We thank the reviewer once more for carefully reading our manuscript and for providing constructive comments, which have further 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.

The authors have addressed most of the issues raised in the first round of reviewing, and the manuscript has improved significantly. There are, however, a few important points to clarify before the manuscript can be accepted for publication.

The term "London van der Waals" is used throughout the manuscript to denote the enhancement of molecular collisions due to intermolecular interactions. While possibly the appropriate term for the large particles studied by Chan and Mozurkevich, the dominant interaction between two sulfuric acid molecules is certainly not the weak London van der Waals force (which scales as r^{-6}), but the interaction between the large (about 3 Debye) permanent dipole moments (which scales as r^{-3}). Thus, "London van der Waals" should, when discussing the specific case of sulfuric acid collisions, be replaced either by "dipole-dipole" or (should the authors prefer a more technical term), Keesom van der Waals (see for example https://en.wikipedia.org/wiki/Van_der_Waals_force). Dipole-dipole interaction is, however, more informative for large fraction of the readers.

Thanks a lot for the clarification. We decided to use the term 'dipole-dipole interaction' and replaced "London van der Waals forces" where necessary.

The computational values for single hydrates from Ding et al (2003) listed in Table 2 are not directly comparable to the experiment-based values reported in this study and by Hanson and Lovejoy. Instead the experiment-based values represent ensemble averages over the hydrate distribution of the evaporating cluster. I would recommend adding these averages to Table 2 to allow direct comparison, as they can easily be computed using the data of Ding et al. as explained for example by Paasonen et al (2012).

According to the referees' suggestion we have calculated the hydrate distribution for the sulfuric acid dimer at the temperatures of 208 and 223 K from the data by Ding et al. (2003). This calculation indicates that almost all sulfuric acid dimers contain 4 water molecules under these conditions. Therefore, the evaporation of the A_2W_4 cluster (two acid molecules A and four water molecules W) can either yield $A_1 + A_1W_4$, $A_1W_1 + A_1W_3$, or $A_1W_2 + A_1W_2$. The evaporation rates for all these reactions are now included in Table 2. The evaporation of A_1 from A_2W_4 has the highest evaporation rate and therefore dominates over the other reactions. The calculated evaporation rates are higher (by about two orders of magnitude) than the experimentally determined ones. This conclusion depends, however, strongly on the hydrate distribution of the sulfuric acid dimer. The data by Temelso et al. (2012) suggest that the sulfuric acid dimer contains on average only about 1 water molecule. The study by Henschel et al. (2014) could not be used because it only provides dG values at 298.15 K and could therefore not be applied to the lower temperatures.

We have added the missing reactions and evaporation rates reported above to Table 2. In addition the following short discussion has been added to the end of section 3.3:

"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. The data by Ding et al. (2003) suggest that almost all sulfuric acid dimers contain four water molecules at the conditions of this study. Therefore, there exist three possibilities for a sulfuric acid monomer ($H_2SO_4(H_2O)_{0-2}$) to dissociate from the dimer with four water molecules. These reactions are listed in the last three rows of Table 2, where the evaporation rates for the monomer of sulfuric acid without water have the highest values. These are about two orders of magnitude faster than the experimentally determined values. One should note, however, that the data by Temelso et al. (2012) indicate a different hydrate distribution and this will have a significant influence on the resulting effective dimer evaporation rate."

The authors should provide a plausible physico-chemical explanation for why they assume that the formation of $H_2SO_4(NO_3^-)$ would proceed at the collision rate, while $H_2SO_4(HSO_4^-)$ would not (despite a greater binding energy, a greater number of degrees of freedom, and the complete absence of any bond-breaking processes in the cluster formation reaction). Alternatively, they should at least state that there is no plausible mechanistic explanation for this assumption.

Unfortunately, we do not have an explanation for this discrepancy. Therefore, we have added the following statement to the end of section 2.4:

"We have no mechanistic explanation why the formation of $HSO_4^-(H_2SO_4)$ should proceed at a rate slower than the collision rate. Comparison with similar ion-molecule reactions shows, e.g., that the formation of $NO_3^-(H_2SO_4)$ proceeds at the collision rate (Viggiano et al., 1997), whereas this does not seem to be the case for the formation of $NO_3^-(HNO_3)$ (Viggiano et al., 1985). Uncertainties regarding the rate of formation for the $HSO_4^-(H_2SO_4)$ cluster remain and these have to be addressed in future studies."

The following reference has been added:

Viggiano, A. A., Dale, F., and Paulson, J. F.: Measurements of some stratospheric ion-molecule association rates: Implications for ion chemistry and derived HNO_3 concentrations in the stratosphere, J. Geophys. Res. Atmos., 90, D5, 7977–7984, doi: 10.1029/JD090iD05p07977, 1985.

The large uncertainties in the literature estimates of collision frequencies should be clearly stated, especially since in their response the authors state that the collision rate between H_2SO_4 and HSO_4^- is a key parameter in their mass spectrometric data analysis. Presumably the collisions parameters used by Hanson and Lovejoy in their instruments data analysis also affect Hanson and Lovejoy dataset and thus the comparison of that data to the data reported in the present manuscript. The kinetic limit is also affected by the neutral–neutral collisions frequencies as well as the wall loss rates used in the model for the molecules and clusters. Since these parameters may have rather large uncertainties, comparing the measurement data to the calculated kinetic limit cannot be used to draw solid conclusions about fundamental quantities such as collision or sticking frequencies.

Part of this comment has been dealt with in the reply to the previous comment. It is true that the kinetic limit calculation depends on the neutral-neutral collision rate but this is also the case (to the same extent) for the derived dimer evaporation rates. This has been discussed in detail in a reply to the first referee report. The wall loss rate in the CLOUD chamber is determined experimentally for H_2SO_4, therefore, the neutral-neutral collision rates used in this study are not relevant for the wall losses.

The authors should make sure they use the terms 'equilibrium' and 'steady-state' consistently: in general steady-state is any time independent situation, whereas equilibrium refer to thermodynamic equilibrium in which there no net growth flux of clusters.

We have changed the term "steady-state" to "equilibrium" where appropriate.

Specific comments:

Table 3: The wall losses (and possibly also their size dependence) in the Hanson and Eisele flow tube experiment are likely to be considerably larger than in the CLOUD experiment. Has this been taken into account in the modeling? Also it should be noted that the vapor concentration in the Hanson and Eisele experiment are so high that the evaporation is likely to play a minor role and thus even a simpler model with evaporation neglected might describe this type of experiment rather well.

The wall loss rate for H_2SO_4 in the CLOUD chamber is approximately 2×10^{-3} s^{-1}. For the flow tube experiment by Hanson and Eisele (2002) this wall loss rate can be approximated by

$$k = \frac{3.66 \cdot D}{r^2} = \frac{3.66 \cdot 0.08 \; cm^2 s^{-1}}{(4.75 \; cm)^2} = 0.014 \; s^{-1},$$

i.e., it is about a factor 7 higher compared to the conditions in CLOUD. So far we had not taken this effect into account but now we have repeated our simulations with a factor 7 higher wall loss rate. This higher wall loss rate leads to concentrations which are less than 1% lower (i.e., the results agree to within better than 99%) than what has been reported in Table 3. Therefore, we consider this effect to be marginal.

Despite the fact that Hanson and Eisele (2002) worked with a high sulfuric acid monomer concentration (1.9×10^9 cm^{-3}) evaporation is still relevant. The forward reaction rate from monomer collisions is ~1 s^{-1}, whereas the evaporation rate for the pure dimer is ~9200 s^{-1} and ~650 s^{-1} for the sulfuric acid-ammonia cluster at 265 K.

Page 15, line 20: 'normalized' should be replaced by 'interpolated'

This has been done.

3

Page 15, lines 28-31: It is somewhat confusing that the authors first refer to the quantum chemical calculations of Temelso et al. and Henschel et al. and then choose the quantum chemical data of Ding et al for their hydration model. Are the significant differences between the newer Temelso data set and the rather old Ding dataset? Why has the older Ding data been chosen?

The data by Ding et al. (2003) has been chosen because it provides data which are relevant for this study. The Ding et al. (2003) paper lists thermochemical data for the reactions $A_1W_i + A_1W_j \rightarrow A_2W_{i+j}$, whereas Temelso et al. (2012) provide the data for $A_2W_i + W_j \rightarrow A_2W_{i+j}$. Henschel et al. (2014) provide dG values only at 298.15 K, from which the evaporation rates at the low temperatures (208 and 223 K) could not be calculated.

Page 23, line 19: It should be stated that the data analysis concerning sulfuric acid-water clusters relies on the assumption that clusters containing more than two sulfuric acid molecules have negligible evaporation rates compared to the two acid clusters.

The following sentence has been added to line 19, page 23:

"This result is obtained when assuming that the evaporation of larger sulfuric acid clusters (trimer and larger) does not contribute significantly to the dimer concentration, which is the case for the conditions of this study."

Page 24, lines 3-4: to make it clear that the model has been fitted to match the date, I would reformulate the sentence 'Using the proposed model, measured dimer concentrations in the ternary system can be reproduced with a high accuracy for the conditions of this study' as 'Using the proposed model with the evaporation rate of the sulfuric acid- ammonia as a fitting parameters, the measured dimer concentrations in the ternary system can be reproduced with a high accuracy for the conditions of this study'

The sentence has been changed according to the referees' suggestion.

References:

Paasonen et al. (2012), On the formation of sulphuric acid - amine clusters in varying atmospheric conditions and its influence on atmospheric new particle formation. Atmospheric Chemistry and Physics, Vol 12, pp 9113-9133.