

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  $dH = -20.1 \pm 1.2$  kcal mol<sup>-1</sup> and  $dS = -46.7 \pm 5.2$  cal mol<sup>-1</sup> K<sup>-1</sup>. The new values are somewhat different from the data by Hanson and Lovejoy (2006) who reported  $dH = -18.3 \pm 1.8$  kcal mol<sup>-1</sup> and  $dS = -39.5 \pm 7.8$  cal mol<sup>-1</sup> K<sup>-1</sup> 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<sup>-1</sup> and  $dS = -51.7$  cal mol<sup>-1</sup> K<sup>-1</sup> for the reaction of  $(\text{H}_2\text{SO}_4)(\text{H}_2\text{O})_2 + (\text{H}_2\text{SO}_4)(\text{H}_2\text{O})$ . 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  $\text{H}_2\text{SO}_4 \cdot \text{NH}_3$  cluster are somewhat different. This results also in updated values for  $dH$  and  $dS$ . These are now  $dH = -16.1 \pm 0.6$  kcal mol<sup>-1</sup> and  $dS = -26.4 \pm 2.6$  cal mol<sup>-1</sup> K<sup>-1</sup>. The previously reported values were  $dH = -16.1$  kcal mol<sup>-1</sup> and  $dS = -26.2$  cal mol<sup>-1</sup> K<sup>-1</sup>; 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  $\pm 100\%$ . Our data indicate a somewhat stronger influence of RH on the evaporation rates, which also seems to be dependent on temperature.

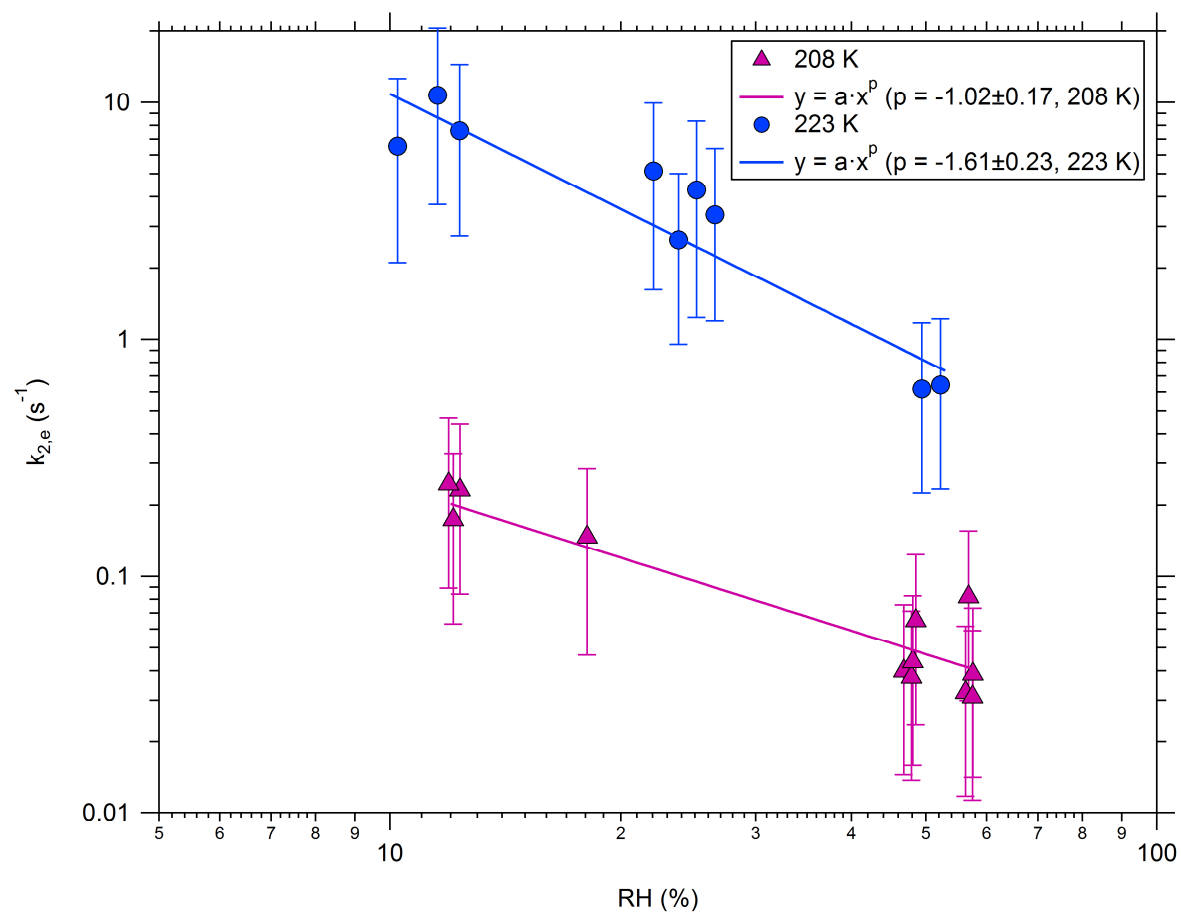
The evaporation rates from Figure 6 with RH between 10 and 30% were normalized to 20% RH using the reported slopes. Figure 7 shows the data from this study and from Hanson and Lovejoy (2006). Fitting the combined data set for 20% RH gives the following formulation for the equilibrium constant

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

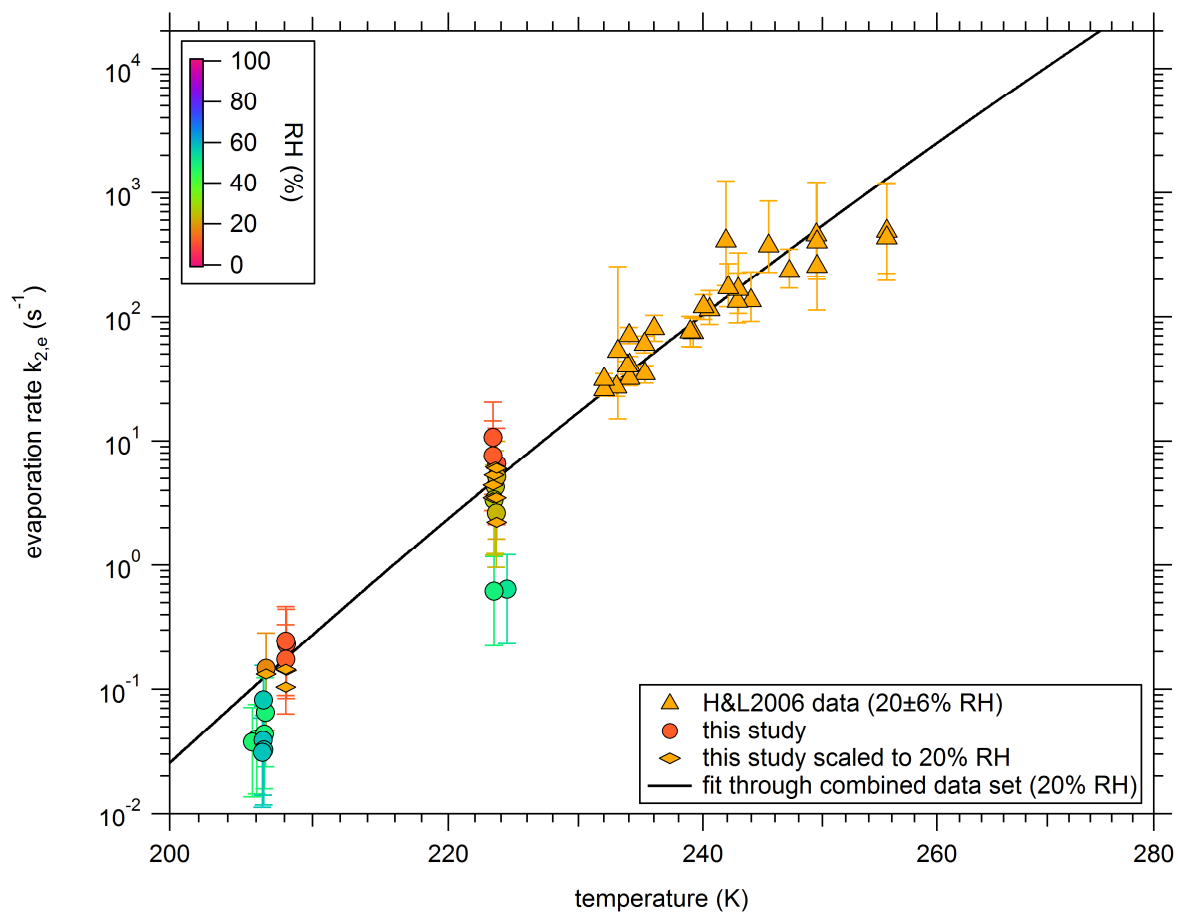
The black line in Fig. 7 shows the dimer evaporation rates derived from equation (9). The uncertainties in equation (9) are based on 95% confidence intervals. Overall, the two data sets are, within errors, consistent with one another, and yield  $dH = -20.1 \pm 1.2$  kcal mol<sup>-1</sup> and  $dS = -46.7 \pm 5.2$  cal mol<sup>-1</sup> K<sup>-1</sup>. 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 <sup>-1</sup> )	$dS$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	$k_{2,e}$ at 208 K (s <sup>-1</sup> )	$k_{2,e}$ at 223 K (s <sup>-1</sup> )
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 <sub>2</sub> SO <sub>4</sub> )(H <sub>2</sub> O) + (H <sub>2</sub> SO <sub>4</sub> )(H <sub>2</sub> O) <sup>a</sup>	-17.8	-48.3	89.3	1550
(H <sub>2</sub> SO <sub>4</sub> )(H <sub>2</sub> O) <sub>2</sub> + (H <sub>2</sub> SO <sub>4</sub> )(H <sub>2</sub> O) <sup>a</sup>	-21.1	-51.7	0.17	5.0
(H <sub>2</sub> SO <sub>4</sub> )(H <sub>2</sub> O) <sub>2</sub> + (H <sub>2</sub> SO <sub>4</sub> )(H <sub>2</sub> O) <sub>2</sub> <sup>a</sup>	-25.6	-55.7	2.4×10 <sup>-5</sup>	1.5×10 <sup>-3</sup>

**Table 2.** Thermodynamic properties ( $dH$  and  $dS$ ) and evaporation rates of the sulfuric acid dimer from this study and from the literature. <sup>a</sup>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  $dH = -20.1 \pm 1.2 \text{ kcal mol}^{-1}$  and  $dS = -46.7 \pm 5.2 \text{ cal mol}^{-1} \text{ K}^{-1}$  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 ( $\text{HSO}_4^-$ )( $\text{H}_2\text{SO}_4$ ) 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<sub>2</sub>SO<sub>4</sub> molecules ( $\sim 1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  including an enhancement factor due to London-van der Waals forces) is faster than the charged-neutral collision rate between bisulfate and H<sub>2</sub>SO<sub>4</sub> ( $8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  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<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>

The collision rate (including the van der Waals correction factor) has been reported as  $\sim 1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  in the ACPD manuscript. However, this value was rounded up and we should have reported the exact value, which is, e.g.  $6.9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  at 208 K. This value consists of two factors; the collision rate calculated from kinetic gas theory ( $2.83 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  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  $3.64 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  and the van der Waals factor is 2.27 (overall collision rate is  $8.26 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ). The value of  $3.64 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  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 (dH and dS) from Fig. 7 (previously Figure 6) for the binary (H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O) system (see below). However, the value of the London-van der Waals 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  $\sim 2.3$ . 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

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

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

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

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

This means that the fitted parameters  $dH = -20.1 \text{ kcal mol}^{-1}$  and  $dS = -46.7 \text{ cal mol}^{-1} \text{ K}^{-1}$  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  $G_{1,1} \cdot K_{1,1}$  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  $\text{HSO}_4^-$  and  $\text{H}_2\text{SO}_4$  (Section 2.3) and between  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$  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  $G_{1,1} \cdot K_{1,1}$ , 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  $G_{1,1} \cdot K_{1,1}$  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  $\text{HSO}_4^-$  and  $\text{H}_2\text{SO}_4$  (denoted as  $k_{21}$ ) is important.

Our current assumption is that this value is  $k_{21} = 8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . 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  $\text{HSO}_4^-$  and  $\text{H}_2\text{SO}_4$  is  $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  (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 ( $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ), 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 ( $dH = -23.0 \pm 1.6 \text{ kcal mol}^{-1}$  and  $dS = -58.5 \pm 6.9 \text{ cal mol}^{-1} \text{ K}^{-1}$  instead of  $dH = -20.1 \pm 1.2 \text{ kcal mol}^{-1}$  and  $dS = -46.7 \pm 5.2 \text{ cal mol}^{-1} \text{ K}^{-1}$ ). 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  $\text{HSO}_4^-$  and  $\text{H}_2\text{SO}_4$  below the collision limit. They found a rate of  $2.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for the reaction between  $\text{NO}_3^-$  and  $\text{HNO}_3$  at the high-pressure limit. This reaction is considered to be similar to the reaction between

$\text{HSO}_4^-$  and  $\text{H}_2\text{SO}_4$  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 ( $\text{HSO}_4^- \bullet \text{H}_2\text{SO}_4$ ) is not known due to the unknown transmission efficiency at masses higher than the sulfuric acid monomer ( $m/z$  97,  $\text{HSO}_4^-$ ) 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  $8.9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , which is close to the currently used value of  $8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  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  $G_{1,1} \bullet K_{1,1}$  the charged-neutral collision rate  $k_{21}$  between  $\text{HSO}_4^-$  and  $\text{H}_2\text{SO}_4$  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  $8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for  $k_{21}$  from Zhao et al. (2010) suggests that this charged-neutral reaction is not proceeding at the collision limit (value of  $\sim 2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ). 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  $dH = -23.0 \pm 1.6 \text{ kcal mol}^{-1}$  and  $dS = -58.5 \pm 6.9 \text{ cal mol}^{-1} \text{ K}^{-1}$ .”



**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  $\text{H}_2\text{SO}_4\cdot\text{NH}_3$  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  $\text{H}_2\text{SO}_4\cdot\text{NH}_3$  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  $[\text{H}_2\text{SO}_4\cdot\text{NH}_3]$  to  $[\text{H}_2\text{SO}_4]$  can be significant (e.g. at 210 K and  $3\times 10^6 \text{ cm}^{-3}$  total sulfuric acid the  $[\text{H}_2\text{SO}_4]$  is  $2\times 10^6$  and  $[\text{H}_2\text{SO}_4\cdot\text{NH}_3]$  is  $\sim 1\times 10^6 \text{ cm}^{-3}$  when  $[\text{NH}_3]$  is  $2\times 10^8 \text{ cm}^{-3}$  according to our model). At higher temperature (248 K) for  $[\text{H}_2\text{SO}_4]$  of  $1\times 10^7 \text{ cm}^{-3}$  and  $[\text{NH}_3] = 2\times 10^8 \text{ cm}^{-3}$ , the  $[\text{H}_2\text{SO}_4\cdot\text{NH}_3]$  is  $2.16\times 10^4 \text{ cm}^{-3}$  and  $[\text{H}_2\text{SO}_4]$  is  $9.98\times 10^6 \text{ cm}^{-3}$ . However, for both temperatures the pathway via  $\text{H}_2\text{SO}_4\cdot\text{NH}_3$  dominates the formation of dimers. At the higher temperature (248 K) the pure dimer concentration ( $[(\text{H}_2\text{SO}_4)_2]$ ) is  $1.04\times 10^2 \text{ cm}^{-3}$ , while the  $[(\text{H}_2\text{SO}_4)_2\cdot\text{NH}_3]$  is  $1.66\times 10^4 \text{ cm}^{-3}$ . The rate of production for  $(\text{H}_2\text{SO}_4)_2\cdot\text{NH}_3$  via the  $\text{H}_2\text{SO}_4\cdot\text{NH}_3$  cluster is a factor of 8 higher than via  $(\text{H}_2\text{SO}_4)_2$ . 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<sub>3</sub>.B<sub>1</sub>: 1034 s<sup>-1</sup> (at 300 K) and 0.70 s<sup>-1</sup> (at 248 K)

B evaporation from SA<sub>3</sub>.B<sub>1</sub>: 5.83x10<sup>-5</sup> s<sup>-1</sup> (at 300 K) and 1.49x10<sup>-9</sup> s<sup>-1</sup> (at 248 K)

A evaporation from SA<sub>3</sub>.B<sub>2</sub>: 0.047 s<sup>-1</sup> (at 300 K) and 3.11x10<sup>-6</sup> s<sup>-1</sup> (at 248 K)

B evaporation from SA<sub>3</sub>.B<sub>2</sub>: 0.065 s<sup>-1</sup> (at 300 K) and 7.33x10<sup>-6</sup> s<sup>-1</sup> (at 248 K)

A evaporation from SA<sub>3</sub>.B<sub>3</sub>: 4.23x10<sup>-8</sup> s<sup>-1</sup> (at 300 K) and 3.73x10<sup>-4</sup> s<sup>-1</sup> (at 248 K)

B evaporation from SA<sub>3</sub>.B<sub>3</sub>: 2.74 s<sup>-1</sup> (at 300 K) and 7.24x10<sup>-14</sup> s<sup>-1</sup> (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<sub>3</sub>.B<sub>3</sub> cluster it results in a SA<sub>3</sub>.B<sub>2</sub> cluster, which has an overall very slow evaporation rate. Therefore, the quantum chemistry data suggest that only the SA<sub>3</sub>.B<sub>1</sub> 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 ~1x10<sup>8</sup> cm<sup>-3</sup>, which results in a forward reaction rate from A<sub>3</sub>.B<sub>1</sub> to A<sub>3</sub>.B<sub>2</sub> of ~0.05 s<sup>-1</sup>. This is not very far away from the evaporation rate of an acid from the A<sub>3</sub>.B<sub>1</sub> cluster (0.7 s<sup>-1</sup>). 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<sub>3</sub>.B<sub>1</sub> 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<sup>8</sup> cm<sup>-3</sup>).

### 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<sup>-1</sup> 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<sup>-1</sup> 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<sup>-1</sup> 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<sub>2</sub>SO<sub>4</sub>)<sub>3</sub>(NH<sub>3</sub>)<sub>1</sub>(H<sub>2</sub>O)<sub>0,1</sub> clusters. While the water molecule lowers the evaporation rate the absolute evaporation rate is higher (2.9x10<sup>4</sup> s<sup>-1</sup> 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?

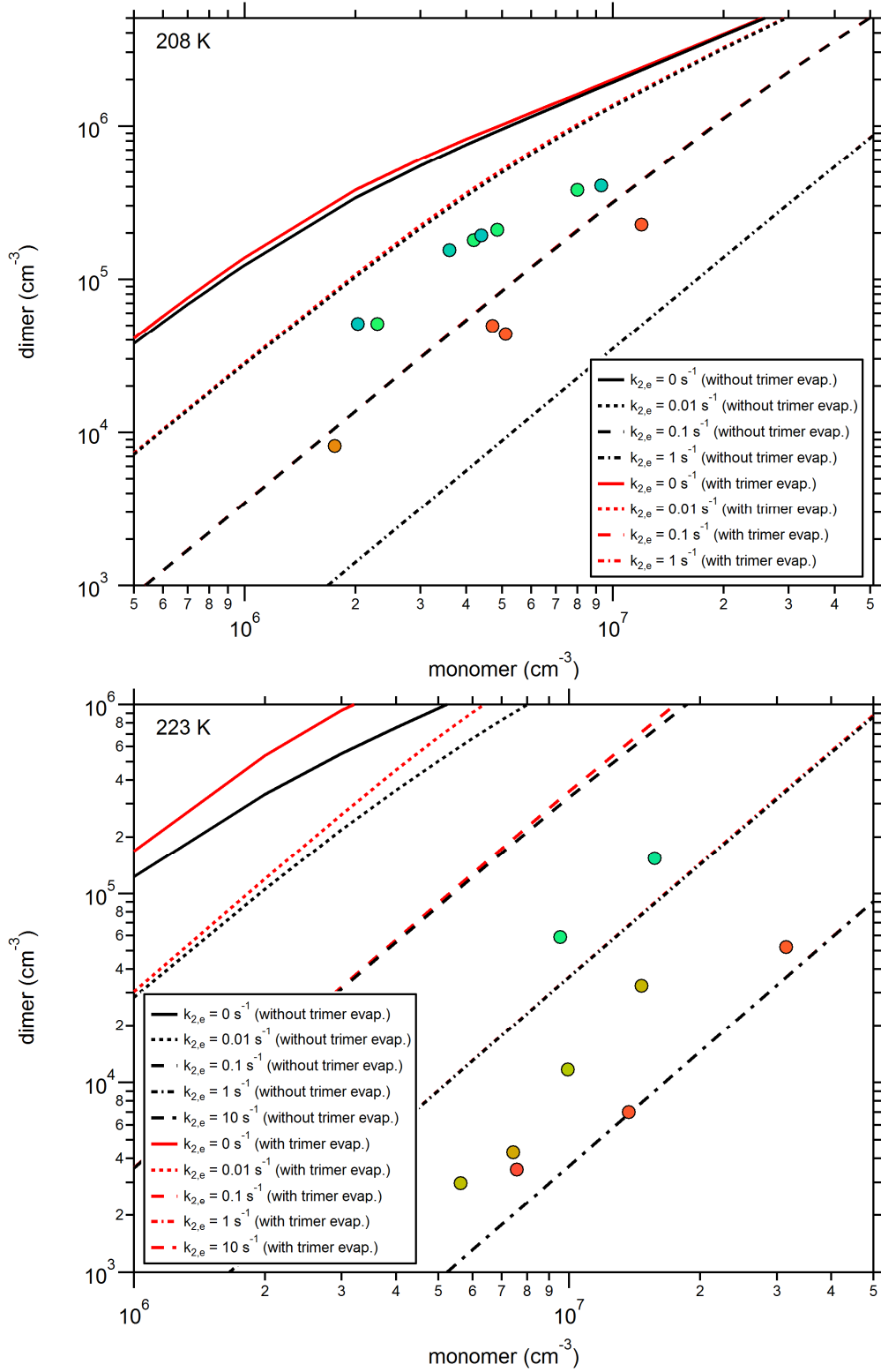
We are not arguing that the trimer (and larger cluster) evaporation rate(s) are zero, we are only saying that the contribution of the second term on the RHS of the following equation is negligible compared to the first term:

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

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  $0.1 \text{ s}^{-1}$  while the trimer evaporation rate is  $1 \times 10^{-3} \text{ s}^{-1}$ . 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  $1 \times 10^{-3} \text{ s}^{-1}$ . Now adding  $1 \times 10^{-3} \text{ s}^{-1}$  to the dimer evaporation rate of  $0.1 \text{ s}^{-1}$  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 ( $k_{3,e} = 1.6 \times 10^{-3} \text{ s}^{-1}$  (208 K),  $k_{3,e} = 5.6 \times 10^{-2} \text{ s}^{-1}$  (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  $1.7 \times 10^7 \text{ cm}^{-3}$  the forward reaction rate (growth by monomers) is approximately  $\sim 10^{-2} \text{ s}^{-1}$ , whereas the dimer evaporation rate is  $\sim 4 \times 10^{-2} \text{ s}^{-1}$ . 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 ( $\text{H}_2\text{SO}_4$ )<sub>2</sub> and in the ternary case for the one sulphuric acid-one ammonia ( $\text{H}_2\text{SO}_4$ )( $\text{NH}_3$ ) 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 ( $\text{H}_2\text{SO}_4$ )<sub>2</sub>( $\text{H}_2\text{O}$ )<sub>0-6</sub> clusters
- Henschel et al. (2014): water content for ( $\text{SA}$ )<sub>1-4</sub> and up to ( $\text{SA}$ )<sub>x=1-3</sub>( $\text{NH}_3$ )<sub>y<x</sub>; ( $\text{H}_2\text{SO}_4$ )( $\text{NH}_3$ ) 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 ( $\text{H}_2\text{SO}_4$ )( $\text{NH}_3$ )( $\text{H}_2\text{O}$ )<sub>0-3</sub> clusters
- Herb et al. (2011): thermodynamic data for ( $\text{H}_2\text{SO}_4$ )<sub>3</sub>( $\text{NH}_3$ )<sub>1</sub>( $\text{H}_2\text{O}$ )<sub>0,1</sub> 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  $\text{H}_2\text{SO}_4 \cdot \text{NH}_3$  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  $dH$  and  $dS$  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  $\text{H}_2\text{SO}_4\cdot\text{NH}_3\cdot(\text{H}_2\text{O})_x$  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  $\text{H}_2\text{SO}_4\cdot\text{NH}_3$  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  $\text{H}_2\text{SO}_4\cdot\text{NH}_3$  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  $0.4 \text{ s}^{-1}$ . 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  $\text{H}_2\text{SO}_4\cdot\text{NH}_3$  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	$dH$ (kcal mol <sup>-1</sup> )	$dS$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	$k_e$ at 210 K (s <sup>-1</sup> )	$k_e$ at 248 K (s <sup>-1</sup> )	$k_e$ at 300 K (s <sup>-1</sup> )
this study <sup>a</sup>	-16.1±0.6	-26.4±2.6	0.11	36	9.8×10 <sup>3</sup>
Torpo et al. (2007) <sup>b</sup>	-15.81	-28.57	0.63	200	4.7×10 <sup>4</sup>
Nadykto and Yu (2007) <sup>b</sup>	-16.72	-30.01	0.15	64	2.1×10 <sup>4</sup>
Nadykto and Yu (2007), $\text{H}_2\text{SO}_4(\text{H}_2\text{O}) + \text{NH}_3$	-15.91	-30.23	1.1	370	9.2×10 <sup>4</sup>
Nadykto and Yu (2007), $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_2 + \text{NH}_3$	-15.27	-30.49	6.0	1.5×10 <sup>3</sup>	3.1×10 <sup>5</sup>
Nadykto and Yu (2007), $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_3 + \text{NH}_3$	-15.44	-32.30	10	2.7×10 <sup>3</sup>	5.8×10 <sup>5</sup>
Ortega et al. (2012) <sup>b</sup>	-16.00	-28.14	0.32	107	2.8×10 <sup>4</sup>
Chon et al. (2014) <sup>b</sup>	-15.43	-29.63	2.7	720	1.5×10 <sup>5</sup>
Jen et al. (2014) <sup>c</sup>	-	-	-	-	400 to 2500

**Table 4.** Thermodynamic properties ( $dH$  and  $dS$ ) and evaporation rates of the  $\text{H}_2\text{SO}_4\cdot\text{NH}_3$  cluster from this study and from the literature. <sup>a</sup>Experiments conducted at ~25% RH (with respect to supercooled water). <sup>b</sup>No effect of water vapor considered. <sup>c</sup>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 sulphuric 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<sub>2</sub>SO<sub>4</sub> 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  $0.06 \text{ cm}^2 \text{ s}^{-1}$  at 298 K, and varies with temperature as  $(298 \text{ K}/T)^{1.75}$ ”. Are this value and temperature dependence derived for a pure dimer (H<sub>2</sub>SO<sub>4</sub>)<sub>2</sub>? 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  $0.06 \text{ cm}^2 \text{ s}^{-1}$  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  $198 \text{ g mol}^{-1}$  but rather 234 or  $270 \text{ g mol}^{-1}$ . 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  $(0.06 \pm 0.01) \text{ cm}^2 \text{ s}^{-1}$ . A variation of the diffusivity by  $0.01 \text{ cm}^2 \text{ s}^{-1}$  results in a variation of the calculated penetration  $L_{\text{dimer}}$  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  $0.06 \pm 0.01 \text{ cm}^2 \text{ s}^{-1}$  at 298 K, and varies with temperature as  $(298\text{K}/T)^{1.75}$ .”

(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  $4 \times 10^5 \text{ cm}^{-3}$  for a monomer concentration of  $8 \times 10^6 \text{ cm}^{-3}$ , i.e., 5% of the dimer. It should also be noted that the dimers can contribute only one monomer (i.e., one  $\text{HSO}_4^-$  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 ( $dG < -12 \text{ kcal mol}^{-1}$ ) at 242 K. This corresponds to an upper limit of the tetramer evaporation rate of  $0.09 \text{ s}^{-1}$  (using a forward reaction rate  $2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  from Hanson and Lovejoy (2006)). The dimer and trimer evaporation rates at this temperature are 83 and  $0.5 \text{ s}^{-1}$ . 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  $117 \text{ s}^{-1}$  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  $(\text{H}_2\text{SO}_4)_2(\text{H}_2\text{O})_x$  and the  $(\text{H}_2\text{SO}_4)(\text{NH}_3)(\text{H}_2\text{O})_y$  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 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<sub>2</sub>O compared to H<sub>2</sub>SO<sub>4</sub>.”

(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):

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

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 (<

Is 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):

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

This loss rate is much higher than what can be expected for loss due to coagulation ( $< 0.01 \text{ s}^{-1}$ ), 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 shortened 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  $5 \times 10^{-3} \text{ cm}^{-3}$  (Kirkby et al., 2011; Franchin et al. 2015) and the  $\text{HSO}_4^-$  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  $\text{HSO}_4^-$  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 off 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 single 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  $dH = -20.1$  kcal mol<sup>-1</sup> and  $dS = -46.7$  cal mol<sup>-1</sup> K<sup>-1</sup>. 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  $dH$  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  $dH$  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  $dH$  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 ( $\sim 1 \times 10^9 \text{ cm}^{-3}$ , 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 ( $\sim 10^9 \text{ cm}^{-3}$ ) whereas in this study the conditions were atmospherically more relevant (sulfuric acid monomer concentration  $\sim 1.7 \times 10^7 \text{ cm}^{-3}$ ). 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, lines 11-14: “In the presence of  $\text{NH}_3$ , 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  $[\text{H}_2\text{SO}_4 \cdot \text{NH}_3]$  to  $[\text{H}_2\text{SO}_4]$  is  $\sim 1/3$  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  $(\text{H}_2\text{SO}_4)$  with  $\text{NH}_3$  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  $\sim 13\%$  overestimation of the monomer would result if  $1/3$  of the total sulfuric acid monomer is present as  $\text{H}_2\text{SO}_4 \cdot \text{NH}_3$ . 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  $\text{H}_2\text{SO}_4\cdot\text{NH}_3$  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  $(\text{H}_2\text{SO}_4)_n(\text{NH}_3)_{n+1}$  clusters. Compared to  $(\text{H}_2\text{SO}_4)_n(\text{NH}_3)_n$  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  $1 \times 10^9 \text{ cm}^{-3}$ ) 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  $\text{AB} + \text{B}$  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  $1 \times 10^7 \text{ cm}^{-3}$  and the ammonia concentration is  $2 \times 10^8 \text{ cm}^{-3}$ . These data indicate that the main path of dimer formation is via the  $\text{H}_2\text{SO}_4 \cdot \text{NH}_3$  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  $\text{SA}_3\text{.B}_1$ :  $1034 \text{ s}^{-1}$  (at 300 K) and  $0.70 \text{ s}^{-1}$  (at 248 K)  
B evaporation from  $\text{SA}_3\text{.B}_1$ :  $5.83 \times 10^{-5} \text{ s}^{-1}$  (at 300 K) and  $1.49 \times 10^{-9} \text{ s}^{-1}$  (at 248 K)

A evaporation from  $\text{SA}_3\text{.B}_2$ :  $0.047 \text{ s}^{-1}$  (at 300 K) and  $3.11 \times 10^{-6} \text{ s}^{-1}$  (at 248 K)  
B evaporation from  $\text{SA}_3\text{.B}_2$ :  $0.065 \text{ s}^{-1}$  (at 300 K) and  $7.33 \times 10^{-6} \text{ s}^{-1}$  (at 248 K)

A evaporation from  $\text{SA}_3\text{.B}_3$ :  $4.23 \times 10^{-8} \text{ s}^{-1}$  (at 300 K) and  $3.73 \times 10^{-4} \text{ s}^{-1}$  (at 248 K)  
B evaporation from  $\text{SA}_3\text{.B}_3$ :  $2.74 \text{ s}^{-1}$  (at 300 K) and  $7.24 \times 10^{-14} \text{ s}^{-1}$  (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  $\text{SA}_3\text{.B}_3$  cluster it results in a  $\text{SA}_3\text{.B}_2$  cluster, which has an overall very slow evaporation rate. Therefore, the quantum chemistry data suggest that only the  $\text{SA}_3\text{.B}$  cluster can be regarded as relatively unstable because an acid molecule can evaporate rapidly.

Furthermore, for the  $(\text{H}_2\text{SO}_4)_{x \geq 2}(\text{NH}_3)_{y \geq 1}(\text{H}_2\text{O})_{z \geq 1}$  cluster data from Herb et al. (2011) is available.

A evaporation from  $\text{A}_3\text{B}_1\text{W}_1$ :  $2.93 \times 10^4 \text{ s}^{-1}$  (at 300 K) and  $50 \text{ s}^{-1}$  (at 248 K)  
A evaporation from  $\text{A}_3\text{B}_1$ :  $1.1 \times 10^6 \text{ s}^{-1}$  (at 300 K) and  $4.1 \times 10^3 \text{ s}^{-1}$  (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  $0.1 \text{ s}^{-1}$  at 300 K). However, it predicts that the trimer containing only one ammonia molecule has a high evaporation rate regarding an acid molecule ( $\sim 1000 \text{ s}^{-1}$  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  $(\text{H}_2\text{SO}_4)_3(\text{NH}_3)_1(\text{H}_2\text{O})_{0,1}$  clusters. While the water molecule lowers the evaporation rate the absolute evaporation rate is higher ( $2.9 \times 10^4 \text{ s}^{-1}$  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  $1.1 \times 10^7 \text{ cm}^{-3}$  when the total sulfuric acid monomer was  $1.9 \times 10^9 \text{ cm}^{-3}$  and ammonia was at  $3.8 \times 10^9 \text{ cm}^{-3}$  (at 265 K and 10% RH). With our model using an evaporation rate of the  $\text{H}_2\text{SO}_4 \cdot \text{NH}_3$  cluster for 265 K, we calculate a total dimer concentration of  $7 \times 10^6 \text{ cm}^{-3}$  (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)	$1.1 \times 10^7 \text{ cm}^{-3}$	$7.0 \times 10^6 \text{ cm}^{-3}$ (-36 %)
$N_3$ (total trimer)	$6.5 \times 10^6 \text{ cm}^{-3}$	$5.6 \times 10^6 \text{ cm}^{-3}$ (-14 %)
$N_4$ (total tetramer)	$6.6 \times 10^6 \text{ cm}^{-3}$	$4.7 \times 10^6 \text{ cm}^{-3}$ (-29 %)
$N_5$ (total pentamer)	$\sim 4 \times 10^6 \text{ cm}^{-3}$	$4.1 \times 10^6 \text{ cm}^{-3}$

**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  $\text{A}_3\text{B}_1$  and  $\text{A}_4\text{B}_1$  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  $1 \text{ s}^{-1}$  and for ammonia  $2 \text{ s}^{-1}$ . This indicates that the acid evaporation rate of the sulfuric acid trimer cannot be higher than  $\sim 1 \text{ s}^{-1}$ . 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.

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