

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  $dH = -20.1 \pm 1.2 \text{ kcal mol}^{-1}$  and  $dS = -46.7 \pm 5.2 \text{ cal mol}^{-1} \text{ K}^{-1}$ . The new values are somewhat different from the data by Hanson and Lovejoy (2006) who reported  $dH = -18.3 \pm 1.8 \text{ kcal mol}^{-1}$  and  $dS = -39.5 \pm 7.8 \text{ cal mol}^{-1} \text{ K}^{-1}$  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  $dH = -21.1 \text{ kcal mol}^{-1}$  and  $dS = -51.7 \text{ cal mol}^{-1} \text{ K}^{-1}$  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  $dH = -16.1 \pm 0.6 \text{ kcal mol}^{-1}$  and  $dS = -26.4 \pm 2.6 \text{ cal mol}^{-1} \text{ K}^{-1}$ . The previously reported values were  $dH = -16.1 \text{ kcal mol}^{-1}$  and  $dS = -26.2 \text{ cal mol}^{-1} \text{ K}^{-1}$ ; 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  $\pm 100\%$ . Our data indicate a somewhat stronger influence of RH on the evaporation rates, which also seems to be dependent on temperature.

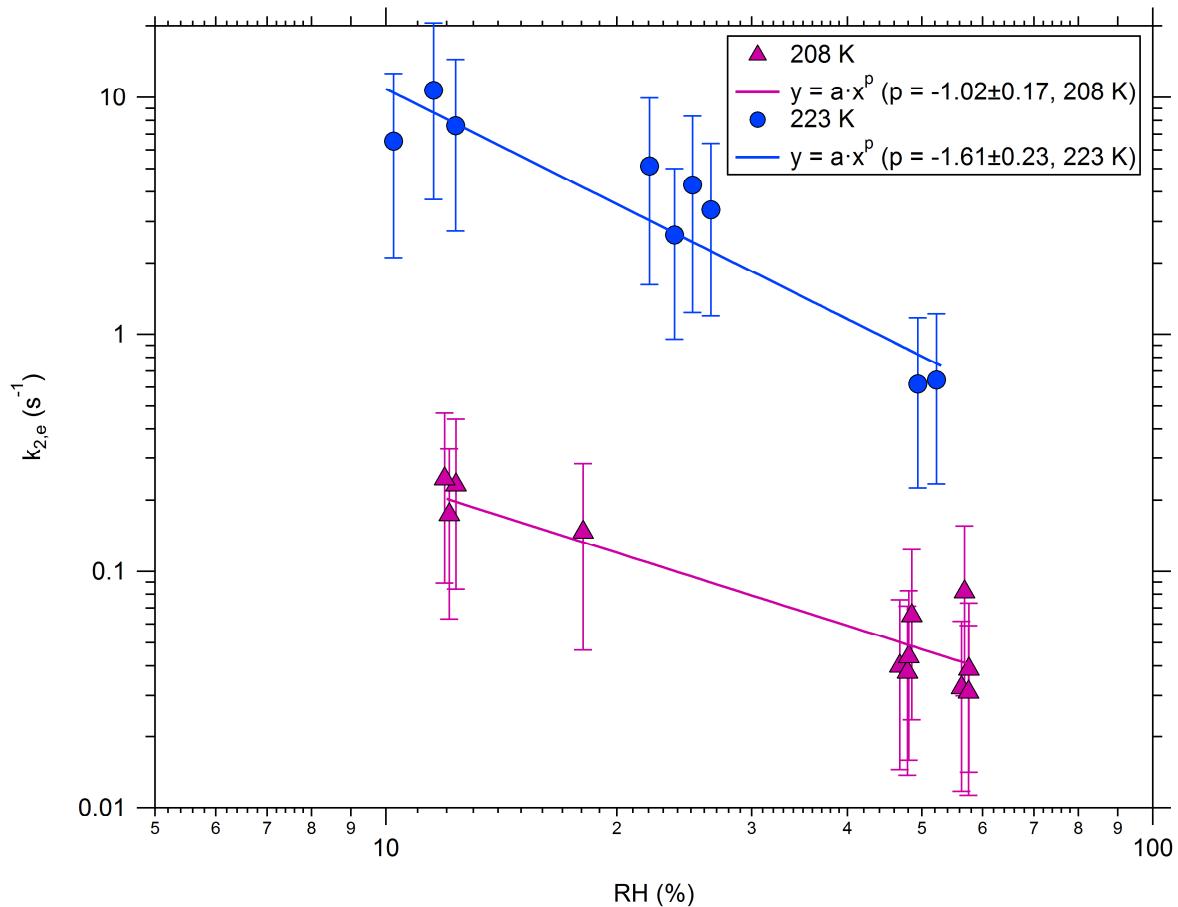
The evaporation rates from Figure 6 with RH between 10 and 30% were normalized to 20% RH using the reported slopes. Figure 7 shows the data from this study and from Hanson and Lovejoy (2006). Fitting the combined data set for 20% RH gives the following formulation for the equilibrium constant

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

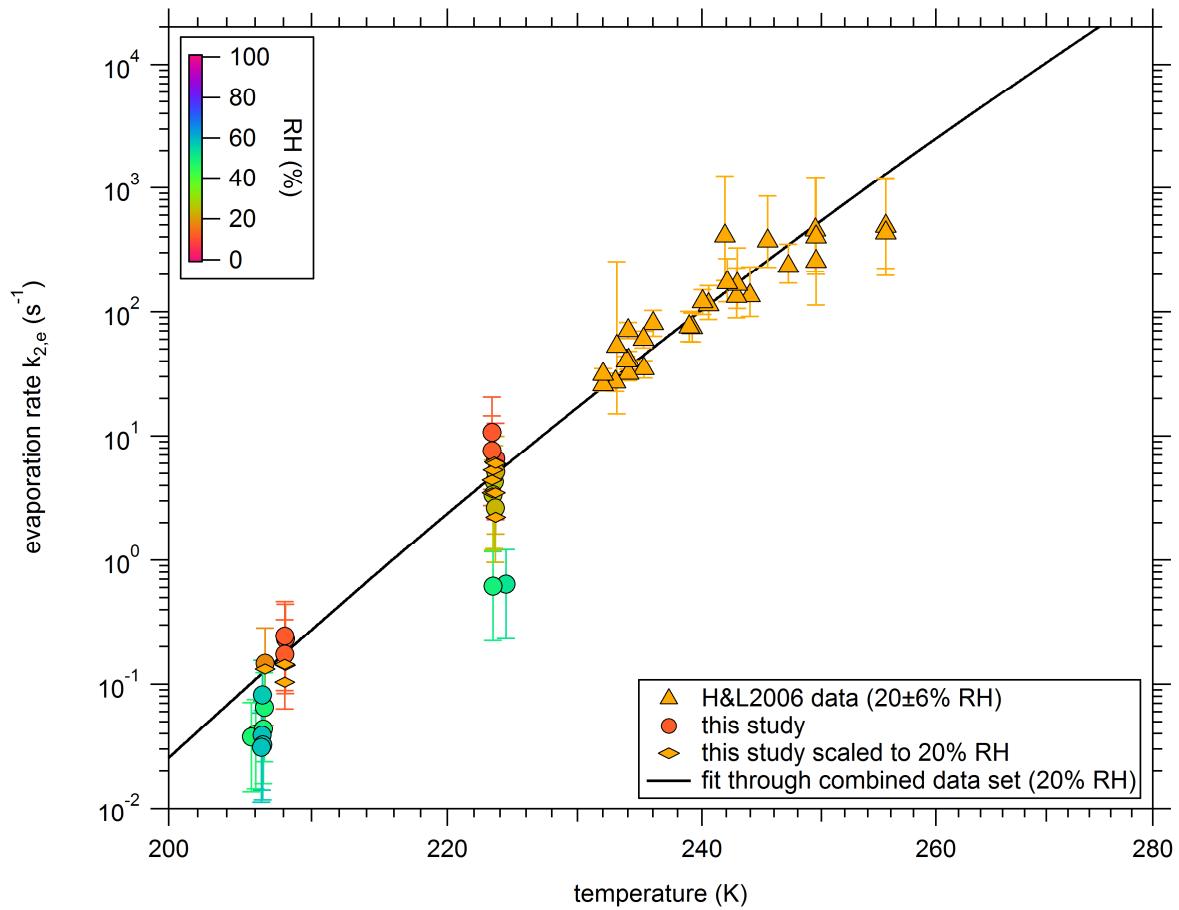
The black line in Fig. 7 shows the dimer evaporation rates derived from equation (9). The uncertainties in equation (9) are based on 95% confidence intervals. Overall, the two data sets are, within errors, consistent with one another, and yield  $dH = -20.1 \pm 1.2 \text{ kcal mol}^{-1}$  and  $dS = -46.7 \pm 5.2 \text{ cal mol}^{-1} \text{ K}^{-1}$ . 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	$dH$	$dS$	$k_{2,e}$ at 208 K	$k_{2,e}$ at 223 K
	(kcal mol <sup>-1</sup> )	(cal mol <sup>-1</sup> K <sup>-1</sup> )	(s <sup>-1</sup> )	(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
$(\text{H}_2\text{SO}_4)(\text{H}_2\text{O}) + (\text{H}_2\text{SO}_4)(\text{H}_2\text{O})^a$	-17.8	-48.3	89.3	1550
$(\text{H}_2\text{SO}_4)(\text{H}_2\text{O})_2 + (\text{H}_2\text{SO}_4)(\text{H}_2\text{O})^a$	-21.1	-51.7	0.17	5.0
$(\text{H}_2\text{SO}_4)(\text{H}_2\text{O})_2 + (\text{H}_2\text{SO}_4)(\text{H}_2\text{O})_2^a$	-25.6	-55.7	$2.4 \times 10^{-5}$	$1.5 \times 10^{-3}$

**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  $dH = -20.1 \pm 1.2$  kcal mol<sup>-1</sup> and  $dS = -46.7 \pm 5.2$  cal mol<sup>-1</sup> K<sup>-1</sup> 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  $\Delta H$  and entropy  $\Delta S$  for the dimer formation. These values are determined for the first time at temperatures  $<232\text{K}$ , 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  $\text{H}_2\text{SO}_4\text{-NH}_3$  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 $\text{H}_2\text{SO}_4\text{-NH}_3$ 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  $\text{H}_2\text{SO}_4\text{-NH}_3$  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  $\text{H}_2\text{SO}_4\text{-NH}_3$  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  $\text{H}_2\text{SO}_4\bullet\text{NH}_3$  cluster formation. These errors originate from the uncertainty in the fitted data and the updated values are  $dH = -16.1 \pm 0.6 \text{ kcal mol}^{-1}$  and  $dS = -26.4 \pm 2.6 \text{ cal mol}^{-1} \text{ K}^{-1}$ .

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)  $dH = -16.1 \pm 0.6 \text{ kcal mol}^{-1}$  and  $dS = -26.4 \pm 2.6 \text{ cal mol}^{-1} \text{ K}^{-1}$  were used. The error in the positive direction (maximum dimer concentration) is calculated with  $dH = -16.1 \pm 0.6 \text{ kcal mol}^{-1}$  and  $dS = -26.4 \pm 2.6 \text{ cal mol}^{-1} \text{ K}^{-1}$ . 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  $\text{H}_2\text{SO}_4\bullet\text{NH}_3$  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.