

We thank the referee for the constructive comments, which are added in full below (in black font). Our replies are given in blue font directly after the comments; text that has been added to the manuscript is shown in red font.

Anonymous Referee #1

This paper presents revised calculations of nucleation rate of CLOUD7 ternary nucleation of sulfuric acid-dimethyl amine-water (278 K, 38% RH, sulfuric acid concentration between $1e6$ and $3e7$ cm^{-3} and dimethylamine mixing ratio of ~ 40 pptv; shown in Almeida et al., Nature 2013), and concludes that under this base-dominant and low temperature conditions, DMA-THN takes place in kinetic regime, that is, collision-limited coagulation of clusters (without nucleation barrier; and no effects of evaporation rates for H_2SO_4 -DMA). The conditions with high concentrations of DMA and low temperatures seem to be plausible for barrier-less nucleation, although it is still difficult to conclude this with limited knowledge of thermodynamics of nucleation (e.g., BHN, THN or IIN). This recalculation is useful to the community. I suggest to tone down other conclusions and remove the simulation of atmospheric NPF with low amines (Section 3.6), as described below.

1) The authors conclude that the CLOUD7 results are consistent with Jen et al. ACP 2016 flow tube THN experiments; the latter was undertaken at a high temperature and acidic conditions ($6e9$ cm^{-3} , tens of pptv of amines, and near 300 K). If they both take place via the same collision-limited coagulation processes, this is most likely because of very different reasons. For CLOUD7, this is due to low temperature and high DMA. And for Jen et al., this is due to exceedingly high sulfuric acid (so that nucleation rates are sensitively dependent on base concentrations). To show they are consistent, the best way is to use the current nucleation algorithm to re-calculate nucleation rates using the experimental data from Jen et al. If even 0.1 pptv DMA makes nucleation kinetic (at both acidic and basic conditions and both low and high temperatures), then di-amines (Jen et al., GRL 2016) should not further enhance nucleation rates, which is not the case. Also, ammonia and amines also should not enhance nucleation (Yu et al., GRL 2012; Glasoe et al., JGR 2015). So, this is an overstatement: “using this model, the findings from the present study and the flow tube experiment can be brought into good agreement.”

First of all, we would like to clarify some of the statements made in the comment:

We do not claim that nucleation is collision-controlled for all conditions of the Jen et al. studies. The reviewer is correct that in some cases (especially at low base to acid ratios), diamines yield even higher formation rates, compared with the amines. This observation alone indicates that sulfuric acid-dimethylamine new particle formation is not entirely collision-controlled for all conditions.

The CLOUD data and the model inter-comparison show, however, that nucleation can proceed at rates that are compatible with collision-controlled nucleation. This is due to the fact that the dimethylamine mixing ratio is ~ 100 times higher (40 pptv, i.e. 1×10^9 cm^{-3}) compared with the highest sulfuric acid concentration ($\sim 1 \times 10^7$ cm^{-3}) in CLOUD. Under these conditions, the modeled cluster concentrations are essentially insensitive to the use of non-zero evaporation rates as long as these are as small as reported by Jen et al. (2016a). This is explained in section 2.5 of the manuscript, where the evaporation rates are listed.

However, when using a low DMA mixing ratio (0.1 pptv), the modeled new particle formation rates (including the evaporation rates from Jen et al., 2016a) are significantly lower than for collision-controlled nucleation (by about a factor of ~100, see Fig. 3, lower panel).

It is true however, that we have not shown yet that our model can replicate all of the flow tube results by Jen et al. (2014, 2016a, 2016b). Still, qualitatively the studies agree very well. This can, e.g., be seen from the experiments by Jen et al. (2016b) for amines and diamines. At high base to acid ratio particle formation reaches a plateau value that is similar for all the different bases. This shows that eventually, the new particle formation rates are indistinguishable from collision-controlled nucleation. Only at low base to acid ratio ($< \sim 0.5$) particle formation decreases with lower base concentrations. For these conditions, the diamines studied by Jen et al. (2016b) can actually lead to even more efficient NPF compared with DMA. However, this can probably be explained by even lower evaporation rates for some of the clusters that can still evaporate at slow rates in the sulfuric acid-DMA system ($k_{e,A1B1} = 0.1 \text{ s}^{-1}$, $k_{e,A3B1} = 1 \text{ s}^{-1}$, $k_{e,A3B2} = 1 \text{ s}^{-1}$, $k_{e,A4B1} = \infty \text{ s}^{-1}$, see section 2.5). The same can be true for the synergistic effects (interaction between amines and NH_3) reported by Glasoe et al. (2015): additional stabilization of some clusters can occur that are still not entirely stable for pure sulfuric acid-DMA nucleation at low base to acid ratio.

These points are now explained in more detail in section 3.5:

“The conditions are only such that, due to the high DMA mixing ratio, most of the clusters (including the monomer) probably contain as many DMA molecules as sulfuric acid molecules; this results in very stable cluster configurations (Ortega et al., 2012). When DMA mixing ratios are low, most sulfuric acid clusters contain, however, only a small number of DMA molecules. As these clusters can evaporate more rapidly, the overall formation rate is slowed down (Ortega et al., 2012; Hanson et al., 2017). For low base to acid ratios, it can therefore matter whether a cluster is stabilized by a dimethylamine, a diamine (Jen et al., 2016) or by both an amine and an ammonia molecule (Glasoe et al., 2015). This can explain the more efficient NPF due to diamines or the synergistic effects involving amines and ammonia at low base to acid ratios. At high base to acid ratios, the differences in the effective evaporation rates become small (Jen et al., 2016b).”

With our model we have not attempted to recalculate all of the Jen et al. (2014, 2016a, 2016b), Glasoe et al. (2015) and Hanson et al. (2017) results as this would be beyond the scope of our manuscript. Rather than this, a comparison is now performed with a formula presented by Hanson et al. (2017) that summarizes their results on sulfuric acid-DMA nucleation from the flow tube studies. This formula, i.e.,

$$J_{1.4nm} = \exp\left(-129 + \frac{16200 \text{ K}}{T}\right) \cdot \left(\frac{N_1}{\text{cm}^{-3}}\right)^3 \cdot \left(\frac{\text{DMA}}{\text{cm}^{-3}}\right)^{1.5}$$

is provided in the revised manuscript (new equation (10) in section 3.3) and a comparison between its values and the results from the present study is shown in Fig. 1 and Fig. 3, lower panel.

In addition to the changes mentioned above, to address the reviewers concern, we have attempted to highlight that the good agreement between our measurements, the model results and the flow tube study is so far only found for the conditions of high base to acid ratios (and DMA). These changes are mentioned in the following.

- We have changed the statement in the abstract

“Using this model, the findings from the present study and the flow tube experiment can be brought into good agreement.”

to

“Using this model, the findings from the present study and the flow tube experiment can be brought into good agreement for the high base to acid ratios (~100) relevant for this study.”

- Section 4:

“Even when evaporation rates for the less stable clusters are introduced in the model (Jen et al., 2016a) the resulting particle formation rates are effectively indistinguishable from the kinetic model results for CLOUD7 conditions”

Changed to:

“Even when evaporation rates for the less stable clusters are introduced in the model (Jen et al., 2016a) the resulting particle formation rates are effectively indistinguishable from the kinetic model results for CLOUD7 conditions (i.e., at the high dimethylamine to acid ratio of ~100).”

- Section 5:

“This indicates that the data from the flow tube study by Jen et al. (2016a) and from CLOUD (Kürten et al., 2014) are consistent.”

Changed to:

“This indicates that the data for sulfuric acid-dimethylamine from the flow tube study by Jen et al. (2016a) and from CLOUD (Kürten et al., 2014) are consistent for the high base to acid ratio relevant for this study (dimethylamine to sulfuric acid monomer ratio of ~100).”

2) The authors also conclude that in the boundary layer (temperature > 245K), even with 0.1 pptv level of dimethylamine, nucleation would proceed with the collision limited process. The section 3.6 is too speculative and should be removed – see below minor comments in detail, to improve the paper quality.

After including the calculated formation rates from a recently published study by Hanson et al. (2017) in Fig. 1 and Fig. 3, lower panel, the following became evident:

The Hanson et al. (2017) equation (now also included in the manuscript, see equation (10) in section 3.3) is predicting lower NPF rates for the small DMA mixing ratios compared with our

model. This indicates that there exists some uncertainty for the low DMA mixing ratios regarding nucleation as no experiments have been made at mixing ratios below 1 pptv.

Therefore, we agree with the referee and have removed Fig. 4 together with the corresponding discussion (section 3.6) from the manuscript.

3) Note, DMA is the only amine that so far CLOUD used and published, but there are other amines that can be as effective as DMA as ternary species, such as trimethylamine (Yu et al., GRL 2012; Glasoe JGR 2015; Jen GRL 2016; Hanson et al., JPC 2017), diamines (Jen GRL 2016) and even methylamine (Chen et al., EST 2017; Chen et al., JPC 2016). And these amines are present in almost everywhere in our environment at anytime, especially within the boundary layer.

We agree with this comment. From what we found from the literature, DMA and TMA behave very similar in terms of nucleation and the tested diamines (ethylene diamine, tetramethylethylene diamine and butanediamine/putrescine) seem to be at least as efficient (Jen et al., 2016b). These substances have been measured at mixing ratios above several pptv and therefore it is a very important question to what extent they are responsible for new particle formation in the atmosphere. We hope that our manuscript can stimulate further research in this direction.

4) Also, some assumptions used in this study have apparent limitations (in addition to evaporation rates at 278 K). For example, RH has significant effects on both nucleation and growth rates of sub-3 nm particles, as shown by flow tube experiments, even within a wide range of temperatures covering both CLOUD7 and Jen et al. conditions (Yu et al., 2017). Yu et al. also showed that growth rates are not constant within the sub-3 nm particle size.

It is true that RH can have a significant effect on new particle formation rates (e.g. Duplissy et al., 2016, etc.). However, the mentioned study by Yu et al. (2017) reported results for the binary system of sulfuric acid and water; base molecules were only present at contaminant level ($\text{NH}_3 < 23$ pptv, methylamine < 1.5 pptv and dimethylamine < 0.52 pptv). The influence of RH on ternary nucleation (involving sulfuric acid, water and NH_3 or amines) is far less studied. However, a recent study based on quantum chemical calculations indicates that RH has only a very small effect on new particle formation rates (only a factor of less than 1.5 over the range of 0 to 100% RH) for dimethylamine (Olenius et al., 2017).

Regarding the growth rates, the study by Yu et al. (2017) showed that the particle growth rate does not change significantly over the range from ~ 1.7 to 2.2 nm (Fig. 1 in Yu et al., 2017). For larger particles, no data were shown in their publication. However, the study by Kürten et al. (2015a) investigated the size dependency of the growth rates for collision-controlled nucleation; no significant size dependency was found within the size range for 1.7 to 3.2 nm.

The growth rate does however change with temperature and relative humidity. This can have several reasons:

- For very low temperatures (or very stable clusters), nucleation will approach the collision-controlled situation. Under such conditions, a significant contribution to growth from clusters is expected (Lehtipalo et al., 2016).

- The base contaminant can increase with higher RH as the contaminants can originate from the water supply or because of wall effects where water displaces base molecules from the chamber or flow reactor walls (e.g. Vaitinen et al., 2014).
- Additional water molecules lead to faster particle growth at higher RH because the water is brought in with the condensing sulfuric acid as sulfuric acid includes more water ligands at increasing RH (Hanson and Eisele, 2000).

While all the factors can contribute to accelerated growth at varying conditions, they indicate nothing about the size-dependency of the growth rate. As stated earlier, the growth rate size-dependency seems to be relatively weak for collision-controlled nucleation. As the data from the present study are consistent with collision-controlled nucleation and new particle formation for the sulfuric acid-dimethylamine-system has been reported to be almost insensitive to RH (Olenius et al., 2017), only brief information about RH effects has been added (to section 4):

“Water could play a role at higher relative humidities, although quantum chemical calculations suggest that it plays only a minor role in NPF for the system of sulfuric acid and dimethylamine (Olenius et al., 2017); this contrasts the sulfuric acid-water system (see e.g. Zollner et al. 2012; Duplissy et al., 2016; Yu et al., 2017).”

Possible effects of water leading to a shift in the particle size distribution are mentioned also in section 4.

5) Please provide detailed tables of variables/values/sources used in models in supporting material, including evaporation rates for clusters.

In the light of this comment, the equations from section 2.5 were moved to an appendix (Appendix A). Furthermore, a new table (Table 1) was added to the manuscript; this table indicates the evaporation rates and for what model calculations they were included.

6) Please remove redundant sentences.

It is not clear to which sentences this comment is referring to. However, in the context of other comments some statements were removed or rewritten. We hope that this adequately addresses the reviewers request.

7) Line 66: At the surface level, in fact sulfuric acid can be as high as the conditions of CLOUD7 (very frequently), and amines/ammonia are abundant (see above). Rather, the problem is high temperatures and high surface area. The question is under these conditions, the very low 0.1 pptv of DMA can make nucleation proceeding kinetically, without any other species?

As stated above (reply to comment 2), we do not claim that new particle formation is kinetic at DMA = 0.1 pptv. In addition, the evaporation rates used in the present study were derived for temperatures at ~300 K (Jen et al., 2016a), therefore, they should well represent the conditions for relatively warm conditions (see also discussion in section 4 of the manuscript).

Regarding the condensation sink, the reviewer is correct. The conditions for the simulations shown in Figure 4 (removed, see comment 2)) are rather clean (condensation sink of $2 \times 10^{-3} \text{ s}^{-1}$

¹). However, the measured condensation sink for the boreal forest in Hyytiälä/Finland are close to this value (see also reply to comment 19)). For a higher condensation sink, the expected new particle formation rates would be reduced and it is possible that this can explain the absence of nucleation even when amine mixing ratios are relatively high.

However, rather than depleting the growing clusters, the condensation sink can also have the effect of depleting the amines. Kürten et al. (2016b) have observed that the amine mixing ratios can be reduced by up to a factor 5 during new particle formation events compared to days when no nucleation is observed. As amines are not produced in the gas phase (unlike sulfuric acid), their clustering with sulfuric acid monomers and small sulfuric acid clusters/particles very likely can lead to significant reduction in the amine mixing ratios. This would indicate that new particle formation involving amines in the atmosphere could be self-limiting, i.e., after an initial burst of particles, new particle formation could be slowed down soon after when amine mixing ratios decrease. This effect could most strongly be caused by the newly formed clusters and particles that can significantly contribute to the condensation sink. However, the CS is most often determined from size-distribution measurements starting above ~3 nm and therefore does not include the newly formed clusters and smallest particles.

Since the section showing the atmospheric simulations has been removed (see comment 2 above) a short summary of this effect is added to the conclusion section (section 5):

“High time resolution (several minutes or better) for the amine measurements during nucleation events is also important. This can show, whether amines can be significantly depleted during NPF. As amines are not produced in the gas phase (unlike sulfuric acid), their clustering with sulfuric acid monomers and small sulfuric acid clusters/particles very likely can lead to a significant reduction in the amine mixing ratios (Kürten et al., 2016b). This would indicate that new particle formation involving amines in the atmosphere could be self-limiting, i.e., after an initial burst of particles, new particle formation could be slowed down soon after when amine mixing ratios decrease.”

8) Line 82: please cite Yu and Lee, EC, 2012; You et al., ACP 2014.

Done.

9) Line 88: clarify that Kirkby et al. Nature 2016 conclusion is based on CLOUD chamber studies, and this yet needs to be verified by atmospheric measurements, in pristine forests during the night, for example.

The sentence was modified as follows to clarify that the Kirkby et al. (2016) study is based on chamber experiments:

“These highly-oxygenated molecules have been found to nucleate efficiently in a chamber study even without the involvement of sulfuric acid, especially when ions take part in the nucleation process (Kirkby et al., 2016).”

10) Line 137: indicate the detection limit and time resolution of the IC method used to detect amines.

The sentence was changed to include the requested information:

“The mixing ratio of dimethylamine was determined by ion chromatography with a detection limit of 0.2 to 1 pptv at a time resolution between 70 and 210 minutes (Praplan et al., 2012; Simon et al., 2016).”

11) Line 148: “time-rate-of-change”?

The expression “time-rate-of-change” was replaced by “time derivative”.

12) Line 264: s_{ij} ?

The factor s_{ij} is 0.5 when $i = j$ and 1 otherwise. It is explained at the end of section 2.2.

13) Lines 320–327: what is the exact sulfuric acid background level (without OH)? Is it dependent on SO₂ or temperature? Why do you have to discount that sulfuric acid?

For the chemical system relevant for the present study (SO₂, O₃, H₂O and DMA without the presence of UV light) we have no evidence for significant dark production of sulfuric acid. Therefore, we consider any measured H₂SO₄ at zero UV as instrumental background. This follows also from a direct comparison between the independently calibrated nitrate CIMS (Kürten et al., 2011; Kürten et al., 2012) and nitrate CI-APi-TOF (Kürten et al., 2014). When UV light produces significant H₂SO₄ both instruments agree quite well, whereas at zero UV the CIMS showed significantly higher [H₂SO₄] compared to the CI-APi-TOF during the DMA experiments. For this reason, it is justified to subtract the CIMS background from the concentrations measured during periods with activated UV light.

The sentence in the last paragraph of section 3.1 was changed to indicate that the CIMS background was an instrumental artifact:

“However, taking into account a subtraction of this instrumental background (reaching sometimes values above $1 \times 10^6 \text{ cm}^{-3}$) leads to a shallower slope for $J_{1.7\text{nm}}$ vs. sulfuric acid and brings the corrected CIMS values in a good agreement with the sulfuric acid measured by the CI-APi-TOF.”

14) How did you know that is not "real" sulfuric acid?

See reply to previous comment.

15) Line 474: $k_{e,A1B1} = 0.1, 1, 10(?) \text{ s}^{-1}$?

We thank the reviewer a lot for realizing this mistake. The sentence should read:

“The evaporation rates considered are $k_{e,A1B1} = 0.1 \text{ s}^{-1}$, $k_{e,A3B1} = 1 \text{ s}^{-1}$ and $k_{e,A3B2} = 1 \text{ s}^{-1}$ (Jen et al., 2016a).”

16) Line 481: 40 or 20 pptv? (earlier it was mentioned as 20 pptv).

Earlier it was mentioned that DMA was always present at 20 pptv or higher. 40 pptv are an average mixing ratio.

17) Line 497: 1 pptv DMA is still larger than $5 \times 10^6 \text{ cm}^{-3}$ sulfuric acid, so this is a base dominant environment. So, this is again quite different from the Jen-ACP-2016 condition.

It is true that 1 pptv (= ca. $2.5 \times 10^7 \text{ cm}^{-3}$) of DMA is higher than $5 \times 10^6 \text{ cm}^{-3}$ of sulfuric acid; therefore, the reviewer is correct that this condition can still be considered base-dominated.

The discussion about Fig. 3, lower panel, includes now the data from Hanson et al. (2017). Their equation was included to the manuscript (new equation (10)) and corresponding data were added to Fig. 1 and Fig. 3 (lower panel). In addition, the statements about the agreement between the flow tube and the CLOUD studies were revised.

18) Line 507: Why would you assume that Hyytiälä has low DMA around 0.1 pptv, because CI-API-TOF did not measure DMA? Remove.

Sipilä et al. (2015) detected no DMA above the detection limit (0.12 pptv) of their instrument in Hyytiälä. Therefore, a mixing ratio of ~0.1 pptv can be regarded as an upper limit for this site.

A very recent study (Hemmilä et al., 2017) reported new amine measurements from Hyytiälä/Finland. While DMA was below the detection limit of the instrument (ca. 0.2 pptv), on some days up to ~3 pptv were measured in the gas phase. For trimethylamine, a monthly average of 0.1 to 0.2 pptv was reported. In the particle phase, the monthly averages ranged from around 0.5 to 4 pptv. These numbers can be taken as evidence that the mixing ratios for DMA and TMA are non-zero in Hyytiälä/Finland – at least on some days – and that their contribution to new particle formation should be considered. An earlier study from Mäkela et al. (2001) found an enrichment of DMA in particles during nucleation events.

However, as mentioned before in response to comment (2) section 3.6 was removed.

19) Line 517: $CS = 2 \times 10^{-3} \text{ s}^{-1}$ is very clean, compared to most of boundary layer conditions.

It is true that this condensation sink is rather low but it is representative of the environment for which this model study was performed. Data shown by Dada et al. (2017) indicate a condensation sink which is on average $\sim 2 \times 10^{-3} \text{ s}^{-1}$ during new particle formation event days in Hyytiälä/Finland. As section 3.6 was removed, this is, however, not further discussed in the manuscript.

20) Line 527–535: why assume DMA is anti-correlated with OH (due to OH oxidation)? In fact, atmospheric measurements, even by the authors (Kürten et al., ACP 2016; Jen et al., GRL 2017) and others (You et al., ACP 2014; Yao et al., ACP 2016), consistently showed that amines have the same diurnal cycles as ambient temperatures, higher concentrations during the day

than at night. This indicates that the main sink of amines in the atmosphere is condensation to aerosols, and not the oxidation by OH or photolysis (You et al., ACP 2014).

In line 527 we suggest that DMA can be depleted by the newly formed particles. OH oxidation would be another possibility (line 525/526). The observed diurnal cycle of amines (higher during the day) can have several reasons, e.g., stronger emissions due to elevated temperature, or some repartitioning of condensed amines from the aerosol to the gas phase. However, this would be the case for the unperturbed atmosphere (without nucleation). If new particles are formed (containing sulfuric acid), these should act as an additional sink for the amines, which could bind to the growing acidic particles. The loss rate of DMA molecules on a sulfuric acid dimer alone is ca. $1 \times 10^{-4} \text{ s}^{-1}$ (product between the collision rate, $10^{-9} \text{ cm}^3 \text{ s}^{-1}$, and a sulfuric acid dimer concentration of $1 \times 10^5 \text{ cm}^{-3}$, see Kürten et al., 2016b). Considering the total loss rate of DMA on nucleating clusters, would correspondingly increase the condensation sink for DMA significantly. Therefore, new particle formation should lead to some depletion of amines, if their mixing ratio does not strongly exceed the sulfuric acid concentration.

In addition, the mentioned publications (You et al., 2014; Kürten et al., 2016b; Yao et al., 2016) showed no clear correlation between temperature (or a clear daily pattern for most of the amines). In fact, the Yao et al. (2016) study showed a maximum for the C2-amines in the morning, which would actually be consistent with the consumption of amines by new particle formation. The other studies (You et al., 2014; Kürten et al., 2016b) showed no significant variation of any of the amines, except for the C4 and C6 amines, which peaked during mid-day. Since these data, however, showed averages over many days including days with and without nucleation it is hard to draw any solid conclusions.

21) Lines 535-541: remove.

The whole section 3.6 was removed (see comment 2 above); therefore, this comment is obsolete.

22) Lines 559–560: reword this conclusion here and at other places.

The whole sentence was deleted.

23) Line 560 and on: Please see Yu et al., JGR 2017 on RH effects on J and GR for sub-3 nm particles. Please cite this paper.

As mentioned before (reply to comment 4) we do not think that RH has a very strong effect on the new particle formation and growth rates for the conditions of the present study (sulfuric acid-dimethylamine system).

However, we have changed the paragraph in section 4 as follows:

“Water could play a role at higher relative humidities, although quantum chemical calculations suggest that it plays only a minor role in NPF for the system of sulfuric acid and dimethylamine (Olenius et al., 2017); this contrasts the sulfuric acid-water system (see e.g. Zollner et al. 2012; Duplissy et al., 2016; Yu et al., 2017). In addition, it is not exactly known how temperature influences the cluster evaporation rates (Hanson et al., 2017).”

24) Line 564 and on: Please see Hanson et al., JPC 2017. Evaporation rates are highly dependent on thermodynamics data. Cite this.

Done (see reply to comment 23).

25) Line 641: Zhao et al., 2014 – if I recall correctly, this cited study intentionally included excessively high sulfuric acid in the inlet of CIMS to see SA-DMA clusters, rather than directly measure the “existing” SA-DMA clusters from ambient air. (This is very similar to Jen et al. flow tube environment, where acid exceeds base. Interesting instrumentation mechanics, if compare cluster-CIMS vs. CI-TOF?)

It is true that some measurements in the Zhao et al. (2011) study were made when H₂SO₄ was added to the cluster-CIMS inlet. However, measurements were also made without the addition of H₂SO₄. The observed signals during these measurements were still consistent with the presence of neutral sulfuric acid amine cluster.

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We thank the referee for the constructive comments, which are added in full below (in black font). Our replies are given in blue font directly after the comments; text that has been added to the manuscript is shown in red font.

Anonymous Referee #2

The study by Kürten et al. presents a revised analysis of their previous study on new particle formation of the sulfuric acid-dimethylamine-water system. The new results show that nucleation is even faster than previously thought and that the derived nucleation rates are in agreement with model simulations. Further, they show that even tiny mixing ratios of dimethylamine are sufficient to explain significant particle nucleation in the boundary layer.

The paper is well written and suitable for publication in ACP after some minor revisions. My comments are listed below:

General comments:

1) Somewhere in the paper it should be stated what the typical concentrations/mixing ratios of dimethylamine and sulfuric acid in the boundary layer are. Are the concentrations that were used in your experiment realistic?

We agree with the referee and have added the following to the end of section 1:

“The reanalyzed data cover sulfuric acid concentrations from ca. 1×10^6 to 3×10^7 cm^{-3} , which fall into the range for most observations of atmospheric boundary layer new particle formation events (e.g. Kulmala et al., 2013). The dimethylamine mixing ratio for most of the data shown in this study is ~ 40 pptv (1×10^9 cm^{-3}), which is within the rather wide range of observations (0.1 to 157 pptv, i.e., 2.5×10^6 to 4×10^9 cm^{-3}) for C2-amines to which dimethylamine belongs to (Yao et al., 2016).”

This indicates that the concentrations of the trace gases in the present study are atmospherically relevant.

2) The difference between the Almeida et al. (2013) study and your study (same holds for the Jen et al. (2016) study) becomes not really clear from the manuscript as it is written now. If I understand your study correct your experiment is the same as the one by Almeida et al. (2013) but with an improved set-up which results in a better agreement between measurement and observations. This is of course very nice, but as you write it, it sounds like “we are doing it right and Almeida et al. did it wrong” which is not correct. I am sure they did their best at the time they performed their study. Of course, with more time and more experience as well with improving knowledge previous studies can be repeated and improved. This should be discussed more clearly and fair in the paper.

The experiment in Almeida et al. (2013) and the present study is the same. The recorded data from both studies are from the CLOUD7 experiment (conducted in fall 2012). The difference between the two studies is the method that was used to analyze the new particle formation rates. In Almeida et al. (2013) the importance of self-coagulation in the small size range (here between 1.7 nm and ~ 3.2 nm) was not known yet. The fact that these small particles have a big impact on the loss rates of the growing small particles became only clear while knowledge about the

high cluster concentrations in the sulfuric acid-dimethylamine-system increased (Kürten et al., 2014) and their impact on particle growth rates was quantified (Lehtipalo et al., 2016). In parallel, the analytical method for taking into account cluster-cluster-collisions in the derivation of new particle formation rates was developed (Kürten et al., 2015a). This allowed us to revisit the previously conducted experiment (CLOUD7 from Almeida et al., 2013) and to re-calculate the formation rates with the new knowledge and analytical tools.

The reviewer is correct, that the analysis in Almeida et al. (2013) was based on the knowledge and analytical tools that were available at that time. In fact, many of the authors of the current study were involved also in the Almeida et al. (2013) study. As knowledge progressed, we are now in a position that allows us to revisit the previously published data and improve the analysis. The results of this analysis are self-consistent, i.e., they confirm what has been concluded earlier (Kürten et al., 2014; Lehtipalo et al., 2016).

In order to avoid the impression that the Almeida et al. (2013) study and the present one are based on different experiments, we have added the following to section 1:

“New particle formation rates as a function of the sulfuric acid concentration from CLOUD7 were previously published (Almeida et al., 2013). However, these data are re-analyzed in the present study using an advanced method that takes into account the effect of self-coagulation in the estimation of new particle formation rates (Kürten et al., 2015a).“

Regarding the suggestion to add further information about the Jen et al. study, we are referring to the reply to comment 12). Information about the method used by Almeida et al. (2013) is provided in the context of comment 9).

Specific comments:

3) P2, 136: add “mobility diameter” so that it reads “... at a mobility diameter of 1.7 nm...”.

Done.

4) P2, 147: The abundances of sulfuric acid and dimethylamine are given in different units (concentrations and mixing ratio, respectively). The same unit should be used for both consequently. However, I would prefer if the amounts of both species would be given as concentration and mixing ratio.

We agree that it is sometimes confusing if the units pptv and cm^{-3} are used for different trace gases. Therefore, we decided to always provide the conversion to cm^{-3} in brackets when DMA mixing ratios are mentioned.

5) P4, 197 and 1111: What the abbreviation CLOUD is standing for should be rather given in the introduction in 197 than in 1111 of the method section.

Done.

6) P5, 1144: The brackets around the reference are obsolete.

Done.

7) P5, 1152: Same here, the brackets around the reference are obsolete.

Done.

8) P5, 1169 and 1172: Is the unit really correct? If yes, why is it $\text{cm}^{-1} \text{s}^{-0.5}$?

The unit is correct. In the equation $k_w = C_w \cdot \text{sqrt}(D)$, the value of C_w is a constant that connects the square root of the diffusivity (unit $\text{cm} \text{s}^{-0.5}$) with the wall loss rate (unit s^{-1}). Therefore, C_w needs to have the unit $\text{cm}^{-1} \text{s}^{-0.5}$.

The expression in equation (2) of the manuscript originates from Crump and Seinfeld (1981). In the original publication it is shown that the wall loss rate is proportional to $\text{sqrt}(k_e \cdot D)/L$ (where k_e is the turbulent energy dissipation rate, unit s^{-1} , and L is a characteristic length, unit cm). From this expression it follows directly that the empirical constant C_w (which combines $\text{sqrt}(k_e)/L$) has the correct unit.

9) P8, 1300: Since you compare your results to Almeida et al. (2013) it would be good if you could write more about the Almeida et al. (2013) study. How were their nucleation rates derived. What are the differences between your experiment and their experiment? Were these experimentally derived or from model simulations?

As outlined in the reply to comment 2), the experiment in Almeida et al. (2013) and in the present study is identical.

The NPF rates from Almeida et al. (2013) were not derived with a model but with equations that can be found in the literature (e.g., in Kürten et al., 2016a, JGR).

The method from Almeida et al. (2013) is now summarized at the end of section 2.3:

“The method introduced here explicitly takes into account losses that occur between particles with d_{p1} and d_{p2} (self-coagulation). These losses have not been taken into account by Almeida et al. (2013). Almeida et al. (2013) derived $J_{3.2\text{nm}}$ from CPC and SMPS measurements by including the corrections for wall loss, dilution and coagulation above 3.2 nm (see also Kürten et al., 2016a). However, the extrapolation to 1.7 nm was made by using the Kerminen and Kulmala equation (Kerminen and Kulmala, 2002), which does not include the effect of self-coagulation. For the system of sulfuric acid and dimethylamine, where a significant fraction of particles reside in the small size range, this process is, however, important.”

10) P10, 1369: Please give to the concentration the corresponding mixing ratio.

We would like to keep the unit cm^{-3} for the sulfuric acid concentration, as this is the unit that is also used in the figures and in many different other publications reporting sulfuric acid concentrations (e.g., Fiedler et al., 2005; Kuang et al., 2008; Kulmala et al., 2013; Almeida et

al., 2013; Jen et al., 2014; etc.). However, related to comment 4) we have provided the numbers in units of cm^{-3} in brackets whenever a DMA mixing ratio is given.

11) P11, L402ff: Concerning the discussion on the differences between model simulation and measurements. I would say that this part could be improved. Although I agree that the agreement is very good you should also admit that the nucleation rates from the model simulation are slightly higher than the measurements which will affect the development of the size distribution. Further, it seems that the differences between the measurements and the model simulation increase with time. Furthermore, the differences are largest at in between the two modes of the size distribution. That is not discussed at all. I would assume that this is caused by an uncertainty in the model. Is the coagulation really correctly calculated? Can't you play around a little with the model and check if the differences get larger/smaller than the nucleation rate is lower/higher (assuming according lower/higher concentrations of dimethylamine and sulfuric acid)? Even larger are the difference between the aerosol volumes, but from the discussion it sounds as that the agreement is perfect which is obviously not true.

We agree with the referee that further discussion and tests regarding the sensitivity of the model would be beneficial for the manuscript. Therefore, further model calculations were performed using the following scenarios (these calculations link to the base-case simulation from Fig. 2 in the manuscript):

- Variation of the sulfuric acid concentration by $\pm 20\%$ to investigate the effect on the evolving size distribution (Fig. 2b).
- Negligence of van der Waals forces in the simulations; van der Waals forces enhance the collision rates by roughly a factor of 2.3 for the smallest particles (Fig. 2c).
- Assumption that the particles grow by the addition of building blocks consisting of 2 dimethylamine molecules and 1 sulfuric acid molecule (2:1 ratio between base and acid, Fig. 2c) rather than due to an equal amount of acid and base (1:1 ratio).

To illustrate the results, the previous version of Fig. 2 was replaced by a new version with four panels instead of two panels (see figure on the next page). In addition, the following discussion was added to section 3.4:

“In order to test the model sensitivity to certain variations quantitatively further simulations were performed (Fig. 2b and Fig. 2c). A variation of the steady-state sulfuric acid monomer concentration by $\pm 20\%$ was achieved by using different monomer production rates for the high sulfuric acid case ($P_1 = 4.17 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$) and for the low sulfuric acid case ($P_1 = 2.01 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$, Fig. 2b). This rather small variation leads to significant mismatches between the modeled and measured size distributions that is also found for the aerosol volumes (Fig. 2d).

Two further scenarios were tested with the model. First, the enhancement due to van der Waals forces were turned off. This scenario results in significantly slower growth rates and the modeled size distributions do not match the measured ones at all anymore (Fig. 2c); the same is found when comparing modeled and measured aerosol volumes (Fig. 2d). Second, the aerosol density and the molecular weight of the condensing “monomer” were changed. In the base-case simulations (Fig. 2a), the density of dimethylaminium-bisulfate is 1470 kg m^{-3} and the molecular weight is $0.143 \text{ kg mol}^{-1}$ because a one to one ratio between DMA and sulfuric acid is assumed. Since full neutralization of sulfuric acid by DMA would require a 2:1-ratio between base and acid, collision-controlled nucleation of $(\text{H}_2\text{SO}_4)((\text{CH}_3)_2\text{NH})_2$ “monomers” instead of $(\text{H}_2\text{SO}_4)((\text{CH}_3)_2\text{NH})$ was tested. Therefore, the density was decreased by 6% to account for the density change between dimethylaminium-bisulfate and dimethylaminium-sulfate (see Qiu and

Zhang, 2011) and the molecular weight was set to $0.188 \text{ kg mol}^{-1}$. As expected, the particle growth is now slightly faster due to the additional volume added by the further DMA molecules (Fig. 2c). However, the changes are rather small and the modeled size distributions move a little further away from the measurements compared to the base case scenario (Fig. 2a).”

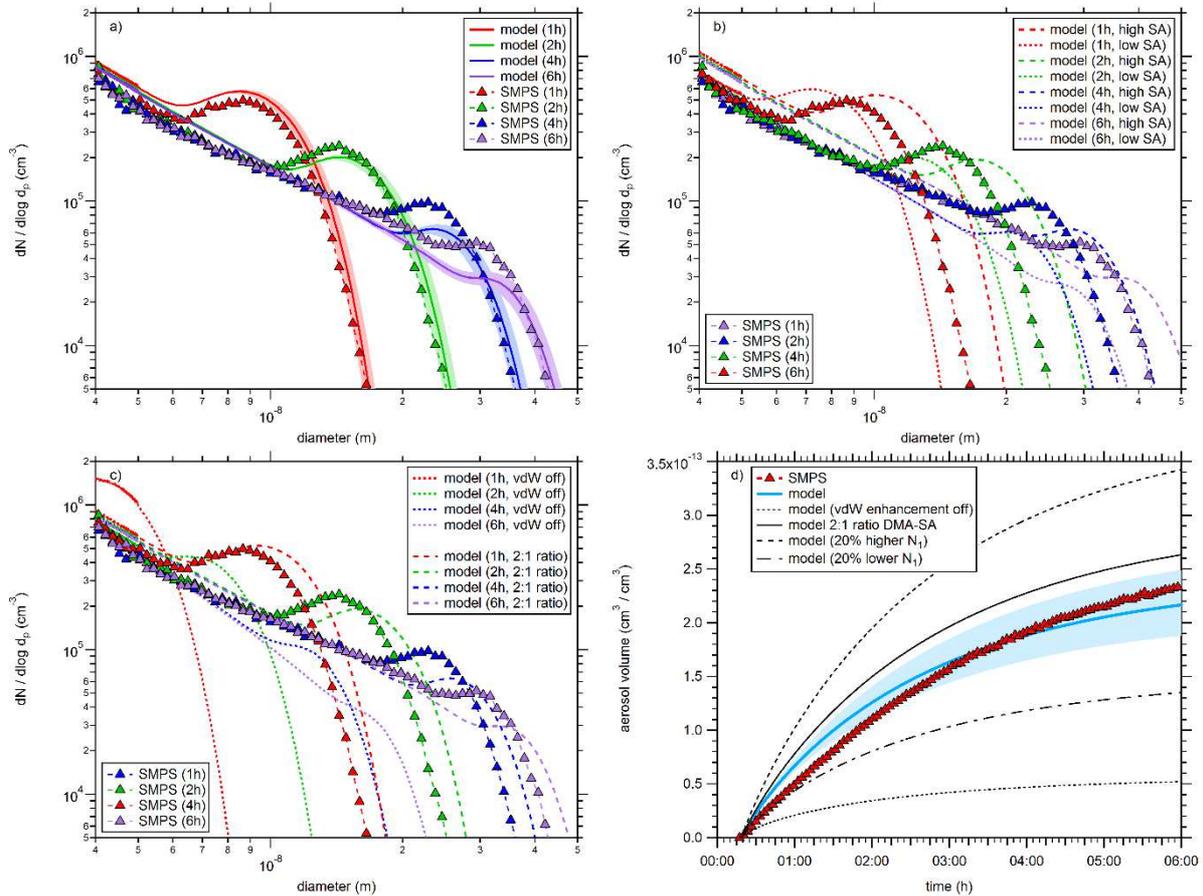


Fig 2 (replacing the previous version of Fig. 2): Comparison between modeled and measured size distributions and aerosol volumes. See text for details.

Regarding the comparison between modeled and measured aerosol volume one of the qualitative statements (“somewhat larger”) was replaced by providing the number of the actual disagreement (section 3.4):

“In the beginning of the experiment the modeled aerosol volume is up to ~40% larger than the measured one, but, towards the end of the experiment (ca. 4h after its start), the volumes agree quite well. Possibly this is because the overestimated modeled particle number density at small diameters is compensated by the underestimated particle concentration in the larger size range (see Fig. 2a).”

In addition, the statement “almost perfectly represented” is replaced by “well represented” in one of the sentences in section 3.4:

“The particle growth rate is well represented by the model given the good agreement between the positions of the local maxima in the size distribution and the intersections between the size distributions and the x -axis.”

12) P11, 1440: Same here as for the Almeida et al. (2013) study, add some more information how Jen et al. (2016) derived their nucleation rates. Was it a similar experiment as the one you performed. If no, what has been done differently etc.

The comparison between our study and the study by Jen et al. (2016a) refers to the measured and simulated clusters concentrations and not to measured new particle formation rates as these were not reported by Jen et al. (2016a, 2016b).

Jen et al. (2016) developed a model that allowed them to retrieve evaporation rates for the sulfuric acid-dimethylamine system from measured cluster signals. The signals were measured at a flow reactor after a reaction time of ~ 3 s, where the initial sulfuric acid monomer concentrations were determined prior to the mixing with the dimethylamine.

The following information was added to section 2.5:

“Within the flow tube experiments dimethylamine was mixed into a gas flow containing a known amount of sulfuric acid monomers. The products, i.e., the sulfuric acid-dimethylamine clusters were measured after a short reaction time (≤ 20 s) with a chemical ionization mass spectrometer. From the measured signals, the cluster evaporation rates were retrieved from model calculations (Jen et al., 2016a). The main differences to the CLOUD study lie within the much shorter reaction time (20 s vs. steady state in CLOUD) and in the much wider range of base to acid ratios used by Jen et al. (2016a, 2016b). This allowed them to retrieve even relatively slow evaporation rates for the sulfuric acid-dimethylamine clusters. The measured cluster/particle concentrations increased with increasing base to acid ratio, eventually approaching a plateau at a dimethylamine to acid ratio of ~ 1 . Therefore, the high dimethylamine to acid ratio used in the CLOUD7 experiment (~ 100) can probably explain why our NPF rates are compatible with collision-controlled nucleation.”

13) P11-12, 1439-478: This text part definitely belongs to the method section than to the result section.

We agree with the referee, and have moved the description of the model (that includes evaporation rates) to the methods section. Therefore, a new section (section 2.5) has been created. However, in that section only a brief overview and description of the extended model is given; the formulae are provided in Appendix A.

14) P12, 1481: The abbreviation DMA has not been introduced yet. I would suggest to keep writing dimethylamine throughout the manuscript. Otherwise, the text is quite difficult to read with all the abbreviations that are already used.

The abbreviation DMA was introduced and defined on page 7, line 230 (section 2.4). As the abbreviation DMA is also used in various other publications (Almeida et al., 2013; Jen et al., 2014; Jen et al., 2016a, etc.) we would like to keep it.

15) P14, 1529 and 1530: Please give the abundances of H₂SO₄ and dimethylamine as concentrations and mixing ratios.

[See replies to comments 4\) and 10\).](#)

16) P15, 1550: I would suggest to write: “This study confirms the results derived in previous studies.”

[Done.](#)

17) P14/P15, 1553, 1575, 1576: please give the according concentrations and mixing ratios.

[See replies to comments 4\) and 10\).](#)

18) P15, 1605: It should read “numerical model”.

[Done.](#)

19) P16, 1608-609: units for *M* and *W* missing or are these dimensionless?

[These parameters are dimensionless; they were introduced by McMurry and Li \(2017\).](#)

20) P30, Figure 3 caption: add DMA in brackets after dimethylamine. Give the abundances for H₂SO₄ and dimethylamine in both concentration and mixing ratio.

[Done \(addition of “DMA” to the figure caption\). Regarding the concentration/mixing ratio values see replies to comments 4\) and 10\).](#)

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We thank the referee for the constructive comments, which are added in full below (in black font). Our replies are given in blue font directly after the comments; text that has been added to the manuscript is shown in red font.

Anonymous Referee #3

In this study, formation rates published by Almeida et al. (2013) for ternary sulfuric acid (SA) nucleation with dimethylamine (DMA) in the CLOUD chamber are re-analyzed with a method that takes into account self-coagulation. The authors argue that particle formation rates at 1.7 nm are more than a factor of 10 higher than those reported by Almeida et al. (2013), which would imply that SA-DMA new particle formation is significant at lower DMA gas-phase concentrations than previously thought. The revised formation rates agree well with rates calculated by a kinetic aerosol model at different particle diameters. Therefore, the authors conclude that nucleation for the conditions studied here proceeds at rates that are collision-controlled.

General comments:

I think this manuscript is well written and contains some interesting results and conclusions that makes it suitable for publication in ACP. However, since the manuscript focuses mainly on a re-evaluation of particle formation rates from the paper by Almeida et al. (2013), I think more information needs to be given on the approach used by Almeida et al. for extrapolating their formation rates. I suggest that the authors add a schematic diagram or a table illustrating how 1) Almeida et al. have calculated their formation rates and 2) how the authors of the present study have calculated their formation rates. Such a diagram should also include information on what instruments were used when deriving the particle formation rates, and the necessary corrections. For instance, the authors state on lines 335-338 that Almeida et al. (2013) made an extrapolation from 3 to 1.7 nm when deriving their formation rates at 1.7 nm. How was this extrapolation done?

Furthermore, the authors of the present study use data from the smallest SMPS size channel to calculate the formation rate. As the authors admit on lines 344-345, “the smallest SMPS size channels need to be corrected by large factors to account for losses and charging probability, which introduces uncertainty”. How were these corrections made, and how large were the corrections relative to the actual measured number concentrations? In addition, the authors assume on line 366 that the growth rate is independent of size which adds more uncertainty. How large are these uncertainties compared to the “error” resulting from the extrapolation method used by Almeida et al. (2013)?

Another general comment I have is related to the fact that there is another recent study focusing on nanoparticle growth for the SA-DMA system in the CLOUD chamber by Ahlm et al. (2016), where most authors of this manuscript were co-authors. In that study, model simulations and measurements with three different instruments indicated an increasing particle-phase DMA/SA molar ratio with increasing particle size due to a decreasing Kelvin-effect of DMA with increasing size, from ~1.5 to 20 nm. The results of that study appear, at least to this reviewer, to be inconsistent with the view provided in this manuscript that nucleation and growth up to ~80 nm are completely collision-controlled. I think there needs to be some explanation, or at least, discussion of this issue.

The first comment refers to the different methods used by Almeida et al. (2013) and in the present study. To add further information regarding the Almeida et al. (2013) method was requested also by reviewer 2 (comment 9). To address this comment, the following paragraph was added to section 2.3:

“The method introduced here explicitly takes into account losses that occur between particles with d_{p1} and d_{p2} (self-coagulation). These losses have not been taken into account by Almeida et al. (2013). Almeida et al. (2013) derived $J_{3.2nm}$ from CPC and SMPS measurements by including the corrections for wall loss, dilution and coagulation above 3.2 nm (see also Kürten et al., 2016a). However, the extrapolation to 1.7 nm was made by using the Kerminen and Kulmala equation (Kerminen and Kulmala, 2002), which does not include the effect of self-coagulation. For the system of sulfuric acid and dimethylamine, where a significant fraction of particles reside in the small size range, this process is, however, important.”

We think this additional information sufficiently addresses the first part of the question and would therefore not like to add another figure to illustrate the methods.

SMPS measurements and uncertainties:

The second part of the comment addresses the SMPS measurements and the uncertainties in the Almeida et al. (2013) and the present study (especially related to the uncertainty in the growth rate).

The SMPS measurements, including the necessary corrections, are further described in the context of comment 2 (see further below).

When discussing uncertainties and errors it is important to note that Almeida et al. (2013) neglected an important process in their derivation of new particle formation rates. When particles grow from small sizes to larger sizes they are subject to several loss processes. For a chamber experiment such as CLOUD three loss processes are important: 1) coagulation, 2) wall loss, and 3) dilution. Due to these losses, the particle number concentrations (and the formation rates) decrease with particle size. Therefore, when retrieving formation rates at small diameters (d_{p1}) from measurements made at larger sizes (d_{p2}), the loss processes need to be accounted for. While Almeida et al. (2013) considered, in principle, all three loss processes; coagulation was only considered with the particles larger than d_{p2} . However, since a large fraction of particles reside in the size range between d_{p1} and d_{p2} for the sulfuric acid-dimethylamine system, their coagulation (self-coagulation) needs to be taken into account as well. The Kerminen and Kulmala equation (Kerminen and Kulmala, 2002) that was used for the correction by Almeida et al. (2013) does, however, not include this effect. This leads to a significant underestimation of the formation rates at J_{dp1} ($J_{1.7nm}$). For this reason, the method from Almeida et al. (2013) could not yield accurate formation rates, which was not known, however, at the time when the analysis was performed (see also comment 2) by referee #2). The differences between the formation rates from Almeida et al. (2013) and the ones calculated with the reconstruction method (section 2.3) can be as high as a factor of 50 (see Fig. 1).

In contrast, the error on the formation rates J_{dp1} ($J_{1.7nm}$) from the method in the present study is not of a systematic nature but is rather due to the uncertainties in the required parameters such as the growth rate. The error on the growth rate is $\pm 20\%$. On the other hand, the growth rate size-dependency found for kinetic nucleation is relatively small in the relevant diameter range

(Kürten et al., 2015a). Therefore, the systematic error caused by this effect does not cause significant deviations. For a sulfuric acid concentration $> 2 \times 10^6 \text{ cm}^{-3}$ and collision-controlled nucleation the size dependent growth rate leads to factor of less than 2 uncertainty (Kürten et al., 2015a), which is much smaller than the factor of 50 due to the use of an incomplete method.

Comparison to Ahlm et al. (2016):

The Ahlm et al. (2016) study showed that the small particles ($< \sim 5 \text{ nm}$) grow by maintaining a 1:1 ratio between base and acid. At least that is the result of the MABNAG model that was used in their study. The APi-TOF and CI-APi-TOF measurements for the charged and neutral clusters support this assumption since the number of acid and DMA molecules do roughly match each other up to a size of ca. 2 nm (see also Almeida et al., 2013; Kürten et al., 2014; Bianchi et al., 2014). For the larger particles ($d_p > 5 \text{ nm}$) and high amine mixing ratios (above ca. 40 pptv) the MABNAG model predicts base to acid ratios between 1.5 and 2, i.e., the particles are rather dimethylammonium-sulfate (2:1 ratio) than dimethylammonium-bisulfate (1:1 ratio). The Ahlm et al. (2016) simulation therefore predicts a transition from a 1:1 to a 2:1 ratio when DMA is sufficiently high and the particles reach $> 5 \text{ nm}$.

The model used in the present study makes use of the assumption that a 1:1 ratio between base and acid is maintained over the full size range. In order to test how the predicted size distribution would change for a 2:1 ratio, this scenario was modeled and the results are shown in the revised version of the manuscript (new panel in Fig. 2, panel c). As expected, the results for the 2:1 ratio simulation indicate a somewhat faster growth. However, the effect is relatively small and makes the comparison between measured and simulated size distribution less good compared to the base-case scenario (1:1 ratio between base and acid). Therefore, we do not think that from the perspective of the kinetic model it makes a significant difference whether a 1:1 or a 2:1 ratio is assumed. As for the new particle formation rates, these are almost certainly better represented by the 1:1 ratio because there is direct evidence from the measurements with the mass spectrometers that the clusters and small particles maintain this ratio up to $\sim 2 \text{ nm}$.

The following discussion was added to section 4:

“It is not yet clear what exact base to acid ratio the particles have for a given diameter. The clusters and small particles ($< \sim 2 \text{ nm}$) seem to grow by maintaining a 1:1 ratio between base and acid, which follows from measurements using mass spectrometers (Almeida et al., 2013; Kürten et al., 2014; Bianchi et al., 2014). The larger particles could eventually reach a 2:1 ratio between base and acid, especially at the DMA mixing ratios relevant for this study (Ahlm, et al., 2016). However, even when a 2:1 ratio is assumed in the model (Fig. 2c) the expected size distributions would not change significantly compared with the base-case scenario (1:1 ratio). Therefore, it is not possible from our comparisons to find out if and at what diameter a transition from 1:1 to 2:1 base to acid ratio takes place.”

Specific comments:

1. In the Almeida et al. (2013) paper, the ACDC model reproduced ternary SA-ammonia formation rates almost perfectly, but somewhat over-predicted ternary SA-DMA formation rates compared to observations in the CLOUD chamber. I think it could be worth mentioning that the conclusion within this manuscript, that ternary SA-DMA formation rates in the CLOUD

chamber were underestimated by Almeida et al., brings the formation rates much closer to predictions by the ACDC model.

We thank the referee for pointing this out. We have added the lines from the ACDC calculation in Almeida et al. (2013) to Fig. 1 for a comparison.

Furthermore, the following discussion was added to section 3.3:

“The higher formation rates are also consistent with calculations from the ACDC (Atmospheric Cluster Dynamics Code) model (McGrath et al., 2012) that were previously published in Almeida et al. (2013). Figure 1 shows the rates calculated by the ACDC model (black lines). It should be noted that these values refer to a mobility diameter of 1.2 to 1.4 nm and therefore, somewhat higher rates are expected due to the smaller diameter compared to $J_{1.7\text{nm}}$. However, the agreement between the measured and predicted rates from ACDC are now in much better agreement than before.”

2. Sect. 2.1: Please describe the SMPS measurements including corrections.

The differential mobility analyzer used for the SMPS measurements is a home-built instrument with a Kr^{85} neutralizer. The corrections required to retrieve the true particle number density for each of the size channels take into account a) the charging efficiency of the particles and b) the diffusion losses within the sampling lines, charger and the differential mobility analyzer as a function of the particle diameter.

The first correction (charging efficiency) yields a factor of ~ 50 , while the second correction (transmission efficiency) requires a factor of ~ 3.6 for the smallest diameter (4.3 nm). The values for the charging efficiency can be determined from Wiedensohler and Fissan (1988) and the transmission can be calculated from Karlsson and Martinsson (2003) using an effective length of 8.1 m and a flow rate of 1.5 liters per minute for this SMPS system.

The following was added to section 2.1:

“The SMPS uses a differential mobility analyzer built by the Paul Scherrer Institute; it includes a Kr^{85} charger to bring the particles into a charge equilibrium before they are classified. The retrieval of the particle size distributions requires corrections for the charging and the transmission efficiency, which were performed according to the literature (Wiedensohler and Fissan, 1988; Karlsson and Martinsson, 2003).”

3. Line 35: The word “advanced” is not very useful for the reader. It is better to try to explain as clearly as possible the difference between the approach used here and the method used by Almeida et al.

In principle, we agree. However, in the abstract we would not like to include too many details about the method. Therefore, the information that it is currently provided:

“...due to earlier approximations in correcting particle measurements made at larger detection threshold.”

should be sufficient. However, further information about the method used by Almeida et al. (2013) was added to the end of section 2.3.

4. Line 40: “modeled and measured size distributions show good agreement”. I think it should be mentioned that this was for one nucleation event that you studied in detail, unless you have analyzed other events as well.

Other events were tested as well and the comparison between model and measurement yielded similar results. The one nucleation event that was studied in further detail (Fig. 2) was chosen because it was one of the longest ones (duration of ~6h) and it was carried out at relatively high sulfuric acid concentrations. Therefore, the particles could grow to large diameters and the comparison between model and experiment covered a wide size range.

The following information was added to section 3.4:

“Comparison between modeled and measured size distributions yielded similar results for other experiments from CLOUD7. However, the experiment shown in Fig. 2 was carried out over a relatively long time (6 h) at high sulfuric acid concentrations. Therefore, the particles could grow to large diameters and the comparison between model and experiment covers a wide size range.”

5. Lines 137-138: To what extent was dimethylamine oxidized by OH within the chamber during these events? Were any oxidation products detected and may these have contributed to new particle formation?

To answer this question we will first estimate the expected OH concentration during the experiments (we refer to the experiment shown in Fig. 2):

The sulfuric acid monomer production rate is

$$P_1 = k_{OH+SO_2} \cdot [OH] \cdot [SO_2] \quad (1)$$

Using a value of $P_1 = 2.9 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$ (see section 3.4), $k_{OH+SO_2} = 9 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ (Atkinson et al., 2004) and $[SO_2] = 1.5 \times 10^{12} \text{ cm}^{-3}$ (60 ppbv of SO_2 were used in the experiment) the estimated OH concentration is $2.1 \times 10^4 \text{ cm}^{-3}$.

This value of OH can be used to estimate the concentration of products from the reaction between DMA and OH (assuming steady-state conditions):

$$C_{DMA+OH \text{ products}} = \frac{k_{OH+DMA} \cdot [OH] \cdot [DMA]}{k_w} \quad (2)$$

Here it is assumed that the products are “sticky”, i.e., they are irreversibly lost to the chamber walls with the rate k_w . The DMA mixing ratio (concentration) is 40 pptv ($1 \times 10^9 \text{ cm}^{-3}$), the reaction rate between OH and DMA is $6.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (Carl and Crowley, 1998) and the wall loss rate is $2 \times 10^{-3} \text{ s}^{-1}$. This results in a concentration of the products of $7 \times 10^5 \text{ cm}^{-3}$.

Compared with the concentration of DMA ($1 \times 10^9 \text{ cm}^{-3}$), the concentration of the products is less than one per mille; compared with the sulfuric acid monomer the products amount ca. 7%.

In fact, if the products would contribute to nucleation and growth, this would even lower their concentration since an additional loss term in the denominator of equation (2) would need to be included. The low concentrations of the DMA oxidation products should therefore rule out a significant contribution to aerosol nucleation and growth during CLOUD.

This is further supported by the fact that no DMA oxidation products were detected in the sulfuric acid clusters measured by the CI-APi-TOF.

In the atmosphere, [OH] can be a factor of ~100 times higher than in the current study. This can lead to higher concentrations of oxidation products of DMA. However, as these products were not observed in CLOUD we have no evidence of their impact on nucleation or growth.

6. Line 321: How high is “relatively high”, and how do the authors know there was no sulfuric acid in the chamber? Do the authors think this is a general problem with using a CIMS for measuring sulfuric acid?

The sulfuric acid background was sometimes higher than $1 \times 10^6 \text{ cm}^{-3}$, while it is usually in the range of $1 \times 10^5 \text{ cm}^{-3}$ for the CIMS instrument. During the DMA experiments in CLOUD 7 there was, however, an instrumental problem with the CIMS, which caused the high background. The measurements made with the CI-APi-TOF verified that the high background was not real, i.e., it did not originate from the CLOUD chamber. This is now mentioned in section 3.1 and the value of the high sulfuric acid background is provided. In principle, however, the CIMS is a great instrument that measured H_2SO_4 reliably during many CLOUD experiments.

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1 **New particle formation in the sulfuric acid-dimethylamine-water system:**
2 **Reevaluation of CLOUD chamber measurements and comparison to an**
3 **aerosol nucleation and growth model**

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5
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30 **Abstract**

31

32 A recent CLOUD (Cosmics Leaving OUtdoor Droplets) chamber study showed that sulfuric
33 acid and dimethylamine produce new aerosols very efficiently, and yield particle formation
34 rates that are compatible with boundary layer observations. These previously published new
35 particle formation (NPF) rates are re-analyzed in the present study with an advanced method.
36 The results show that the NPF rates at 1.7 nm are more than a factor of 10 faster than previously
37 published due to earlier approximations in correcting particle measurements made at larger
38 detection threshold. The revised NPF rates agree almost perfectly with calculated rates from a
39 kinetic aerosol model at different sizes (1.7 nm and 4.3 nm mobility diameter). In addition,
40 modeled and measured size distributions show good agreement over a wide range (up to ca. 30
41 nm). Furthermore, the aerosol model is modified such that evaporation rates for some clusters
42 can be taken into account; these evaporation rates were previously published from a flow tube
43 study. Using this model, the findings from the present study and the flow tube experiment can
44 be brought into good agreement **for the high base to acid ratios (~100) relevant for this study**.
45 This confirms that nucleation proceeds at rates that are compatible with collision-controlled
46 (a.k.a. kinetically-controlled) new particle formation for the conditions during the CLOUD7
47 experiment (278 K, 38% RH, sulfuric acid concentration between 1×10^6 and 3×10^7 cm^{-3} and
48 dimethylamine mixing ratio of ~40 pptv, **i.e., 1×10^9 cm^{-3}**).

49 1. INTRODUCTION

50

51 The formation of new particles by gas-to-particle conversion (nucleation or new particle
52 formation, NPF) is important for a variety of atmospheric processes and for human health.

53 It has been shown in numerous studies that sulfuric acid (H_2SO_4) is often associated with
54 NPF (Weber et al., 1997; Kulmala et al., 2004; Fiedler et al., 2005; Kuang et al., 2008; Kirkby
55 et al., 2011) and indeed it can explain some of the observed particle formation together with
56 water vapor for neutral (uncharged) and ion-induced conditions when temperatures are low,
57 e.g., in the free troposphere (Lee et al., 2003; Lovejoy et al., 2004; Duplissy et al., 2016; Ehrhart
58 et al., 2016; Dunne et al., 2016). However, at least one additional stabilizing compound is
59 required in order to explain boundary layer nucleation at warm temperatures. Acid-base
60 nucleation, which involves a ternary compound, e.g., ammonia, besides sulfuric acid and water,
61 can lead to much higher NPF rates compared to the binary system (Weber et al., 1998; Ball et
62 al., 1999; Kürten et al., 2016a). Nevertheless, for most conditions close to the surface, the
63 concentrations of H_2SO_4 and NH_3 are too low, or temperatures are too high, to allow significant
64 ternary nucleation of these compounds (Kirkby et al., 2011; Kürten et al., 2016a). However, the
65 substitution of ammonia by amines, e.g., dimethylamine ($((\text{CH}_3)_2\text{NH})$), leads to NPF rates that
66 can explain the atmospheric observations over a wide range of sulfuric acid concentrations,
67 even when the amine mixing ratios are in the low pptv-range (Kurtén et al., 2008; Nadykto et
68 al., 2011; Ortega et al., 2012; Chen et al., 2012; Almeida et al., 2013; Glasoe et al., 2015). A
69 recent study even showed that NPF is collision-controlled, i.e., that it proceeds at the maximum
70 possible speed (Rao and McMurry, 1989), when amine mixing ratios are above ~ 20 pptv (5×10^8
71 cm^{-3}), and sulfuric acid concentrations are between $1 \times 10^6 \text{ cm}^{-3}$ and $3 \times 10^7 \text{ cm}^{-3}$ at 278 K and
72 38% RH (Kürten et al., 2014). Indications that NPF can be collision-limited were reported more
73 than 30 years ago based on the analysis of chamber nucleation experiments (McMurry, 1980),
74 although the involvement of amines, which were probably present as a contaminant during
75 those experiments, was not considered. Indications that atmospheric nucleation might occur by
76 a collision-limited process have also been previously presented (Weber et al., 1996). Despite
77 the strong evidence that sulfuric acid-amine nucleation is very efficient, it has rarely been
78 observed in the atmosphere. Only one study has so far reported sulfuric acid-amine nucleation
79 (Zhao et al., 2011) despite amine mixing ratios of up to tens of pptv at some sites (Yu and Lee,
80 2012; You et al., 2014; Freshour et al., 2014; Yao et al., 2016). A global modelling study of
81 sulfuric acid-amine nucleation has been carried out so far (Bergman et al., 2015) applying a
82 nucleation parametrization based on the measurements of Almeida et al. (2013) and Glasoe et
83 al. (2015).

84 Atmospheric boundary layer nucleation can also be explained by the existence of highly-
85 oxygenated organic molecules (Crouse et al., 2013; Ehn et al., 2014), e.g., from α -pinene.
86 These highly-oxygenated molecules have been found to nucleate efficiently in a chamber study
87 even without the involvement of sulfuric acid, especially when ions take part in the nucleation
88 process (Kirkby et al., 2016).

89 Even though oxidized organics seem to be globally important for NPF (Jokinen et al., 2015;
90 Gordon et al., 2016; Dunne et al., 2016), the formation of new particles by sulfuric acid and
91 amines should still be considered because sulfuric acid-amine nucleation rates exceed those
92 from oxidized organics as soon as the concentrations of the precursor gases (sulfuric acid and

93 amines) are high enough (Berndt et al., 2014). Therefore, at least locally or regionally, i.e., close
94 to sources, amines should be relevant.

95 In this study, we reanalyze data from CLOUD (Cosmics Leaving OUtdoor Droplets)
96 chamber experiments conducted at CERN during October/November 2012 (CLOUD7
97 campaign). New particle formation rates as a function of the sulfuric acid concentration from
98 CLOUD7 were previously published (Almeida et al., 2013). However, these data are re-
99 analyzed in the present study using an advanced method that takes into account the effect of
100 self-coagulation in the estimation of new particle formation rates (Kürten et al., 2015a). The re-
101 analyzed data and NPF rates obtained from Scanning Mobility Particle Sizer (SMPS)
102 measurements are compared to results from a kinetic aerosol model. Modeling is also used for
103 a comparison between results from a flow tube study (Jen et al., 2016a) and CLOUD.

104 The reanalyzed data cover sulfuric acid concentrations from ca. 1×10^6 to 3×10^7 cm^{-3} , which
105 fall into the range for most observations of atmospheric boundary layer new particle formation
106 events (e.g. Kulmala et al., 2013). The dimethylamine mixing ratio for most of the data shown
107 in this study is ~ 40 pptv (1×10^9 cm^{-3}), which is within the rather wide range of observations
108 (0.1 to 157 pptv, i.e., 2.5×10^6 to 4×10^9 cm^{-3}) for C2-amines to which dimethylamine belongs to
109 (Yao et al., 2016).

110
111

112 2. METHODS

113

114 2.1 CLOUD experiment and instruments

115

116 The CLOUD (Cosmics Leaving OUtdoor Droplets) experiment at CERN was designed to
117 investigate nucleation and growth of aerosol particles in chemically diverse systems.
118 Additionally, the influence of ions on new particle formation (NPF) and growth can be studied
119 inside the 26.1 m^3 electro-polished stainless steel chamber (Kirkby et al., 2011). For the
120 experiments discussed in this paper, NPF is initiated by illuminating the air inside the chamber
121 with UV light by means of a fiber-optic system (Kupc et al., 2011), which produces sulfuric
122 acid (H_2SO_4) photolytically from reactions involving O_3 , H_2O , SO_2 and O_2 . Diluted
123 dimethylamine and sulfur dioxide are taken from gas bottles; inside the chamber, these trace
124 gases mix with clean synthetic air (i.e., O_2 and N_2 with a ratio of 21:79 from evaporated
125 cryogenic liquids). To ensure homogenous conditions, the air is mixed with magnetically driven
126 fans installed at the top and bottom of the chamber (Voigtländer et al., 2012). A thermal housing
127 controls the chamber temperature to 278.15 K within several hundredths of a degree. The
128 temperature was not varied for the experiments relevant for this study. The relative humidity
129 was kept constant at 38% by humidifying a fraction of the inflowing air with a humidification
130 system (Duplissy et al., 2016). In order to keep the pressure inside the chamber at 1.005 bar,
131 the air that is taken by the instruments has to be continuously replenished. Therefore, a flow of
132 150 l/min of the humidified air is continuously supplied to the chamber. For the sulfuric acid,
133 dimethylamine and water system, ions do not have a strong enhancing effect on the nucleation
134 rates for most conditions (Almeida et al., 2013); therefore, we do not distinguish between the
135 neutral and charged pathway in such runs.

136 A suite of instruments is connected to the CLOUD chamber to measure particles, ions,
 137 clusters and gas concentrations. A summary of these instruments is provided elsewhere (Kirkby
 138 et al., 2011; Duplissy et al., 2016). For this study, measured sulfuric acid and particle
 139 concentrations are relevant. A Chemical Ionization-Atmospheric Pressure interface-Time Of
 140 Flight Mass Spectrometer (CI-APi-TOF) was employed to measure sulfuric acid and its neutral
 141 clusters in this study (Jokinen et al., 2012; Kürten et al., 2014). The particle concentrations
 142 originate from a scanning mobility particle sizer (SMPS, Wang and Flagan, 1990), which
 143 measured the particle size distribution between ~4 and ~80 nm. The SMPS uses a differential
 144 mobility analyzer built by the Paul Scherrer Institute; it includes a Kr⁸⁵ charger to bring the
 145 particles into a charge equilibrium before they are classified. The retrieval of the particle size
 146 distributions requires corrections for the charging and the transmission efficiency, which were
 147 performed according to the literature (Wiedensohler and Fissan, 1988; Karlsson and
 148 Martinsson, 2003). The mixing ratio of dimethylamine was determined by ion chromatography
 149 with a detection limit of 0.2 to 1 pptv (5×10^6 to 2.5×10^7 cm⁻³) at a time resolution between 70
 150 and 210 minutes (Praplan et al., 2012; Simon et al., 2016).

151

152 2.2 Calculation of particle formation rates

153

154 Particle formation rates J (cm⁻³ s⁻¹) are calculated from the measured size distributions (assumed
 155 to consist of n bins). For the size bin with the index m , the rate at which particles with a diameter
 156 equal or larger than d_m are formed can be calculated according to Kürten et al., 2015a:

157

$$158 J_{\geq m} = \frac{dN_{\geq m}}{dt} + \sum_{i=m}^n (k_{w,i} \cdot N_i) + k_{dil} \cdot N_{\geq m} + \sum_{i=m}^n (\sum_{j=i}^n s_{i,j} \cdot K_{i,j} \cdot N_j \cdot N_i). \quad (1)$$

159

160 This equation takes into account the time derivative of the number density of all particles for
 161 which $d_p \geq d_m$, i.e., $N_{\geq m}$, and corrects for the effects of wall loss (size dependent wall loss rates
 162 $k_{w,i}$), dilution (dilution rate k_{dil}), and coagulation (collision frequency function $K_{i,j}$), where N_i
 163 and N_j are the particle number densities in different size bins. The rate of losses to the chamber
 164 walls can be expressed by Crump and Seinfeld, 1981:

165

$$166 k_w(d_p) = C_w \cdot \sqrt{D(d_p)}, \quad (2)$$

167

168 where $D(d_p)$ is the diffusivity of a particle of diameter d_p , which is given by the Stokes-Einstein
 169 relation (Hinds, 1999),

170

$$171 D(d_p) = \frac{k_B \cdot T \cdot C_C}{3 \cdot \pi \cdot \eta \cdot d_p}, \quad (3)$$

172

173 where k_b , T , η , are the Boltzmann constant, the temperature, and the gas viscosity, respectively.
 174 The Cunningham slip correction factor, C_C , is a function of the particle Knudsen number, $Kn =$
 175 $2\lambda/d_p$, and λ is the mean-free-path of the gas molecules. The empirically derived proportionality
 176 coefficient, C_w , depends upon the chamber dimensions and on the intensity of turbulent mixing.

177 The rate of loss of sulfuric acid to the chamber walls is generally used to characterize C_w . The
 178 diffusivity of sulfuric acid is $0.0732 \text{ cm}^2 \text{ s}^{-1}$ at 278 K and 38% RH (Hanson and Eisele, 2000).
 179 The measured life time, determined from the decay of sulfuric acid when the UV light is turned
 180 off, was 554 s (wall loss rate 0.00181 s^{-1}), with the experimentally determined diffusivity this
 181 yields a factor C_w of $0.00667 \text{ cm}^{-1} \text{ s}^{-0.5}$. However, in this study diffusivities were calculated
 182 according to equation (3), so the calculated monomer diffusivity (for a monomer with a density
 183 of 1470 kg m^{-3} and a molecular weight of $0.143 \text{ kg mol}^{-1}$, see section 2.4) required a different
 184 scaling, resulting in a value of $C_w = 0.00542 \text{ cm}^{-1} \text{ s}^{-0.5}$ that was used throughout this study.

185 Dilution is taken into account by a loss rate that is independent of size and equals $k_{\text{dil}} =$
 186 $9.6 \times 10^{-5} \text{ s}^{-1}$. Correcting for particle-particle collisions requires the calculation of the collision
 187 frequency function. We used the method from Chan and Mozurkewich (2001). This method
 188 includes the effect of enhanced collision rates through van der Waals forces. A value of
 189 $6.4 \times 10^{-20} \text{ J}$ was used for the Hamaker constant (Hamaker, 1937), leading to a maximum
 190 enhancement factor of ~ 2.3 for the smallest clusters, relative to the collision rate in the absence
 191 of van der Waals forces. The factor of 2.3 has previously been shown to give good agreement
 192 between measured and modeled cluster and particle concentrations for the chemical system of
 193 sulfuric acid and dimethylamine (Kürten et al., 2014; Lehtipalo et al., 2016). In order to consider
 194 the collisions of particles in the same size bin, a scaling factor $s_{i,j}$ is used in equation (1), which
 195 is 0.5 when $i = j$ and 1 otherwise.

196

197 **2.3 Reconstruction method**

198

199 Recently a new method was introduced, that makes it possible to retrieve new particle formation
 200 rates at sizes below the threshold of the instrument used to determine the particle number
 201 density. This method is capable of considering the effect of self-coagulation (Kürten et al.,
 202 2015a). It requires introducing new size bins below the threshold of the SMPS (termed d_{p2} in
 203 the following; d_{p2} corresponds to the index $m = 1$). The method starts by calculating the number
 204 density in the first newly introduced smaller size bin (index $m = 0$, diameter $d_{p2} - dd_p$):

205

$$206 \quad N_{m-1} = (d_{p,m} - d_{p,m-1}) \cdot \frac{J_{\geq m}}{GR_{m-1}} \approx dd_p \cdot \frac{J_{\geq m}}{GR}. \quad (4)$$

207

208 Here, the particle growth rate GR (nm s^{-1}) needs to be used as well as the difference between
 209 two adjacent size bins (dd_p). Once the number density in the newly introduced bin is known
 210 this information can be used to calculate J_{m-1} . In the further steps, the numbers N_{m-2} and J_{m-2} are
 211 calculated and so on. In this way, the size distribution can be extrapolated towards smaller and
 212 smaller sizes in a stepwise process until eventually reaching the diameter d_{p1} .

213 The method has so far only been tested against simulated data but not against measured size
 214 distributions (Kürten et al., 2015a). In this study the smallest measured SMPS diameter is $d_{p2} =$
 215 4.3 nm ; 26 new size bins with $dd_p = 0.1 \text{ nm}$ were introduced and this enabled the calculation of
 216 the NPF rates at $d_{p1} = 1.7 \text{ nm}$ in the smallest size bin. This size was chosen since previously
 217 published particle formation rates from the CLOUD experiment were reported for this diameter
 218 (e.g. Kirkby et al., 2011; Almeida et al., 2013; Riccobono et al., 2014).

219 **The method introduced here explicitly takes into account losses that occur between particles**
 220 **with d_{p1} and d_{p2} (self-coagulation). These losses have not been taken into account by Almeida**

221 et al. (2013). Almeida et al. (2013) derived $J_{3,2\text{nm}}$ from CPC and SMPS measurements by
 222 including the corrections for wall loss, dilution and coagulation above 3.2 nm (see also Kürten
 223 et al., 2016a). However, the extrapolation to 1.7 nm was made by using the Kerminen and
 224 Kulmala equation (Kerminen and Kulmala, 2002), which does not include the effect of self-
 225 coagulation. For the system of sulfuric acid and dimethylamine, where a significant fraction of
 226 particles reside in the small size range, this process is, however, important.

227

228 2.4 Kinetic new particle formation and growth model

229

230 The measured particle formation rates are compared to modeled formation rates assuming
 231 collision-limited particle formation, i.e., all clusters are not allowed to evaporate. McMurry
 232 (1980) was the first to show that number concentrations and size distributions of particles
 233 formed photochemically from SO₂ in chamber experiments (Clark and Whitby, 1975) are
 234 consistent with collision-controlled nucleation; results from updated versions of this model
 235 have recently been presented (Kürten et al., 2014; McMurry and Li, 2017). The model used
 236 here has been described previously (Kürten et al., 2014; Kürten et al., 2015a, Kürten et al.
 237 2015b) but only brief introductions were reported; therefore, more details are provided in the
 238 following.

239 As outlined in Kürten et al. (2014), collision-controlled new particle formation accurately
 240 described the measured cluster distributions for the sulfuric acid-dimethylamine system up to
 241 the pentamer (cluster containing five sulfuric acid molecules). In this model, it was assumed
 242 that the clusters consist of “monomeric” building blocks, each containing one dimethylamine
 243 and one sulfuric acid molecule. Evidence that this 1:1-ratio between base and acid is
 244 approximately maintained for the small clusters was presented from neutral and charged cluster
 245 measurements (Almeida et al., 2013; Kürten et al., 2014; Bianchi et al., 2014; Glasoe et al.,
 246 2015). The molecular weight was, therefore, chosen as 0.143 kg mol⁻¹ (sum of sulfuric acid
 247 with 0.098 kg mol⁻¹ and dimethylamine with 0.045 kg mol⁻¹), and the density as 1470 kg m⁻³
 248 (Qiu and Zhang, 2012).

249 During the reported experiments (CLOUD7 in fall 2012), dimethylamine was always present
 250 at mixing ratios above ca. 20 pptv ($5 \times 10^8 \text{ cm}^{-3}$). Dimethylamine (DMA) was supplied from a
 251 certified gas bottle and diluted with synthetic air before it was introduced into the chamber to
 252 achieve the desired mixing ratios. Sulfuric acid was generated in situ from the reactions between
 253 SO₂ and OH whenever the UV light was turned on (see section 2.1). Since the UV light intensity
 254 and the gas concentrations were kept constant throughout each individual experiment, it is
 255 justified to assume a constant monomer production rate P_1 . The equation describing the
 256 temporal development of the monomer concentration, N_1 , is

257

$$258 \frac{dN_1}{dt} = P_1 - (k_{1,w} + k_{dil} + \sum_{j=1}^{N_{max}} K_{1,j} \cdot N_j) \cdot N_1 \quad (5)$$

259

260 and, for the clusters containing two or more sulfuric acid molecules ($k \geq 2$),

261

$$262 \frac{dN_k}{dt} = \frac{1}{2} \cdot \sum_{i+j=k} K_{i,j} \cdot N_i \cdot N_j - (k_{w,k} + k_{dil} + \sum_{j=1}^N K_{k,j} \cdot N_j) \cdot N_k. \quad (6)$$

263

264 The same loss mechanisms (wall loss, dilution and coagulation) as for the calculation of the
 265 particle formation rates (section 2.2) are considered when modeling the cluster concentrations.
 266 In this study, the particle size distribution was calculated from the monomer up to a diameter
 267 of ~84 nm, which corresponds to the upper size limit of the SMPS used in CLOUD7. Tracking
 268 each individual cluster/particle up to this large size would be computationally too demanding,
 269 so the size distribution was divided into so-called molecular size bins (tracking each individual
 270 cluster), and geometric size bins, where the mid-point diameters of two neighboring size bins
 271 differ by a constant factor. The number of molecular size bins was set to 400 (which results in
 272 a diameter of ~5 nm for the largest molecular bin), while the number of geometric size bins was
 273 set to 190 with a geometric factor of 1.015 (maximum diameter of the last bin is 83.7 nm). The
 274 treatment of the geometric size bins was similar to the molecular bins, except that the collision
 275 products were distributed between the two closest size bins. Two smaller particles with
 276 diameters $d_{p,i}$ and $d_{p,j}$ generate a cluster with size

$$277 \quad d_{p,x} = (d_{p,i}^3 + d_{p,j}^3)^{1/3}. \quad (7)$$

278 If it is assumed that the collision product falls into the size range covered by the geometric bins,
 281 its diameter will be between two size bins $d_{p,k}$ and $d_{p,k+1}$. The production rate of particles with
 282 diameter $d_{p,x}$ is

$$283 \quad P_x = s_{i,j} \cdot K_{i,j} \cdot N_i \cdot N_j. \quad (8)$$

284 For the geometric size range, the resulting particles are distributed between the two bins to
 285 conserve mass, i.e.,

$$286 \quad P_k = \left(\frac{d_{p,k+1}^3 - d_{p,x}^3}{d_{p,k+1}^3 - d_{p,k}^3} \right) \cdot P_x, \quad (9a)$$

$$287 \quad P_{k+1} = \left(1 - \frac{d_{p,k+1}^3 - d_{p,x}^3}{d_{p,k+1}^3 - d_{p,k}^3} \right) \cdot P_x. \quad (9b)$$

288 When the collision product falls into the molecular size bin regime the calculation is
 289 straightforward because the diameter of the product agrees exactly with a molecular bin and
 290 does not need to be distributed between two bins (see the production term in equation (6)). In
 291 case the collision products exceed the largest bin diameter, the product is entirely assigned to
 292 the largest bin, while taking into account the scaling such that the total mass is conserved.

293 In the model, no free parameter is used as the concentration of monomers is constrained by
 294 the measurements. Therefore, the production rate P_1 is adjusted such that the resulting monomer
 295 concentration in the model matches the measured sulfuric acid concentration. The model is used
 296 to simulate the experiments for a duration of 10,000 s with a time resolution of 1 s. For the
 297 small clusters and particles this leads to a steady-state between production and loss; therefore,
 298 the resulting concentrations are essentially time-independent.

299 The model introduced here was compared with the model described in McMurry and Li
 300 (2017) and yielded almost indistinguishable results for several scenarios when the same input
 301 parameters were used. We take this as an indication that both models correctly describe

306 collision-controlled nucleation, especially since the models were independently developed and
307 do not share the same code. The model in this paper is based on defining size bins according to
308 their diameter, while the model by McMurry and Li (2017) uses particle volume.

309

310 **2.5 Nucleation and growth model involving selected evaporation rates**

311

312 Measured cluster concentrations for the sulfuric acid-dimethylamine system from flow tube
313 experiments indicated that finite evaporation rates exist for some clusters (Jen et al., 2014; Jen
314 et al., 2016a). This was supported by the observation that diamines can yield even higher
315 formation rates than amines for some conditions (Jen et al., 2016b). Within the flow tube
316 experiments dimethylamine was mixed into a gas flow containing a known amount of sulfuric
317 acid monomers. The products, i.e., the sulfuric acid-dimethylamine clusters were measured
318 after a short reaction time (≤ 20 s) with a chemical ionization mass spectrometer. From the
319 measured signals, the cluster evaporation rates were retrieved from model calculations (Jen et
320 al., 2016a). The main differences to the CLOUD study lie within the much shorter reaction time
321 (20 s vs. steady state in CLOUD) and in the much wider range of base to acid ratios used by
322 Jen et al. (2016a, 2016b). This allowed them to retrieve even relatively slow evaporation rates
323 for the sulfuric acid-dimethylamine clusters. The measured cluster/particle concentrations
324 increased with increasing base to acid ratio, eventually approaching a plateau at a
325 dimethylamine to acid ratio of ~ 1 . Therefore, the high dimethylamine to acid ratio used in the
326 CLOUD7 experiment (~ 100) can probably explain why our NPF rates are compatible with
327 collision-controlled nucleation.

328 However, this was further tested by incorporating the evaporation rates from Jen et al.
329 (2016a) in our model. For this purpose, the model described in section 2.4 was modified in a
330 way that allows retrieving the cluster concentrations of the monomer, dimer, trimer and tetramer
331 as a function of their dimethylamine content (see Appendix A). The abbreviation A_xB_y denotes
332 the concentration of a cluster containing x sulfuric acid ($x = 1$ for the monomer) and y base
333 (dimethylamine) molecules. It is assumed that $x \geq y$ for all clusters, i.e., the number of bases is
334 always smaller or equal to the number of acid molecules. The reported cluster concentrations
335 (Fig. 3) refer to the number of acid molecules in the cluster, i.e., $N_1 = A_1 + A_1B_1$, $N_2 = A_2B_1 +$
336 A_2B_2 and $N_3 = A_3B_1 + A_3B_2 + A_3B_3$.

337 The evaporation rates considered are $k_{e,A_1B_1} = 0.1 \text{ s}^{-1}$, $k_{e,A_3B_1} = 1 \text{ s}^{-1}$, $k_{e,A_3B_2} = 1 \text{ s}^{-1}$ (Jen et al.,
338 2016a). Jen et al. (2016a) suggested that the formation of stable tetramers requires at least two
339 base molecules. In this case the evaporation rate of k_{e,A_4B_1} is infinity. In the model, this was
340 solved by not taking into account the formation of clusters A_4B_1 (from A_3B_1 and A_1) at all.
341 Further details about the modeling involving evaporation rates can be found in Appendix A and
342 in Table 1, which gives a summary over the different model studies.

343

344

345 **3. RESULTS**

346

347 **3.1 Comparison between Almeida et al. (2013) and SMPS derived NPF rates**

348

349 Using the model described in section 2.4, a comparison between the previously published NPF
350 rates from Almeida et al. (2013) and the modeled rates was performed. Almeida et al. (2013)
351 derived NPF rates for a particle mobility diameter of 1.7 nm. Using a density of 1470 kg m^{-3}
352 and a molecular weight of $0.143 \text{ kg mol}^{-1}$, it can be calculated that a spherical cluster containing
353 nine monomers (nonamer) has a geometric diameter of $\sim 1.4 \text{ nm}$, i.e., a mobility diameter of 1.7
354 nm (Ku and Fernandez de la Mora, 2009, see also Appendix A); therefore, the modeled nonamer
355 formation rates were used for the comparison.

356 Figure 1 shows the modeled formation rates at 1.7 nm and the Almeida et al. (2013) data as
357 a function of the sulfuric acid concentration (which is equivalent to the monomer concentration
358 in the model, see section 2.4, since it is assumed that all sulfuric acid is bound to DMA). It can
359 be seen that the modeled NPF rates are significantly higher. This indicates that the previously
360 published formation rates underestimate the true formation rates if sulfuric acid-dimethylamine
361 nucleation is indeed proceeding at the collision-limit. Previously published results indicated
362 that this is the case (Kürten et al., 2014; Lehtipalo et al., 2016); however, we will provide further
363 evidence that this assumption accurately describes the experiments in the present study and
364 provide an explanation why Almeida et al. (2013) underestimated the formation rates.

365 It should be noted that the displayed experimental $J_{1.7\text{nm}}$ values (open red triangles in Fig. 1)
366 are identical to the values from Almeida et al. (2013), while the sulfuric acid concentration has
367 been corrected. In Almeida et al. (2013) data were shown from CLOUD4 (spring 2011) and
368 CLOUD7 (fall 2012). For consistency, the sulfuric acid concentrations from the chemical
369 ionization mass spectrometer (Kürten et al., 2011) were used, as the CI-APi-TOF was not
370 available during CLOUD4. Especially during CLOUD7, the chemical ionization mass
371 spectrometer (CIMS) showed relatively high sulfuric acid concentrations even when no sulfuric
372 acid was produced from the UV light system inside the CLOUD chamber; no correction was
373 applied for this effect in Almeida et al. (2013). However, taking into account a subtraction of
374 this instrumental background (reaching sometimes values above $1 \times 10^6 \text{ cm}^{-3}$) leads to a
375 shallower slope for $J_{1.7\text{nm}}$ vs. sulfuric acid and brings the corrected CIMS values in a good
376 agreement with the sulfuric acid measured by the CI-APi-TOF. In the present study, the data
377 from the CI-APi-TOF were used. The slope for $J_{1.7\text{nm}}$ vs. sulfuric acid now yields a value of
378 close to 2, while the previously reported value was ~ 3.7 (Almeida et al., 2013). The higher
379 value resulted from the bias in the sulfuric acid concentration and the consideration of data
380 points at low sulfuric acid concentration, where new particle formation is significantly affected
381 by losses to the chamber walls, which tends to bias the slope towards higher values (Ehrhart
382 and Curtius, 2013).

383

384 **3.2 Comparison between NPF rates from the kinetic model and SMPS measurements**

385

386 The formation rates in Almeida et al. (2013) were calculated from measured particle number
387 densities with a condensation particle counter that has a lower cut-off diameter of $\sim 3 \text{ nm}$. The
388 derivation of particle formation rates at 1.7 nm therefore required an extrapolation to the smaller
389 diameter (Kerminen and Kulmala, 2002). With the available model, we are now, in principle,
390 able to calculate NPF rates for any particle diameter and compare the result to directly measured
391 rates. This was done for the SMPS size channel corresponding to a mobility diameter of 4.3 nm
392 ($J_{4.3\text{nm}}$) with the method described in section 2.2. Using the SMPS data has the advantage that

393 the size-dependent loss rates can be accurately taken into account, which is not possible when
394 only the total (non size-resolved) concentration from a condensation particle counter is
395 available. On the other hand, the smallest SMPS size channels need to be corrected by large
396 factors to account for losses and charging probability (section 2.1), which introduces
397 uncertainty.

398 The result for $J_{4.3\text{nm}}$ is shown in Figure 1 together with the modeled particle formation rates
399 for the same diameter. The agreement between modeled and measured NPF rates is very good
400 indicating that the collision-controlled model accurately describes 4.3 nm particle production
401 rates for these experiments. This is further evidence that particles are formed at the collision-
402 limit. However, it is also an indication that the Almeida et al. (2013) data underestimate the
403 NPF rates, which is further discussed in the following section.

404

405 **3.3 Reconstruction model results**

406

407 Recently, a new method was introduced, which allows the extrapolation of NPF rates
408 determined at a larger size (d_{p2}) to a smaller diameter (d_{p1}). The advantage of that method is
409 that the effect of cluster-cluster collisions (self-coagulation) can be accurately taken into
410 account (Kürten et al., 2015a). So far, the method has not been tested for measured particle size
411 distributions. However, the effect of cluster-cluster collisions should be largest in the case of
412 collision-controlled nucleation since it results in the highest possible cluster (particle)
413 concentrations for a given production rate of nucleating molecules. Therefore, the current data
414 set is ideal for testing the new method. It requires the measured growth rate as an input
415 parameter (equation (4)); this growth rate was derived from fitting a linear curve to the mode
416 diameter determined from the SMPS size distribution (Hirsikko et al., 2005). It was then used
417 as a constant (i.e., it was assumed that it is independent of size) for the full reconstruction of
418 the size distribution, in order to obtain a formation rate at 1.7 nm. The growth rate could only
419 be accurately determined for experiments with relatively high sulfuric acid concentration
420 (above $\sim 5 \times 10^6 \text{ cm}^{-3}$); therefore, the reconstruction method was only tested for these conditions
421 (Figure 1). The comparison with the modeled formation rates at the same size (1.7 nm) shows
422 that the reconstruction method yields quite accurate results, highlighting the importance of
423 cluster-cluster collisions in this chemical system. This explains why the Almeida et al. (2013)
424 data strongly underestimate the particle formation rates.

425 While the reconstruction method gives good results in the present study, it needs to be
426 mentioned that the errors for this method can become quite large. Small inaccuracies in the
427 growth rate, can be blown up to very large uncertainties due to the non-linear nature of the
428 method. This can be seen for some of the data points with large error bars in the positive
429 direction. The errors are calculated by repeating the reconstruction with growth rates $GR \pm dGR$,
430 where dGR ($\pm 20\%$) is the error from the fitted growth rate. Therefore, the accuracy of the
431 method strongly depends on good growth rate measurements, and relies on the assumption that
432 the growth rate does not change as a function of size. This seems to be a reasonable
433 approximation for collision-controlled nucleation under the present conditions (Kürten et al.,
434 2015a), but it could be different in other chemical systems.

435 The higher formation rates are also consistent with calculations from the ACDC
436 (Atmospheric Cluster Dynamics Code) model (McGrath et al., 2012) that were previously

437 published in Almeida et al. (2013). Figure 1 shows the rates calculated by the ACDC model
 438 (black lines). It should be noted that these values refer to a mobility diameter of 1.2 to 1.4 nm
 439 and therefore, somewhat higher rates are expected due to the smaller diameter compared to
 440 $J_{1.7\text{nm}}$. However, the agreement between the measured and predicted rates from ACDC are now
 441 in much better agreement than before.

442 Hanson et al. (2017) recently reported an expression for the calculation of particle formation
 443 rates as a function of the sulfuric acid concentration, dimethylamine concentration and
 444 temperature. According to their formula the formation rate of tetramers (mobility diameter of
 445 ~ 1.4 nm, see Appendix A) follows the expression

$$447 J_{1.4\text{nm}} = \exp\left(-129 + \frac{16200\text{ K}}{T}\right) \cdot \left(\frac{N_1}{\text{cm}^{-3}}\right)^3 \cdot \left(\frac{\text{DMA}}{\text{cm}^{-3}}\right)^{1.5} \quad (10)$$

448
 449 The formation rates $J_{1.4\text{nm}}$ are shown in Fig. 1 (green line) for a DMA mixing ratio of 40 pptv
 450 ($1 \times 10^9 \text{ cm}^{-3}$) and a temperature of 278 K. At the first glance, the agreement between the
 451 experimental CLOUD data and the ACDC simulation is remarkably good. However, one should
 452 note that Hanson et al. (2017) recommended to use their equation only for DMA between 2
 453 pptv ($5 \times 10^7 \text{ cm}^{-3}$) and 16 pptv ($4 \times 10^8 \text{ cm}^{-3}$) if sulfuric acid is present between $1 \times 10^6 \text{ cm}^{-3}$ and
 454 $2 \times 10^7 \text{ cm}^{-3}$. Using the equation in this range avoids that the formation rates can exceed the
 455 kinetic limit. When using larger concentrations, the kinetic limit is eventually exceeded due to
 456 the power dependency of 3 regarding sulfuric acid and the 1.5 power dependency for DMA.
 457 Further comparison between equation (10) and the results from the present study are shown in
 458 Fig. 3 (lower panel).

460 3.4 Size distribution comparison between model and SMPS

461
 462 Further comparison between modeled and measured data was performed for one experimental
 463 run (CLOUD7 run 1036.01) in which the particles were grown to sizes beyond 20 nm.
 464 Therefore, the time-dependent cluster/particle concentrations were modeled for a monomer
 465 production rate of $2.9 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$, which results in a steady-state monomer concentration of
 466 $1.07 \times 10^7 \text{ cm}^{-3}$ for the model; this is the same as the measured sulfuric acid concentration. The
 467 measured and modeled size distributions are shown in Fig. 2 (panels a, b and c) at four different
 468 times, i.e., at 1h, 2h, 4h and 6h after the start of the experiment. Given that there is no free
 469 parameter used in the model, the agreement between the base case simulation and the
 470 measurement is very good (Fig. 2a). For the earliest time shown (1h) the modeled
 471 concentrations overestimate the measured concentrations by up to 30%, whereas for the later
 472 times (≥ 4 h) the model underestimates the measured concentrations by up to 30%. It is unclear
 473 whether these discrepancies are due to SMPS measurement uncertainties, or if the model does
 474 not include or accurately describe all the relevant processes. If, for example, the SMPS would
 475 underestimate the concentrations of the smaller particles ($< \text{ca. } 15 \text{ nm}$) and overestimate those
 476 of the larger particles, the observed difference between modeled and measured concentrations
 477 could also be explained.

478 A comparison between measured and modeled aerosol volume concentrations is shown
 479 in Fig. 2d. In order to enable direct comparison, the modeled size distribution was integrated

480 starting at 4.3 nm since the SMPS did not capture smaller particles. In the beginning of the
481 experiment the modeled aerosol volume is up to ~40% larger than the measured one, but,
482 towards the end of the experiment (ca. 4h after its start), the volumes agree quite well. Possibly
483 this is because the overestimated modeled particle number density at small diameters is
484 compensated by the underestimated particle concentration in the larger size range (see Fig. 2a).

485 This trend leads eventually to a slight underestimation of the aerosol volume by the model.

486 If one assumes that the SMPS is not responsible for the slight disagreement, then the
487 following conclusions can be drawn regarding the accuracy of the model. The particle growth
488 rate is well represented by the model given the good agreement between the positions of the
489 local maxima in the size distribution and the intersections between the size distributions and
490 the x -axis. This good agreement between measured and modeled growth rates has already been
491 demonstrated in Lehtipalo et al. (2016) for a particle diameter of 2 nm. The results shown here
492 indicate that no significant condensation of other trace gases contribute to the growth of
493 particles because, in this case, the measured particle size distributions would be shifted towards
494 larger diameters compared to the model.

495 The good agreement between model and measurement is also a confirmation of the effect of
496 van der Waals forces, when a Hamaker constant of 6.4×10^{-20} J is used, a value that has been
497 demonstrated previously to represent particle size distribution dynamics correctly (McMurry,
498 1980; Chan and Mozurkewich, 2001; Kürten et al., 2014; Lehtipalo et al., 2016). Regarding the
499 underestimation of the modeled size distribution for diameters ≥ 15 nm, one explanation could
500 be that the size-dependent particle loss rates in the CLOUD chamber are weaker than assumed
501 ($k_w \sim D^{0.5}$; see equation (2)). A weaker size dependence would lead to higher predicted particle
502 concentrations at larger sizes (Park et al., 2001). However, no evidence was found from the
503 existing CLOUD data that this is the case. Dedicated wall loss experiments could be performed
504 in the future to investigate this hypothesis further.

505 In order to test the model sensitivity to certain variations quantitatively further simulations
506 were performed (Fig. 2b and Fig. 2c). A variation of the steady-state sulfuric acid monomer
507 concentration by $\pm 20\%$ was achieved by using different monomer production rates for the high
508 sulfuric acid case ($P_1 = 4.17 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$) and for the low sulfuric acid case ($P_1 = 2.01 \times 10^5$
509 $\text{cm}^{-3} \text{ s}^{-1}$, Fig. 2b). This rather small variation leads to significant mismatches between the
510 modeled and measured size distributions that is also found for the aerosol volumes (Fig. 2d).

511 Two further scenarios were tested with the model. First, the enhancement due to van der
512 Waals forces were turned off. This scenario results in significantly slower growth rates and the
513 modeled size distributions do not match the measured ones at all anymore (Fig. 2c); the same
514 is found when comparing modeled and measured aerosol volumes (Fig. 2d). Second, the aerosol
515 density and the molecular weight of the condensing “monomer” were changed. In the base-case
516 simulations (Fig. 2a), the density of dimethylammonium-bisulfate is 1470 kg m^{-3} and the
517 molecular weight is $0.143 \text{ kg mol}^{-1}$ because a one to one ratio between DMA and sulfuric acid
518 is assumed. Since full neutralization of sulfuric acid by DMA would require a 2:1-ratio between
519 base and acid, collision-controlled nucleation of $(\text{H}_2\text{SO}_4)((\text{CH}_3)_2\text{NH})_2$ “monomers” instead of
520 $(\text{H}_2\text{SO}_4)((\text{CH}_3)_2\text{NH})$ was tested. Therefore, the density was decreased by 6% to account for the
521 density change between dimethylammonium-bisulfate and dimethylammonium-sulfate (see Qiu and
522 Zhang, 2011) and the molecular weight was set to $0.188 \text{ kg mol}^{-1}$. As expected, the particle
523 growth is now slightly faster due to the additional volume added by the further DMA molecules

524 (Fig. 2c). However, the changes are rather small and the modeled size distributions move a little
525 further away from the measurements compared to the base case scenario (Fig. 2a).

526 Comparison between modeled and measured size distributions yielded similar results for
527 other experiments from CLOUD7. However, the experiment shown in Fig. 2 was carried out
528 over a relatively long time (6 h) at high sulfuric acid concentrations. Therefore, the particles
529 could grow to large diameters and the comparison between model and experiment covers a wide
530 size range.

531

532 **3.5 Sensitivity of cluster concentrations and NPF rates regarding DMA**

533

534 The data presented in the previous sections provide evidence that the new particle formation in
535 the sulfuric acid-dimethylamine system during CLOUD7 proceeds at rates that are consistent
536 with collision-controlled nucleation, in agreement with results for this data set obtained using
537 different approaches (Kürten et al., 2014; Lehtipalo et al., 2016). In this section, we compare
538 whether for CLOUD conditions the collision-controlled assumption is consistent with the Jen
539 et al. (2016a) results that showed that some clusters evaporate at the rates given in section 2.5
540 and Table. 1.

541 For the following discussion, both versions of the nucleation and growth model (section 2.4
542 and section 2.5) were used. Figure 3 shows a comparison between calculated cluster (dimer,
543 trimer, tetramer and pentamer) concentrations using collision-controlled nucleation (section
544 2.4) and the model described in section 2.5. When a DMA mixing ratio of 40 pptv ($1 \times 10^9 \text{ cm}^{-3}$)
545 is used (this was the average mixing ratio of DMA during the CLOUD7 experiments), there is
546 almost no difference between the two scenarios. This indicates that, under the CLOUD7
547 conditions, new particle formation proceeded at almost the same rates that result for collision-
548 controlled nucleation. Nevertheless, this does not imply that all cluster evaporation rates are
549 zero. The conditions are only such that, due to the high DMA mixing ratio, most of the clusters
550 (including the monomer) probably contain as many DMA molecules as sulfuric acid molecules;
551 this results in very stable cluster configurations (Ortega et al., 2012). When DMA mixing ratios
552 are low, most sulfuric acid clusters contain, however, only a small number of DMA molecules.
553 As these clusters can evaporate more rapidly, the overall formation rate is slowed down (Ortega
554 et al., 2012; Hanson et al., 2017). For low base to acid ratios, it can therefore matter whether a
555 cluster is stabilized by a dimethylamine, a diamine (Jen et al., 2016) or by both an amine and
556 an ammonia molecule (Glasoe et al., 2015). This can explain the more efficient NPF due to
557 diamines or the synergistic effects involving amines and ammonia at low base to acid ratios. At
558 high base to acid ratios, the differences in the effective evaporation rates become small (Jen et
559 al., 2016b).

560 The effect of the dimethylamine concentration on the cluster concentrations and on the
561 particle formation rate was further investigated. The lower panel of Fig. 3 shows that the cluster
562 concentrations and the NPF rate at 1.7 nm decrease with decreasing DMA levels. The figure
563 shows the concentrations and the NPF rate normalized by the results for the collision-limit. The
564 NPF rate drops by about a factor of three when DMA is reduced to $2.5 \times 10^7 \text{ cm}^{-3}$ (~ 1 pptv).
565 Below that level, the reduction in J and in the trimer, tetramer, and pentamer concentrations is
566 approximately linear with DMA. The dimer is less affected since, in the model, its evaporation
567 rates are set to zero while the evaporating trimers contribute to the dimer concentration. From

568 this perspective, very high particle formation rates should be observed even at DMA mixing
569 ratios around 1 pptv ($2.5 \times 10^7 \text{ cm}^{-3}$), which should be almost indistinguishable from rates
570 calculated for collision-controlled nucleation. Possibilities why such high rates have so far not
571 been observed are discussed in section 4.

572 For a comparison, the expected formation rates from equation (10) are shown in Fig. 3, lower
573 panel, by the grey line. The values were scaled similar to the simulated data by setting the value
574 for 40 pptv ($1 \times 10^9 \text{ cm}^{-3}$) to 1. Although this DMA mixing ratio is outside the range for which
575 the Hanson et al. (2017) formulation is recommended for (between $5 \times 10^7 \text{ cm}^{-3}$ and $4 \times 10^8 \text{ cm}^{-3}$),
576 from Fig. 1 it can be concluded that both, the Hanson et al. (2017) equation and the kinetic
577 model agree quite well at this DMA mixing ratio. The slope of J vs. DMA seems to be, however,
578 different in the relevant range of DMA ($5 \times 10^7 \text{ cm}^{-3}$ and $4 \times 10^8 \text{ cm}^{-3}$). This is due to the fact,
579 that the model predicts a steep slope (close to the value of 1.5 in equation (10)) only for much
580 lower DMA ($< 2.5 \times 10^6 \text{ cm}^{-3}$), for higher DMA the slope flattens out and reaches eventually a
581 plateau, when the value for collision-controlled nucleation is approached. This flattening of the
582 curve is not reflected in the simple formulation from Hanson et al. (2017). However, in contrast
583 to the three constant evaporation rates used in our modeling approach, Hanson et al. (2017)
584 used a more sophisticated nucleation scheme involving many different evaporation rates, not
585 only regarding sulfuric acid but also for dimethylamine. This more complex scheme was,
586 however, not implemented in our model.

587 Further experiments are required to derive accurate values for evaporation rates in the
588 sulfuric acid-dimethylamine system; these experiments should especially target DMA
589 concentrations with low base to acid ratios (< 10).

590
591

592 4. DISCUSSION

593

594 This study confirms the results derived in previous studies that new particle formation in the
595 sulfuric acid-dimethylamine-water system can proceed at or close to the collision-controlled
596 limit (Kürten et al., 2014; Lehtipalo et al., 2016). This is the case for sulfuric acid concentrations
597 between 1×10^6 and $3 \times 10^7 \text{ cm}^{-3}$ and dimethylamine mixing ratios around 40 pptv ($1 \times 10^9 \text{ cm}^{-3}$)
598 at 278 K and 38% RH. For these conditions particle formation rates and size distributions can
599 be reproduced with high accuracy by an aerosol model that assumes that particle growth is
600 exclusively due the irreversible addition of $\text{H}_2\text{SO}_4 \cdot (\text{CH}_3)_2\text{NH}$ “monomers” and coagulation.
601 Even when evaporation rates for the less stable clusters are introduced in the model (Jen et al.,
602 2016a) the resulting particle formation rates are effectively indistinguishable from the kinetic
603 model results for CLOUD7 conditions (i.e., at the high dimethylamine to acid ratio of ~ 100).
604 The fact that the measured particle size distribution can be reproduced with good accuracy
605 shows that neither water nor other species contribute significantly to particle growth during
606 these CLOUD chamber experiments. Water could play a role at higher relative humidities,
607 although quantum chemical calculations suggest that it plays only a minor role in NPF for the
608 system of sulfuric acid and dimethylamine (Olenius et al., 2017); this contrasts the sulfuric acid-
609 water system (see e.g. Zollner et al. 2012; Duplissy et al., 2016; Yu et al., 2017). In addition, it
610 is not exactly known how temperature influences the cluster evaporation rates (Hanson et al.,
611 2017). The evaporation rates from Jen et al. (2016a) were derived at temperatures close to 300

612 K; therefore the simulation of nucleation in the CLOUD chamber (278 K) using the Jen et al.
613 (2016a) rate parameters is likely to overestimate the effect of cluster evaporation.

614 It is not yet clear what exact base to acid ratio the particles have for a given diameter. The
615 clusters and small particles ($< \sim 2$ nm) seem to grow by maintaining a 1:1 ratio between base
616 and acid, which follows from measurements using mass spectrometers (Almeida et al., 2013;
617 Kürten et al., 2014; Bianchi et al., 2014). The larger particles could eventually reach a 2:1 ratio
618 between base and acid, especially at the DMA mixing ratios relevant for this study (Ahlm, et
619 al., 2016). However, even when a 2:1 ratio is assumed in the model (Fig. 2c) the expected size
620 distributions would not change significantly compared with the base-case scenario (1:1 ratio).
621 Therefore, it is not possible from our comparisons to find out if and at what diameter a transition
622 from 1:1 to 2:1 base to acid ratio takes place.

623 The question of why sulfuric acid-amine nucleation is rarely observed in the atmosphere is
624 still open. Jen et al. (2016a) reported that clusters that contain equal numbers of dimethylamine
625 and sulfuric acid molecules are ionized at reduced efficiencies than more acidic clusters with
626 the commonly used $\text{NO}_3^-(\text{HNO}_3)_{0.2}$ reagent ions. Still, Kürten et al. (2014) observed high
627 concentrations for large clusters containing acid and base at an average ratio of 1:1. A reduced
628 detection efficiency was also reported but the reduced sensitivity (in relation to the monomer)
629 was, e.g., only a factor of 3 for the trimer containing DMA. Using the model results from section
630 3.5 the expected trimer concentration at $5 \times 10^6 \text{ cm}^{-3}$ of sulfuric acid and 1 pptv ($2.5 \times 10^7 \text{ cm}^{-3}$)
631 of DMA should be $\sim 1 \times 10^5 \text{ cm}^{-3}$. Even when the detection efficiency for the trimer was reduced
632 by a factor of 3, such a concentration should still be well above the detection limit of a CI-API-
633 TOF. However, no sulfuric acid trimers could be detected in a field study where amines were
634 present at levels above 1 pptv ($2.5 \times 10^7 \text{ cm}^{-3}$, Kürten et al., 2016b). It is, therefore, possible that
635 any amines present were not suitable for nucleation. Therefore, application of methods capable
636 of amine speciation should be applied more widely in atmospheric measurements (Place et al.,
637 2017).

638 Several CLOUD papers reported particle formation rates for a diameter of 1.7 nm. Some of
639 these published formation rates were derived from direct measurements using particle counters
640 with cut-off diameters close to 1.7 nm (Riccobono et al., 2014; Duplissy et al., 2016), while
641 other reported NPF rates were derived from process models describing the nucleation process
642 in the CLOUD chamber (Kirkby et al., 2011; Kirkby et al., 2016). Therefore, no extrapolation
643 of the NPF rates from a larger threshold diameter was performed, which could have led to an
644 underestimation due to missing self-coagulation. Besides Almeida et al. (2013), the data set
645 reported by Dunne et al. (2016) and Kürten et al. (2016a) did make use of the NPF rate
646 extrapolation method from 3.2 to 1.7 nm without taking into account the effect of self-
647 coagulation. However, the reported formation rates are, in almost all cases, considerably slower
648 than those for the collision-controlled limit at a given sulfuric acid concentration since no
649 dimethylamine was present in the CLOUD chamber (Dunne et al., 2016; Kürten et al., 2016a).
650 The chemical system in these studies was the binary system, (H_2SO_4 and H_2O) and the ternary
651 system involving ammonia. The conditions only approached the collision-controlled limit at
652 the lowest temperature (210 K) when the highest ammonia mixing ratio of ~ 6 pptv (1.5×10^8
653 cm^{-3}) was investigated (Kürten et al., 2015b). However, even under these conditions, the
654 reported rates are only about a factor of 2 slower than the collision-controlled limit (Kürten et
655 al., 2016a). This is probably related to the low acid concentrations ($\leq 3 \times 10^6 \text{ cm}^{-3}$) in these

656 experiments, where the self-coagulation effect is not as strong as at higher acid concentration
657 (see Fig. 1) when wall loss and dilution lead to decreased cluster concentrations relative to the
658 monomer. This indicates that previously published CLOUD results, other than the Almeida et
659 al. (2013) data, are most likely not significantly affected.

660 McMurry and Li (2017) have recently investigated the effect of the wall loss and dilution
661 rate on new particle formation with their **numerical** model, which uses dimensionless
662 parameters. In order to allow for a comparison between McMurry and Li (2017) and the present
663 study, information on the **dimensionless** parameters W (describing wall loss) and M (describing
664 dilution) is provided (see McMurry and Li, 2017, for the exact definitions). These parameters
665 range from 0.04 to 0.7 (W) and 2×10^{-3} to 4×10^{-2} (M) for the experiments shown in this study
666 (Fig. 1). The monomer production rate (P_1) ranges from 7×10^3 to 2×10^6 $\text{cm}^{-3} \text{s}^{-1}$.

667
668

669 5. SUMMARY AND CONCLUSIONS

670

671 New particle formation rates from CLOUD chamber measurements for the sulfuric acid-
672 dimethylamine-water system were re-analyzed. It was found that the previously published rates
673 by Almeida et al. (2013) underestimate the NPF rates by up to a factor of ~ 50 at high acid
674 concentrations ($\sim 1 \times 10^7$ cm^{-3}). The reason for this underestimation is the effect of self-
675 coagulation that contributes efficiently to the loss of small particles in the size range relevant
676 for the data analysis (between 1.7 and 3.2 nm). The previously used method for extrapolating
677 the NPF rates from 3.2 nm to 1.7 nm did not include this effect and therefore the correction
678 factors were too small. Using an advanced reconstruction method that accounts for the effect
679 of self-coagulation yields much higher NPF rates (Kürten et al., 2015a). These corrected NPF
680 rates are in good agreement with rates calculated from an aerosol model assuming collision-
681 controlled nucleation and with measured NPF rates from SMPS data. Furthermore, the model
682 can reproduce the measured size distribution with good accuracy up to ~ 30 nm.

683 Extending the aerosol model by including evaporation rates for some clusters (see Jen et al.,
684 2016a) still yields good agreement between modeled and measured CLOUD NPF rates and
685 cluster concentrations. This indicates that the data **for sulfuric acid-dimethylamine** from the
686 flow tube study by Jen et al. (2016a) and from CLOUD (Kürten et al., 2014) are consistent **for**
687 **the high base to acid ratio relevant for this study (dimethylamine to sulfuric acid monomer ratio**
688 **of ~ 100).**

689 The above findings raise some further conclusions and questions. These are in part related
690 to the rare detection of sulfuric acid-amine nucleation in the atmosphere. Only one study has so
691 far reported sulfuric acid-amine nucleation (Zhao et al., 2011). The nucleation of sulfuric acid-
692 amines could occur, however, more often than currently thought.

693

694 – It is unclear to what extent previously published atmospheric NPF rates are affected by
695 incomplete J extrapolations. Some J measurements were made at diameters close to 3 nm
696 and extrapolated to a smaller size. If self-coagulation were important, the formation rates at
697 the small sizes could be significantly underestimated, and, therefore, in reality be much
698 closer to rates consistent with collision-controlled nucleation than previously thought. In
699 such a case, DMA (or other equally effective amines) could have been responsible for

700 nucleation as they are among the most potent nucleation precursors (in combination with
701 sulfuric acid). To avoid such ambiguities, the NPF rates should, in the future, be directly
702 measured at small diameters whenever possible.

703

704 – Better gas-phase amine (base) measurements are needed. Detection limits need to reach
705 mixing ratios even below 0.1 pptv ($2.5 \times 10^6 \text{ cm}^{-3}$); ideally the methods should also be
706 capable of speciating the amines (discriminate e.g. dimethylamine from ethylamine, which
707 have the same mass when measured by mass spectrometry but probably behave differently
708 in terms of their contribution to NPF). High time resolution (several minutes or better) for
709 the amine measurements during nucleation events is also important. This can show, whether
710 amines can be significantly depleted during NPF. As amines are not produced in the gas
711 phase (unlike sulfuric acid), their clustering with sulfuric acid monomers and small sulfuric
712 acid clusters/particles very likely can lead to a significant reduction in the amine mixing
713 ratios (Kürten et al., 2016b). This would indicate that new particle formation involving
714 amines in the atmosphere could be self-limiting, i.e., after an initial burst of particles, new
715 particle formation could be slowed down soon after when amine mixing ratios decrease.

716

717 – It is not clear why no clusters containing three or more sulfuric acid molecules are frequently
718 observed during atmospheric new particle formation when amines are expected to be
719 present. This could be due to incorrect assumptions about the amine concentrations, the
720 amine identities, or a reduced detection efficiency of chemical ionization mass
721 spectrometers (Jen et al., 2016a). The potential formation of complex multi-species clusters
722 (containing sulfuric acid, amines, ammonia and oxidized organics) in the atmosphere could
723 distribute the clusters over many different identities and therefore result in concentrations
724 too low to be detected by the current instrumentation for the individual species.

725

726 The overall contribution of amines to atmospheric nucleation can only be quantified after these
727 issues are understood. Besides further atmospheric measurements, controlled laboratory
728 measurements are necessary. Of special interest are the temperature dependent evaporation
729 rates of the relevant sulfuric-acid amine (and diamine) clusters.

730 Appendix A:

731

732 Model that includes selected evaporation rates

733

734 The kinetic model described in section 2.4 was expanded in a way that allows calculating the
735 concentrations of the monomer, dimer, trimer and tetramer as a function of their dimethylamine
736 content. Here, A_xB_y denotes the concentration of a cluster containing x sulfuric acid ($x = 1$ for
737 the monomer) and y base ($y = 1$ for dimethylamine monomer) molecules; $x \geq y$ for all clusters,
738 i.e., the number of bases is always smaller or equal to the number of acid molecules. When the
739 total monomer concentration (N_1) is fixed, i.e., $A_1 = N_1 - A_1B_1$ at each time step, then the
740 following equations result, i.e., for the A_1B_1 cluster

741

$$742 \frac{dA_1B_1}{dt} = K_{1,1} \cdot B_1 \cdot A_1 - (k_{1,w} + k_{dil} + k_{e,A_1B_1} + \sum_{j=1}^{N_{max}} K_{1,j} \cdot N_j) \cdot A_1B_1, \quad (A1)$$

743

744 for the two different identities of the sulfuric acid dimer

745

$$746 \frac{dA_2B_1}{dt} = (K_{1,1} \cdot A_1 \cdot A_1B_1 + k_{e,A_3B_1} \cdot A_3B_1) - (k_{w,2} + k_{dil} + K_{1,2} \cdot B_1 + \sum_{j=1}^N K_{j,2} \cdot N_j) \cdot$$

747 $A_2B_1,$ (A2)

748

$$749 \frac{dA_2B_2}{dt} = (0.5 \cdot K_{1,1} \cdot A_1B_1 \cdot A_1B_1 + K_{1,2} \cdot B_1 \cdot A_2B_1 + k_{e,A_3B_2} \cdot A_3B_2) - (k_{w,2} + k_{dil} +$$

750 $\sum_{j=1}^N K_{j,2} \cdot N_j) \cdot A_2B_2,$ (A3)

751

752 and for the three different identities of the sulfuric acid trimer

753

$$754 \frac{dA_3B_1}{dt} = (K_{1,2} \cdot A_1 \cdot A_2B_1) - (k_{w,3} + k_{dil} + k_{e,A_3B_1} + K_{1,3} \cdot B_1 + \sum_{j=1}^N K_{j,3} \cdot N_j - K_{1,3} \cdot A_1) \cdot$$

755 $A_3B_1,$ (A4)

756

$$757 \frac{dA_3B_2}{dt} = (K_{1,2} \cdot A_1B_1 \cdot A_2B_1 + K_{1,2} \cdot A_1 \cdot A_2B_2 + K_{1,3} \cdot B_1 \cdot A_3B_1) - (k_{w,3} + k_{dil} + k_{e,A_3B_2} +$$

758 $K_{1,3} \cdot B_1 + \sum_{j=1}^N K_{j,3} \cdot N_j) \cdot A_3B_2,$ (A5)

759

$$760 \frac{dA_3B_3}{dt} = (K_{1,2} \cdot A_1B_1 \cdot A_2B_2 + K_{1,3} \cdot B_1 \cdot A_3B_2) - (k_{w,3} + k_{dil} + \sum_{j=1}^N K_{j,3} \cdot N_j) \cdot A_3B_3. \quad (A6)$$

761

762 Since the formation of stable A_4B_1 clusters is not allowed (see Jen et al., 2016), the loss due to
763 the A_1 and A_3B_1 collision is subtracted from the coagulation loss term in equation (A4).

764 Tetramers can be formed from trimers and dimers:

765

$$766 \frac{dN_4}{dt} = (K_{1,3} \cdot A_1B_1 \cdot A_3B_1 + K_{1,3} \cdot N_1 \cdot (A_3B_2 + A_3B_3) + 0.5 \cdot K_{2,2} \cdot N_2 \cdot N_2) - (k_{w,4} +$$

767 $k_{dil} + \sum_{j=1}^N K_{j,4} \cdot N_j) \cdot N_4. \quad (A7)$

768

769 Note that the formation of A_4B_1 (from A_3B_1) is not included in the formation rate for tetramers
770 (see also further below). The concentrations of larger clusters and particles are calculated with

771 the same method as described in section 2.4. The cluster concentrations reported in section 3.5
772 refer to the number of acid molecules in the cluster, i.e., $N_1 = A_1 + A_1B_1$, $N_2 = A_2B_1 + A_2B_2$ and
773 $N_3 = A_3B_1 + A_3B_2 + A_3B_3$.

774 The evaporation rates considered are $k_{e,A_1B_1} = 0.1 \text{ s}^{-1}$, $k_{e,A_3B_1} = 1 \text{ s}^{-1}$, $k_{e,A_3B_2} = 1 \text{ s}^{-1}$ (Jen et al.,
775 2016a). Pure acid clusters are assumed to evaporate rapidly (at 278 K and higher) and are,
776 therefore, not considered (Hanson and Lovejoy, 2006). Jen et al. (2016a) suggested that the
777 formation of stable tetramers requires two base molecules. Therefore, this would indicate that
778 the evaporation rate k_{e,A_4B_1} is infinity (or very fast), which is also shown by Hanson et al. (2017).
779 However, the A_4B_1 formation (and its evaporation) is not explicitly treated in equations (A4)
780 and (A7).

781 In summary, three different evaporation rates were included in this model version (equations
782 (A1) to (A7)), i.e., $k_{e,A_1B_1} = 0.1 \text{ s}^{-1}$ (cluster A_1B_1), $k_{e,A_3B_1} = 1 \text{ s}^{-1}$ (cluster A_3B_1) and $k_{e,A_3B_2} = 1$
783 s^{-1} (cluster A_3B_2). All other evaporation rates were not explicitly included in the model, i.e.,
784 their rates were assumed to be zero (except for A_4B_1 , which is assumed to be infinity). Table 1
785 gives an overview of the different model configurations used to generate the model data in the
786 figures.

787
788

789 **Calculation of particle mobility diameters**

790

791 The mobility diameter of a cluster containing i sulfuric acid molecules (and i DMA molecules)
792 can be calculated according to

$$793 \quad d_{p,i} = \left(\frac{6 \cdot i \cdot M_w}{\pi \cdot N_A \cdot \rho} \right)^{1/3} + 0.3 \cdot 10^{-9} \text{ m}. \quad (\text{A8})$$

794

795 M_w is the molecular weight of the “monomer”, i.e., $0.143 \text{ kg mol}^{-1}$, ρ is the density of 1470 kg
796 m^{-3} (see section 2.4) and N_A is the Avogadro number, i.e., $6.022 \times 10^{23} \text{ mol}^{-1}$. The addition of
797 0.3 nm in equation (A8) is used to convert the geometric diameter (first term in equation (A8))
798 to a mobility diameter (Ku and Fernandez de la Mora, 2009).

799 **DATA AVAILABILITY**

800

801 Data used in this study can be obtained by sending an email to the corresponding author.

802

803

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805

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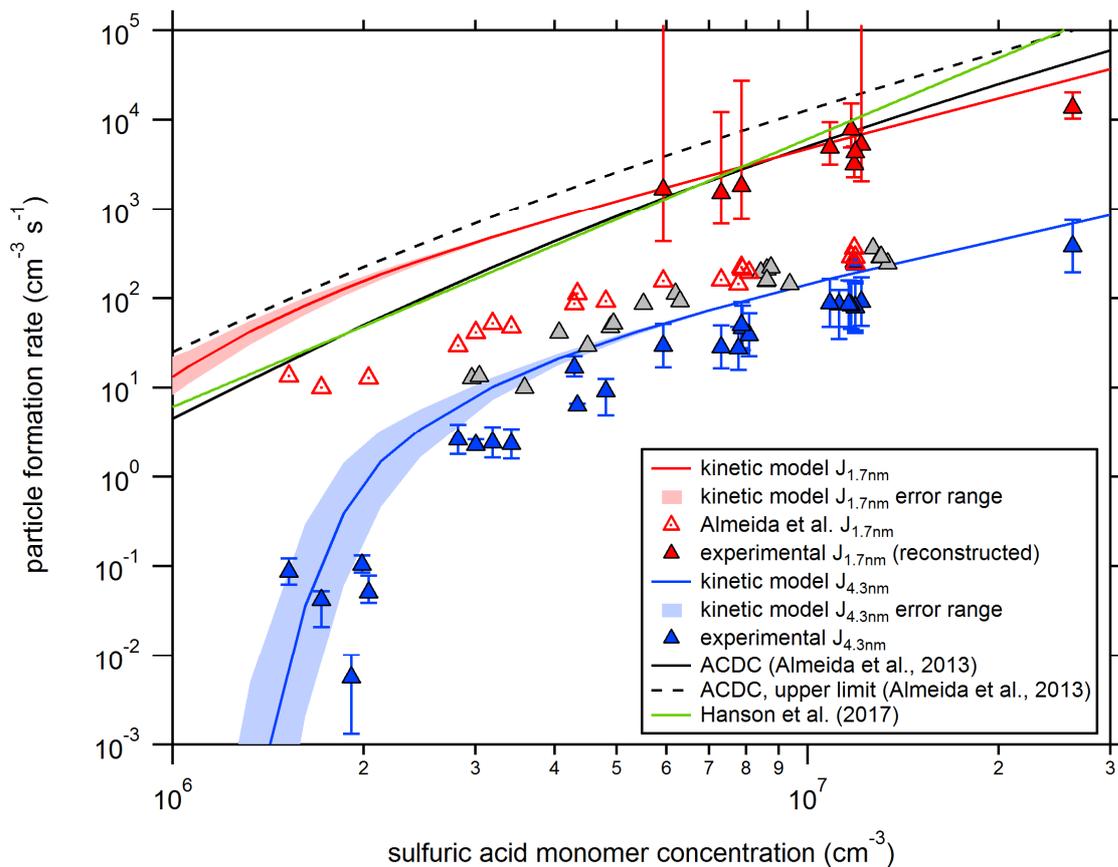
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1242 **Table 1.** Overview of the two different model versions used to generate the data in the figures.
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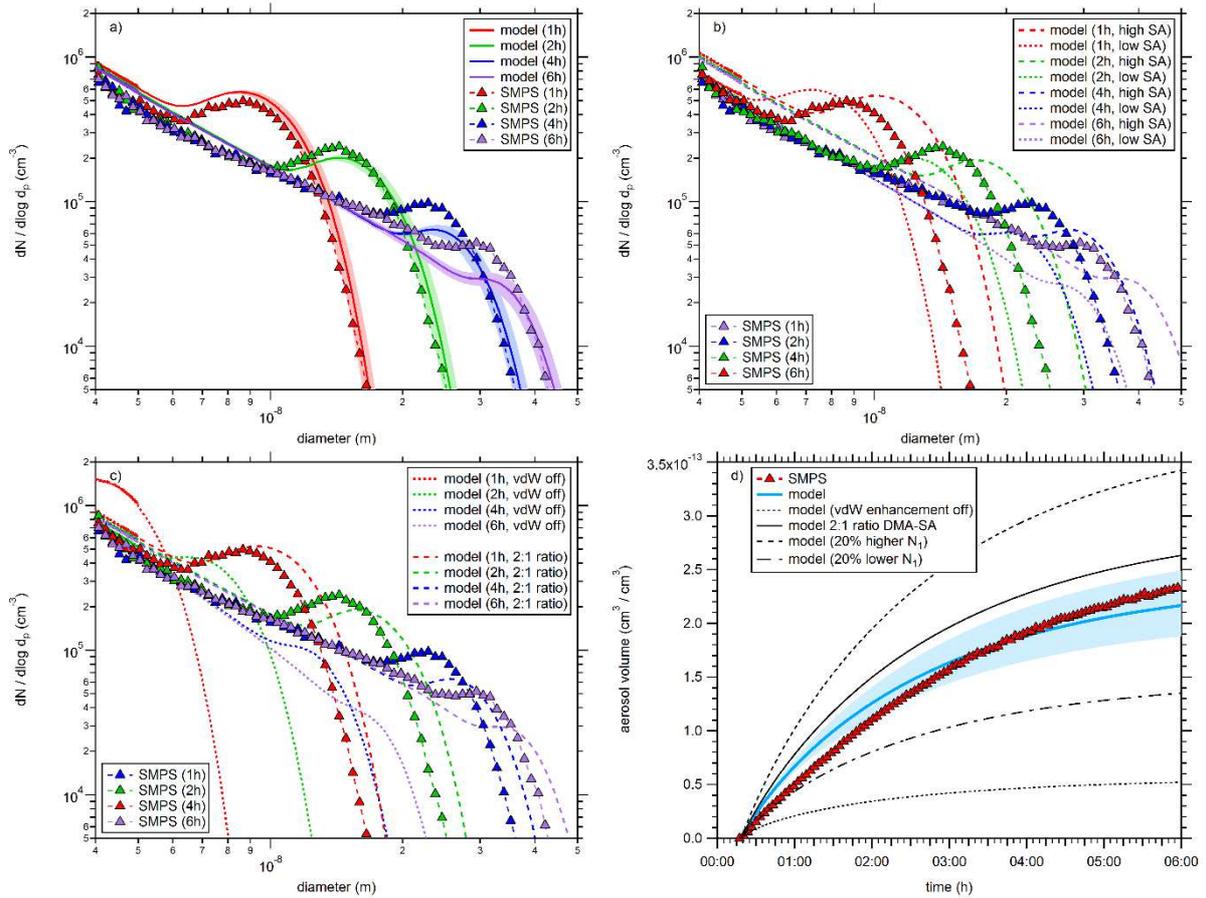
	kinetic model	model with evaporation rates
used for	Fig. 1, Fig. 2, Fig. 3 upper panel (black lines)	Fig. 3 upper panel (colored lines), Fig. 3 lower panel
described in	section 2.4	section 2.5, Appendix A
evaporation rates	all zero	$k_{e,A1B1} = 0.1 \text{ s}^{-1}$ $k_{e,A3B1} = 1 \text{ s}^{-1}$ $k_{e,A3B2} = 1 \text{ s}^{-1}$ $(k_{e,A4B1} = \infty \text{ s}^{-1})$ all others zero

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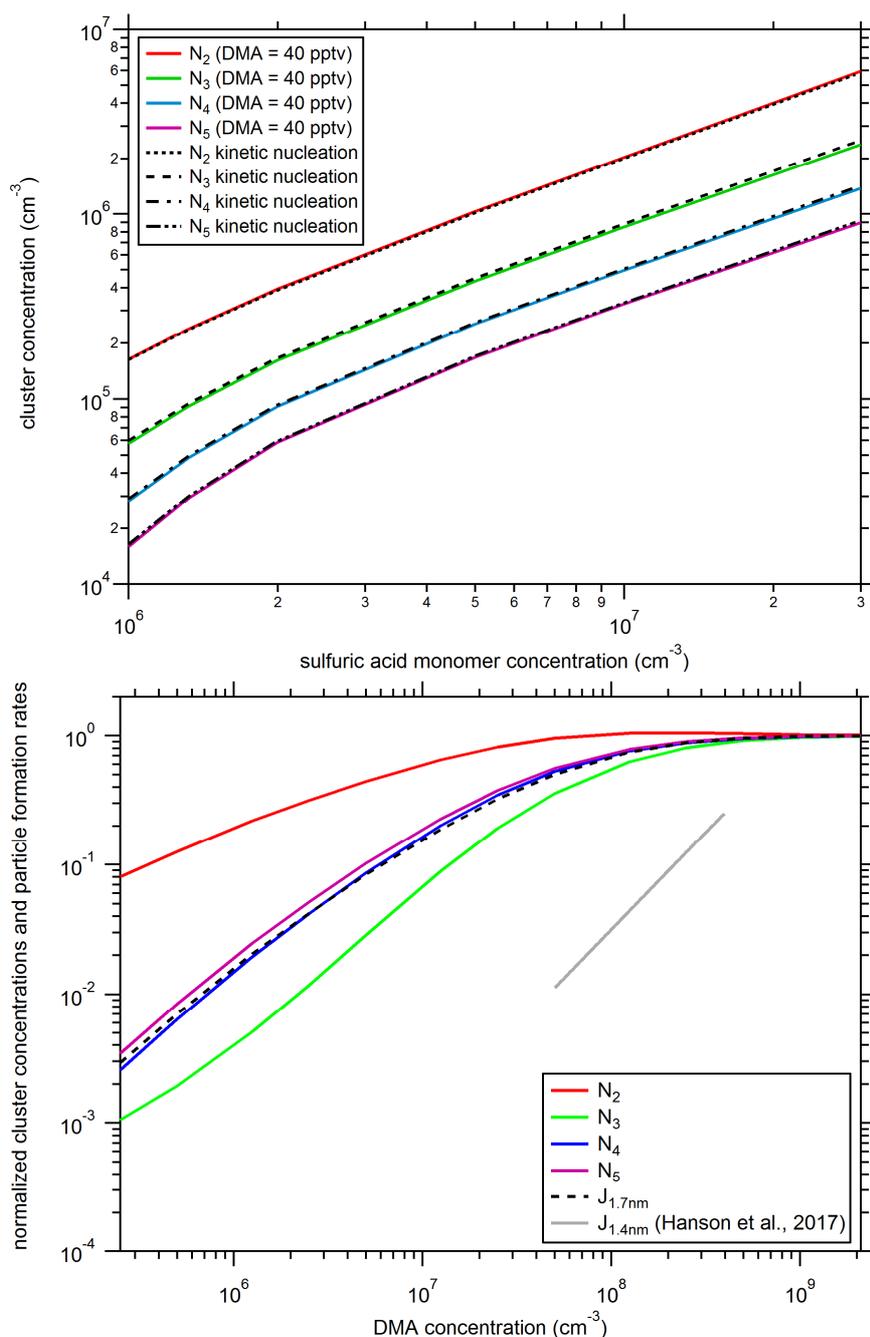
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Fig. 1. Comparison between experimental and theoretical particle formation rates at different sizes (mainly at mobility diameters of 1.7 nm and 4.3 nm). The lines indicate calculated particle formation rates from the collision-controlled aerosol model described in section 2.4 for CLOUD chamber conditions. The shaded regions show the model uncertainties when using an error of $\pm 20\%$ for the wall loss coefficient (C_w , see equation (2)). The open red symbols show previously published CLOUD7 data for the sulfuric acid-dimethylamine-water system (Almeida et al., 2013), while the blue symbols show the rates derived from SMPS size distribution measurements (this study). The data shown by the closed red symbols were derived with the method introduced by Kürten et al. (2015a) by extrapolating the SMPS data starting at 4.3 nm. The black lines show the calculated formation rates from the ACDC model for a mobility diameter of 1.2 to 1.4 nm (Almeida et al., 2013). Equation (10) from Hanson et al. (2017) is used to generate the green line.



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Fig. 2. Comparison between simulated and measured particle size distributions for one experiment (CLOUD7, run 1036.01). The comparison is shown for four different times (1h, 2h, 4h and 6h) after the start of the experiment (panels a, b and c). Panel d shows a comparison between modeled and measured aerosol volume as a function of time. The shaded regions in panel a show the model uncertainties when using an error of $\pm 20\%$ for the wall loss coefficient (C_w , see equation (2)). Panel b shows the change in the size distributions when the sulfuric acid monomer concentration is varied by $\pm 20\%$. The effect of van der Waals forces on the size distribution is shown in panel c along with the assumption that particles grow by the addition of 2 DMA and 1 sulfuric acid molecule (2:1 ratio instead of 1:1 ratio). See text for further details.



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Fig. 3. Upper panel: Comparison of modeled cluster ($N_2 =$ dimer, $N_3 =$ trimer, $N_4 =$ tetramer and $N_5 =$ pentamer) concentrations using different scenarios. The dashed black lines use the collision-controlled nucleation scheme with all evaporation rates set to zero (section 2.4); while the colored solid lines are calculated based on the model from section 2.5 with a dimethylamine (DMA) mixing ratio of 40 pptv ($1 \times 10^9 \text{ cm}^{-3}$), which was the average mixing ratio during the CLOUD7 campaign. Lower panel: Variation in modeled cluster concentration and $J_{1.7\text{nm}}$ as a function of the dimethylamine mixing ratio. The data were normalized to the values from the collision-controlled limit calculation (upper panel). For the calculations, a sulfuric acid monomer concentration of $N_1 = 5 \times 10^6 \text{ cm}^{-3}$ was used. An expression from Hanson et al. (2017) to calculate NPF rates as a function of DMA is shown by the grey line. See text for further details.