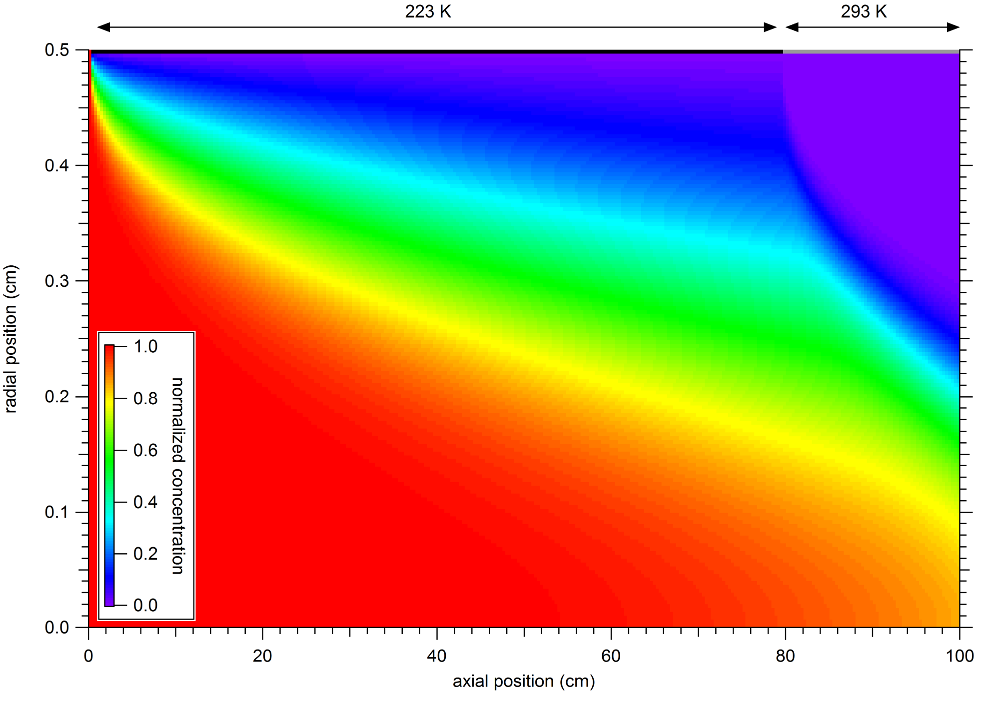


Fig. 1. Simulated transmission of dimers through the CIMS sampling line at a temperature of 223 K for the incoming air. The temperature of the sampling line is fixed to 223 K for the first 80 cm (black color at top axis) and to 293 K for the last 20 cm (grey color at top axis). Wall loss is the dominant loss process over the first 80 cm, whereas evaporation is an additional loss process for the last 20 cm. The overall transmission (diffusion loss and evaporation) is 22.8% at a flow rate of 7.6 liter min^{-1}, while it is 47.5% when evaporation is neglected (diffusion loss only). See text for details.

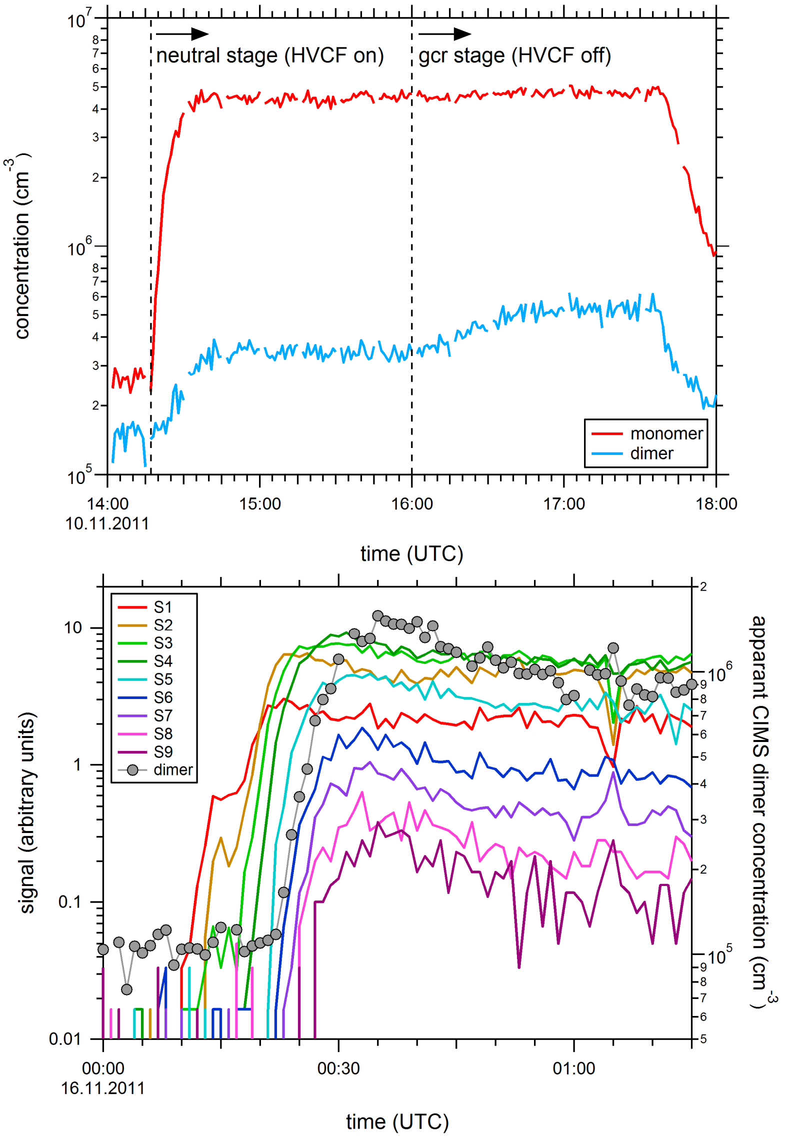


Fig. 2. Upper panel: observed ion effect on CIMS sulfuric acid dimer (*m*/*z* 195) measurements at 223 K. The first part of the experiment is under neutral conditions, the second part is a GCR run with ions present in the chamber. The increase in the dimer signal during the GCR stage is due to ions detected by the CIMS and not due to neutral dimers. Lower panel: comparison between the APi-TOF signals and the CIMS dimer measurements for a different ion-induced experiment at 223 K. The ion clusters (S6, i.e., $HSO_4^-(H_2SO_4)_5$ and larger) show a clear correlation with the apparent dimer signal, which indicates that fragmented cluster ions contribute to the CIMS dimer measurement (Pearson's correlation coefficient between dimer and S6 is 0.93).

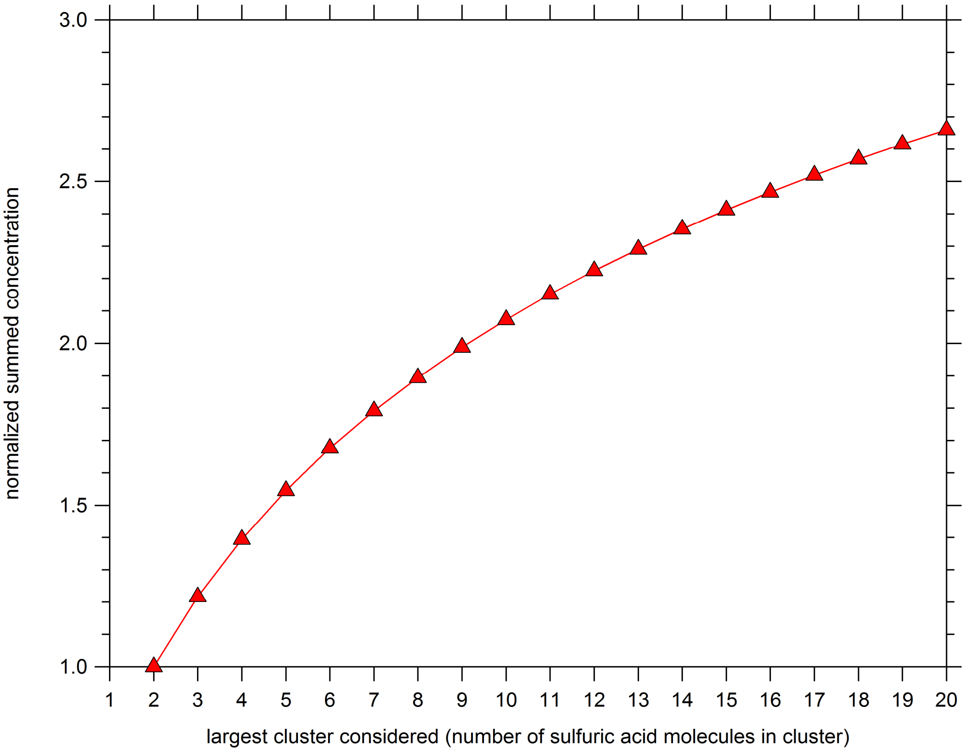


Fig. 3. Simulated ~~integrated~~ summed cluster concentrations at 223 K and 20% RH ($k_{2,e}$ = 5.8 s^{-1} and $k_{3,e}$ = 0.056 s^{-1}; all larger evaporation rates are zero). The cluster concentrations are ~~integrated~~ summed up to a certain number of sulfuric acid molecules in a cluster starting with the dimer concentration. The values on the *x*-axis indicate the number of sulfuric acid molecules in the largest cluster considered in the ~~integration~~summation. All concentrations are normalized by the dimer concentration (at 2.0×10^7 cm^{-3} monomer concentration).

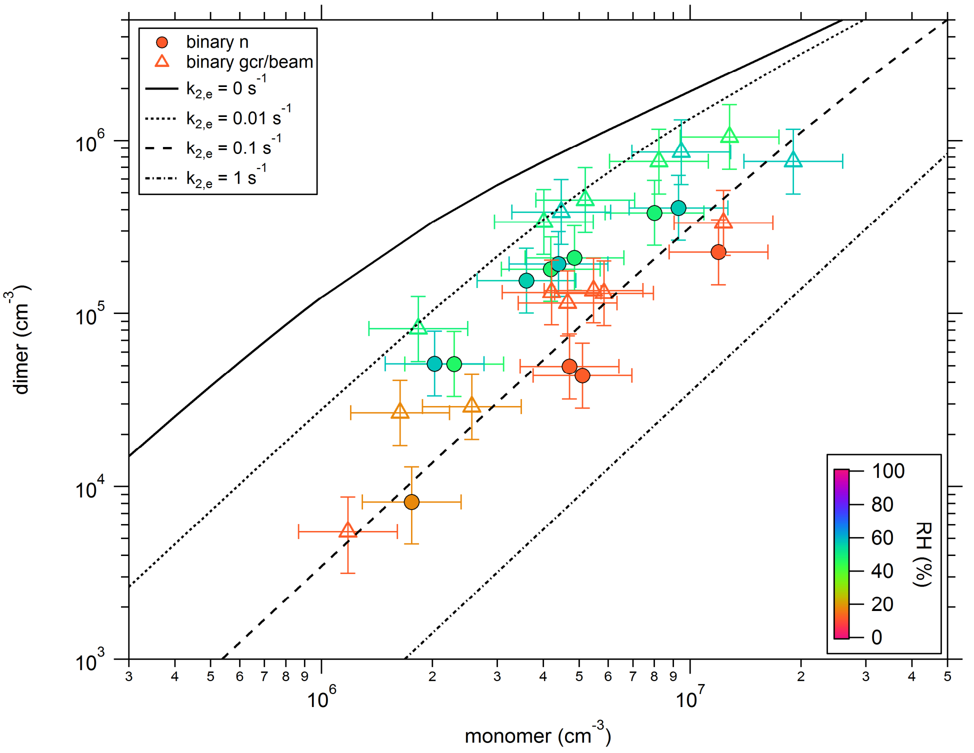


Fig. 4. Sulfuric acid dimer concentration of as a function of the monomer concentration at 208 K for binary conditions. The full circles are from neutral experiments obtained at steady-state and the open triangles from ion-induced experiments. The black lines indicate the modeled dimer concentration for a given dimer evaporation rate with all other cluster evaporation rates set to zero. The color code indicates the relative humidity over supercooled water.

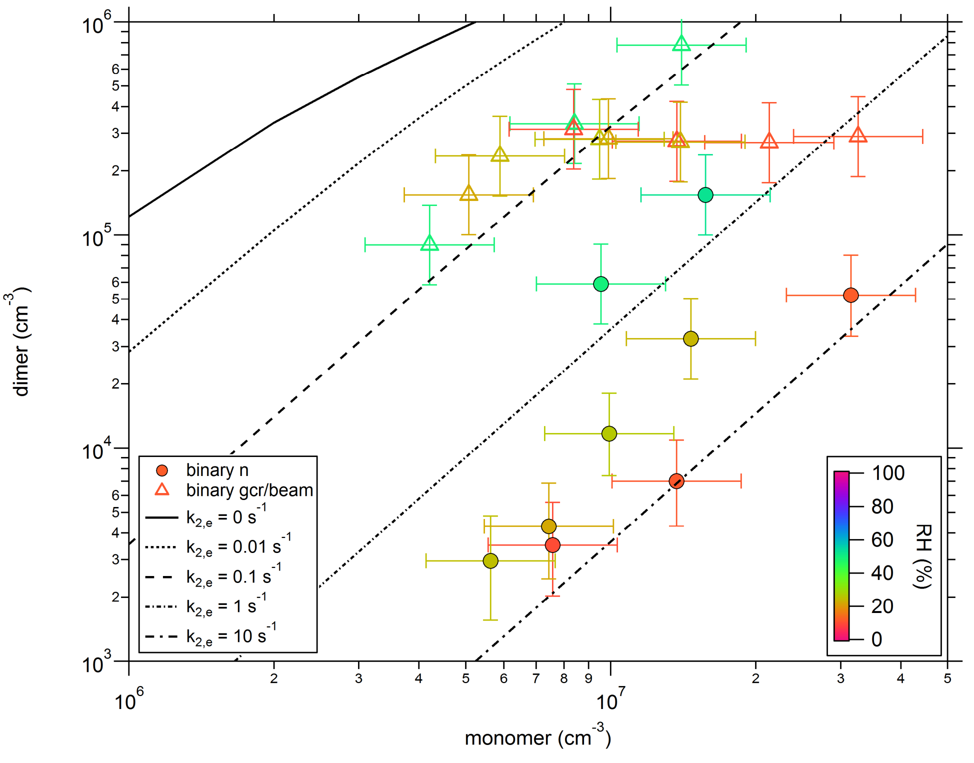
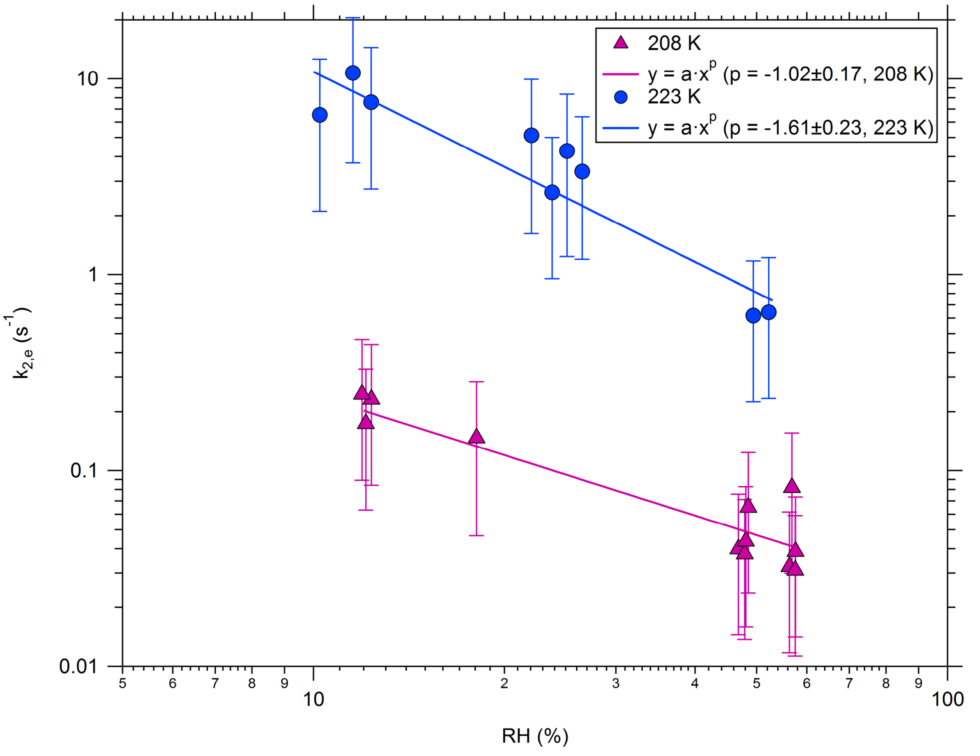


Fig. 5. Same as Fig. 4 but for a temperature of 223 K.



5 **Fig. 6.** Dimer evaporation rate as a function of the RH for two different temperatures (208 and 223 K). Power law fit curves are shown and the slopes *p* are indicated in the figure legend.

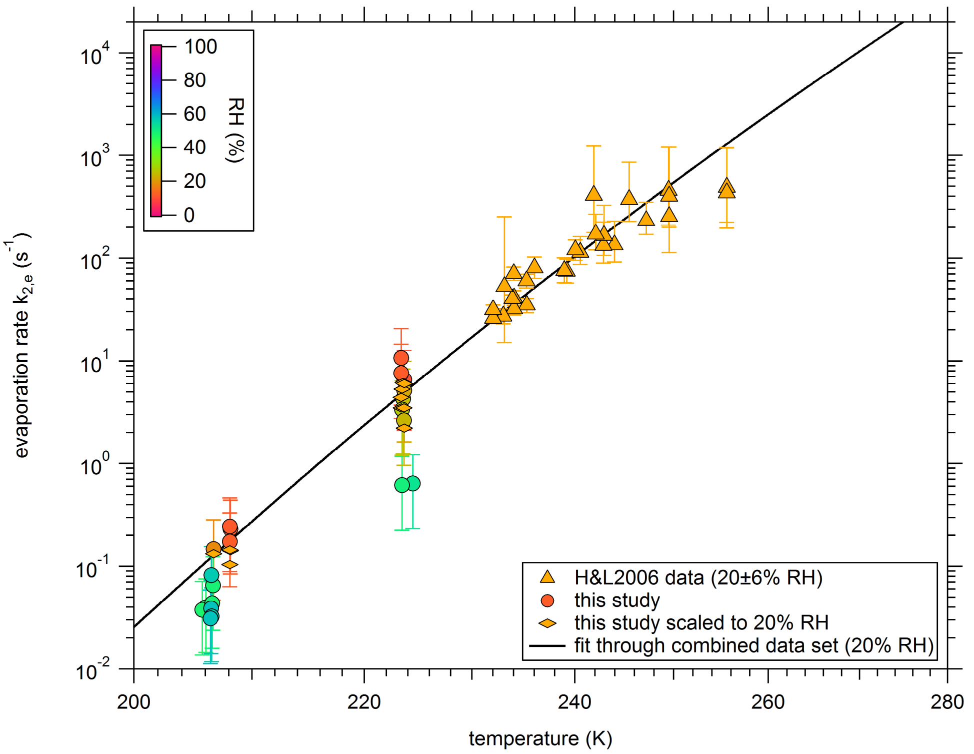


Fig. ~~6~~7. Comparison of the sulfuric acid dimer evaporation rates from this study (circles) and from the literature (triangles, see Hanson and Lovejoy, 2006) as a function of temperature. The color code indicates the relative humidity during the experiments. Diamond symbols represent the data from this study scaled to 20% RH. The solid line shows a best fit through the data with the thermodynamic properties d*H* = -20.1±1.2 kcal mol^{-1} and d*S* = -46.7±5.2 cal mol^{-1} K^{-1} at 20% RH.~~The solid line represents a best fit through the data with the thermodynamic properties d*H* = –18.6±1.3 kcal mol^{-1} and d*S* = –40.7±5.5 cal mol^{-1} K^{-1} at 20% RH. The dashed line shows the dimer evaporation rates for a relative humidity of 100% assuming a power dependency of $k_{2,e}$ ~ RH^{-1}.~~

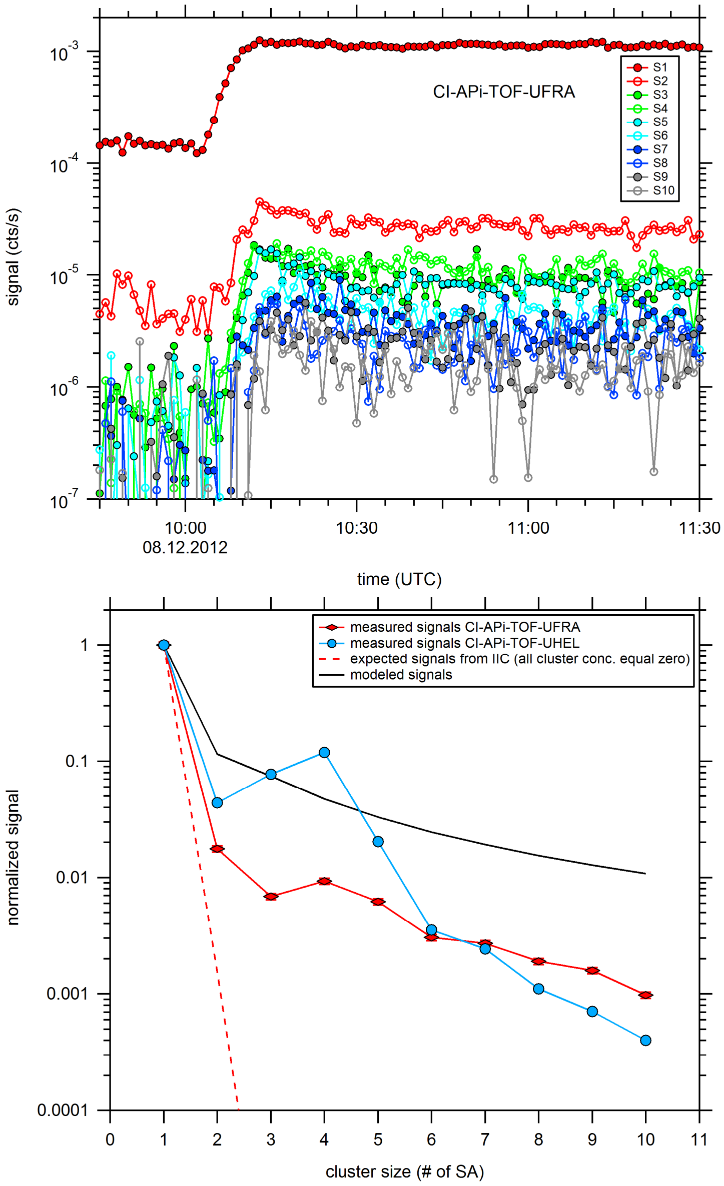


Fig. ~~7~~8. Cluster measurements for the binary system at 206 K and a RH close to 100% over ice measured with two CI-APi-TOFs (UFRA and UHEL instruments). The upper panel shows the monomer (S1) and the cluster signals (Si, $i \geq 2$) normalized by the nitrate ion signals as a function of time (1 minute time resolution) for the CI-APi-TOF-UFRA. The lower panel shows the measured steady-state signals as well as expected signals using different assumptions as function of the cluster size. See text for details.

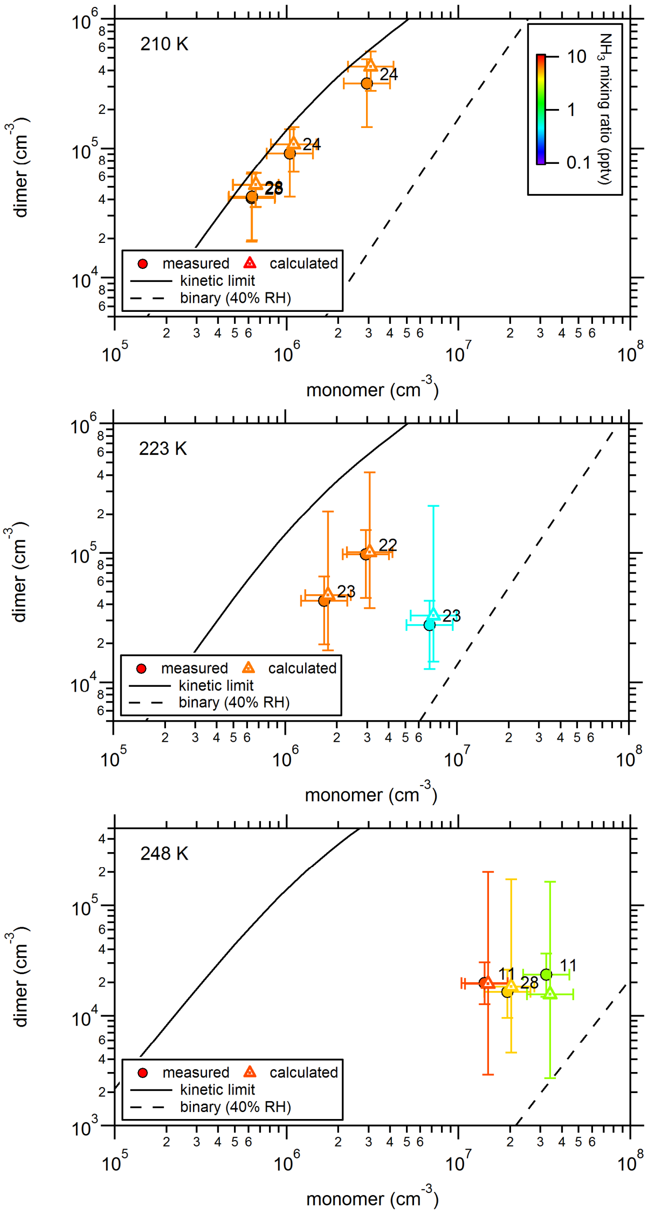


Fig. ~~8~~9. Sulfuric acid dimer concentrations as a function of the sulfuric acid monomer concentration at three different temperatures for the ternary system involving ammonia (ammonia mixing ratio indicated by the color code). The colored circles are the measured concentrations. Lines are from model calculations indicating the expected concentrations for the binary system (dashed line) and the kinetic limit (solid line). The numbers indicate the RH (in %) during an experiment. Open colored triangles are the simulated dimer concentrations using the reaction scheme from Fig. ~~9~~10. These are slightly offset to the right in order to improve readability.

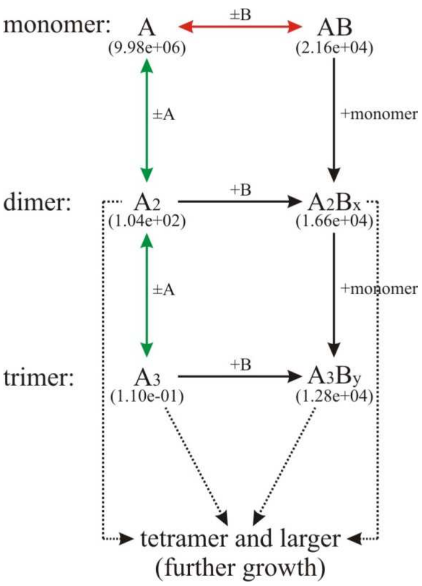


Fig. ~~9~~10. Reaction scheme for the sulfuric acid dimer formation in the ternary system at a low temperature. ‘A’ denotes a sulfuric acid molecule, and ‘B’ an ammonia molecule. ‘Monomer’ is the sum of the concentration of the pure sulfuric acid (A) and the sulfuric acid bound to an ammonia (AB). ‘Dimer’ is the sum of all clusters containing two sulfuric acid molecules ($A_2 + A_2B + A_2B_2$) and the same applies for the ‘trimer’ with three sulfuric acid molecules. The arrows indicate the relevant reactions and whether only collisional growth (single-ended arrow) or growth as well as evaporation (double-ended arrow) are important. Losses due to walls, dilution and coagulation are included in the model but not indicated. Small numbers represent concentrations for an example calculation at a temperature of 248 K, a [monomer] of $1\text{x}10^7$ cm^{-3} and a [NH_3] of $2\text{x}10^8$ cm^{-3}. See text for details.