

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  $\sim 40$  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  $\sim 100$  times higher (40 pptv, i.e.  $1 \times 10^9$   $cm^{-3}$ ) 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 (< ~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  $\text{NH}_3$ ) 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  $\text{NH}_3$  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  $\sim 1.7$  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  $2 \times 10^{-3} \text{ s}^{-1}$

<sup>1</sup>). 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 SO<sub>2</sub> or temperature? Why do you have to discount that sulfuric acid?

For the chemical system relevant for the present study (SO<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O and DMA without the presence of UV light) we have no evidence for significant dark production of sulfuric acid. Therefore, we consider any measured H<sub>2</sub>SO<sub>4</sub> 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 H<sub>2</sub>SO<sub>4</sub> both instruments agree quite well, whereas at zero UV the CIMS showed significantly higher [H<sub>2</sub>SO<sub>4</sub>] 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 H<sub>2</sub>SO<sub>4</sub> was added to the cluster-CIMS inlet. However, measurements were also made without the addition of H<sub>2</sub>SO<sub>4</sub>. The observed signals during these measurements were still consistent with the presence of neutral sulfuric acid amine cluster.

## References

Almeida, J., et al.: Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere, *Nature*, 502, 359–363, doi: 10.1038/nature12663, 2013.

Chen, H., and Finlayson-Pitts, B. J.: New Particle Formation from Methanesulfonic Acid and Amines/Ammonia as a Function of Temperature, *Env. Science Technol.*, 51, 243–252, 2017.

Chen, H., et al.: Reactions of Methanesulfonic Acid with Amines and Ammonia as a Source of New Particles in Air, *J. Phys. Chem. B*, 120, 1526–1536, 2016.

Dada, L., et al.: Long-term analysis of clear-sky new particle formation events and nonevents in Hyytiälä, *Atmos. Chem. Phys.*, 17, 6227–6241, doi: 10.5194/acp-17-6227-2017, 2017.

Duplissy, J., et al.: Effect of ions on sulfuric acid-water binary particle formation II: Experimental data and comparison with QC-normalized classical nucleation theory, *J. Geophys. Res.-Atmos.*, 121, 1752–1775, doi: 10.1002/2015JD023539, 2016.

Glacoe, W. A., et al.: Sulfuric acid nucleation: An experimental study of the effect of seven bases, *J. Geophys. Res.-Atmos.*, 120, 1933–1950, doi: 10.1002/2014JD022730, 2015.

Hanson, D. R., and Eisele, F.: Diffusion of H<sub>2</sub>SO<sub>4</sub> in humidified nitrogen: Hydrated H<sub>2</sub>SO<sub>4</sub>, *J. Phys. Chem. A*, 104, 1715–1719, doi: 10.1021/jp993622j, 2000.

Hanson, D. R., et al.: Computational Fluid Dynamics Studies of a Flow Reactor: Free Energies of Clusters of Sulfuric Acid with NH<sub>3</sub> or Dimethyl Amine, *J. Phys. Chem. A*, 121, 3976–3990, doi: 10.1021/acs.jpca.7b00252, 2017.

Hemmilä, M., et al.: Amines in Boreal Forest Air at SMEAR II Station in Finland, *Atmos. Chem. Phys. Discuss.*, doi: 10.5194/acp-2017-958, in review, 2017.

Jen, C. N., et al.: Chemical ionization of clusters formed from sulfuric acid and dimethylamine or diamines, *Atmos. Chem. Phys.*, 16, 12513–12529, doi: 10.5194/acp-16-12513-2016, 2016a.

Jen, C. N., et al.: Diamine-sulfuric acid reactions are a potent source of new particle formation, *Geophys. Res. Lett.*, 43, 867–873, doi: 10.1002/2015GL066958, 2016b.

Kirkby, J., et al.: Ion-induced nucleation of pure biogenic particles, *Nature*, 533, 521–526, doi: 10.1038/nature17953, 2016.

Kürten, A., et al.: Performance of a corona ion source for measurement of sulfuric acid by chemical ionization mass spectrometry, *Atmos. Meas. Tech.*, 4, 437–443, doi: 10.5194/amt-4-437-2011, 2011.

Kürten, A., et al.: Calibration of a chemical ionization mass spectrometer for the measurement of gaseous sulfuric acid, *J. Phys. Chem. A*, 116(24), 6375–6386, doi: 10.1021/jp212123n, 2012.

Kürten, A., et al.: Neutral molecular cluster formation of sulfuric acid-dimethylamine observed in real-time under atmospheric conditions, *P. Natl. Acad. Sci. USA*, 111, 15019–15024, doi: 10.1073/pnas.1404853111, 2014.

Kürten, A., et al.: On the derivation of particle nucleation rates from experimental formation rates, *Atmos. Chem. Phys.*, 15, 4063–4075, doi: 10.5194/acp-15-4063-2015, 2015a.

Kürten, A., et al.: Observation of new particle formation and measurement of sulfuric acid, ammonia, amines and highly oxidized organic molecules at a rural site in central Germany, *Atmos. Chem. Phys.*, 16, 12793–12813, doi: 10.5194/acp-16-12793-2016, 2016b.

Lehtipalo, K., et al.: The effect of acid–base clustering and ions on the growth of atmospheric nano-particles, *Nature Commun.*, 7, 11594, doi: 10.1038/ncomms11594, 2016.

Mäkelä, J. M., et al.: Chemical composition of aerosol during particle formation events in boreal forest, *Tellus*, 53B, 380–393, doi: 10.1034/j.1600-0889.2001.530405.x, 2001.

Olenius, T., et al.: New particle formation from sulfuric acid and amines: Comparison of monomethylamine, dimethylamine, and trimethylamine, *J. Geophys. Res. Atmos.*, 122, 7103–7118, doi: 10.1002/2017JD026501, 2017.

Praplan, A. P., et al.: Dimethylamine and ammonia measurements with ion chromatography during the CLOUD4 campaign, *Atmos. Meas. Tech.*, 5, 2161–2167, doi: 10.5194/amt-5-2161-2012, 2012.

Simon, M., et al.: Detection of dimethylamine in the low pptv range using nitrate chemical ionization atmospheric pressure interface time-of-flight (CI-APi-TOF) mass spectrometry, *Atmos. Meas. Tech.*, 9, 2135–2145, doi: 10.5194/amt-9-2135-2016, 2016.

Sipilä, M., et al.: Bisulfate – cluster based atmospheric pressure chemical ionization mass spectrometer for high-sensitivity (< 100 ppqV) detection of atmospheric dimethyl amine: proof-of-concept and first ambient data from boreal forest, *Atmos. Meas. Tech.*, 8, 4001–4011, doi: 10.5194/amt-8-4001-2015, 2015.

Vaaitinen, O., et al.: Adsorption of ammonia on treated stainless steel and polymer surfaces, *Appl. Phys. B*, 115(2), 185–196, doi: 10.1007/s00340-013-5590-3, 2014.

Yao, L., et al.: Detection of atmospheric gaseous amines and amides by a high-resolution time-of-flight chemical ionization mass spectrometer with protonated ethanol reagent ions, *Atmos. Chem. Phys.*, 16, 14527–14543, doi: 10.5194/acp-16-14527-2016, 2016.

You, Y., et al.: Atmospheric amines and ammonia measured with a chemical ionization mass spectrometer (CIMS), *Atmos. Chem. Phys.*, 14, 12181–12194, doi: 10.5194/acp-14-12181-2014, 2014.

Yu, H., and Lee, S.-H.: Chemical ionisation mass spectrometry for the measurement of atmospheric amines, *Environ. Chem.*, 9, 190–201, doi: 10.1071/EN12020, 2012.

Yu, H., et al.: Effects of amines on formation of sub-3 nm particles and their subsequent growth, *Geophys. Res. Lett.*, 39, L02807, doi: 10.1029/2011GL050099, 2012.

Yu, H., et al.: Laboratory observations of temperature and humidity dependencies of nucleation and growth rates of sub-3 nm particles, *J. Geophys. Res. Atmos.*, 122, 1919–1929, doi: 10.1002/2016JD025619, 2017.

Zhao, J., et al.: Observation of neutral sulfuric acid-amine containing clusters in laboratory and ambient measurements, *Atmos. Chem. Phys.*, 11, 10823–10836, doi: 10.5194/acp-11-10823-2011, 2011.

Zollner, J. H., et al.: Sulfuric acid nucleation: power dependencies, variation with relative humidity, and effect of bases, *Atmos. Chem. Phys.*, 12, 4399–4411, doi: 10.5194/acp-12-4399-2012, 2012.

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.  $1 \times 10^6$  to  $3 \times 10^7$   $\text{cm}^{-3}$ , 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  $\sim 40$  pptv ( $1 \times 10^9$   $\text{cm}^{-3}$ ), which is within the rather wide range of observations (0.1 to 157 pptv, i.e.,  $2.5 \times 10^6$  to  $4 \times 10^9$   $\text{cm}^{-3}$ ) 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  $\sim 3.2$  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  $\text{cm}^{-3}$  are used for different trace gases. Therefore, we decided to always provide the conversion to  $\text{cm}^{-3}$  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  $\text{s}^{-1}$ ). 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  $\text{s}^{-1}$ , 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  $\text{cm}^{-3}$  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  $\text{cm}^{-3}$  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).

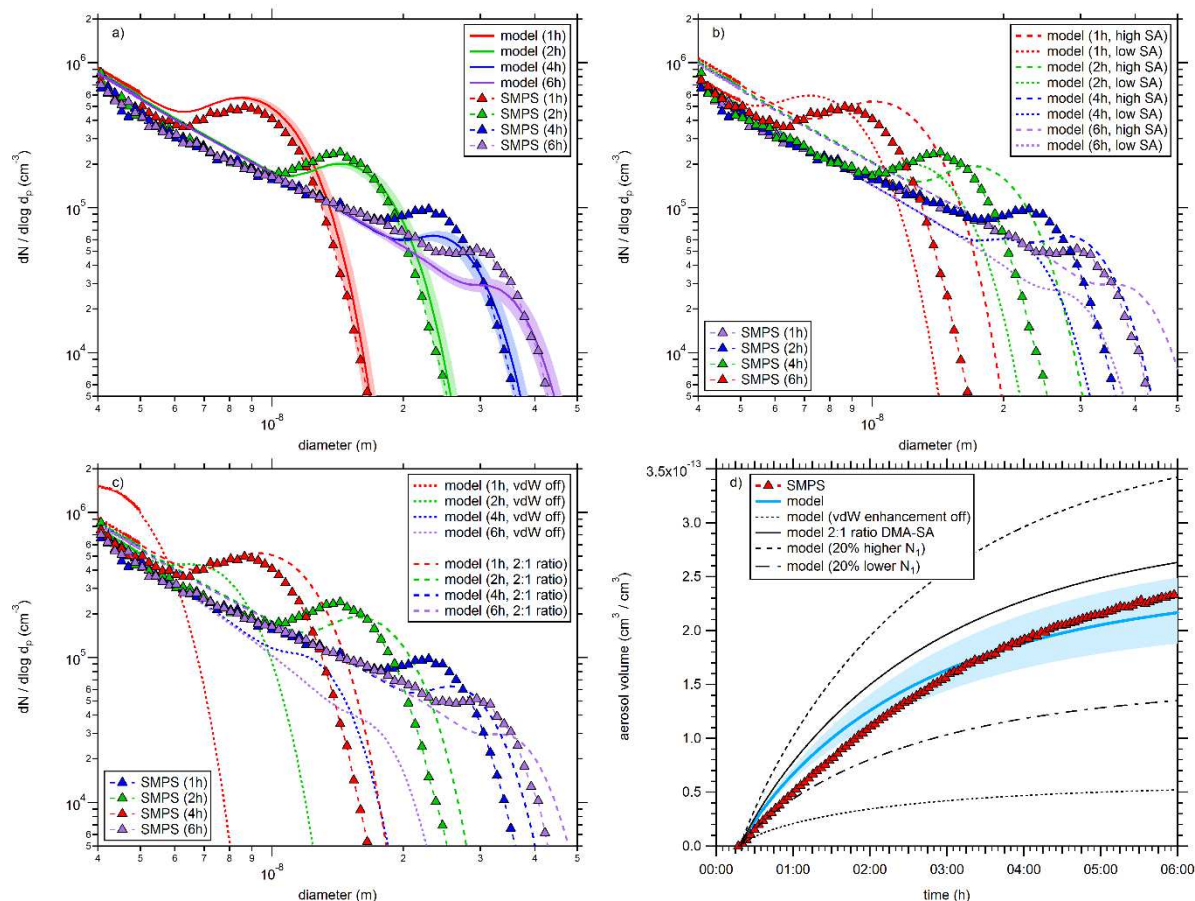
To illustrate the results, the previous version of Fig. 2 was replaced by a new version with four panels instead of two panels (see figure on the next page). In addition, the following discussion was added to section 3.4:

“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  $1470 \text{ kg m}^{-3}$  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  $\sim 3$  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 ( $\leq 20$  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  $\sim 1$ . Therefore, the high dimethylamine to acid ratio used in the CLOUD7 experiment ( $\sim 100$ ) 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 H<sub>2</sub>SO<sub>4</sub> 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 H<sub>2</sub>SO<sub>4</sub> 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\).](#)

## References

Ahlm, L., et al.: Modeling the thermodynamics and kinetics of sulfuric acid-dimethylamine-water nanoparticle growth in the CLOUD chamber, *Aerosol Sci. Technol.*, 50, 1017–1032, doi: 10.1080/02786826.2016.1223268, 2016.

Almeida, J., et al.: Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere, *Nature*, 502, 359–363, doi: 10.1038/nature12663, 2013.

Crump, J. G., and Seinfeld, J. H.: Turbulent deposition and gravitational sedimentation of an aerosol in a vessel of arbitrary shape, *J. Aerosol Sci.*, 12, 405–415, doi: 10.1016/0021-8502(81)90036-7, 1981.

Fiedler, V., et al.: The contribution of sulphuric acid to atmospheric particle formation and growth: a comparison between boundary layers in Northern and Central Europe, *Atmos. Chem. Phys.*, 5, 1773–1785, doi: 10.5194/acp-5-1773-2005, 2005.

Jen, C., et al.: Stabilization of sulfuric acid dimers by ammonia, methylamine, dimethylamine, and trimethylamine, *J. Geophys. Res.-Atmos.*, 119, 7502–7514, doi: 10.1002/2014JD021592, 2014.

Jen, C. N., et al.: Chemical ionization of clusters formed from sulfuric acid and dimethylamine or diamines, *Atmos. Chem. Phys.*, 16, 12513–12529, doi: 10.5194/acp-16-12513-2016, 2016a.

Jen, C. N., et al.: Diamine-sulfuric acid reactions are a potent source of new particle formation, *Geophys. Res. Lett.*, 43, 867–873, doi: 10.1002/2015GL066958, 2016b.

Kerminen, V.-M., and Kulmala, M.: Analytical formulae connecting the “real” and the “apparent” nucleation rate and the nuclei number concentration for atmospheric nucleation events, *J. Aerosol Sci.*, 33, 609–622, doi: 10.1016/S0021-8502(01)00194-X, 2002.

Kuang, C., et al.: Dependence of nucleation rates on sulfuric acid vapor concentration in diverse atmospheric locations, *J. Geophys. Res.-Atmos.*, 113, D10209, doi: 10.1029/2007JD009253, 2008.

Kulmala, M., et al.: Direct observations of atmospheric aerosol nucleation, *Science*, 339, 943–946, doi: 10.1126/science.1227385, 2013.

Kürten, A., et al.: Neutral molecular cluster formation of sulfuric acid-dimethylamine observed in real-time under atmospheric conditions, *P. Natl. Acad. Sci. USA*, 111, 15019–15024, doi: 10.1073/pnas.1404853111, 2014.

Kürten, A., et al.: On the derivation of particle nucleation rates from experimental formation rates, *Atmos. Chem. Phys.*, 15, 4063–4075, doi: 10.5194/acp-15-4063-2015, 2015a.

Kürten, A., et al.: Experimental particle formation rates spanning tropospheric sulfuric acid and ammonia abundances, ion production rates and temperatures, *J. Geophys. Res.-Atmos.*, 121, 12377–12400, doi: 10.1002/2015JD023908, 2016a.

Lehtipalo, K., et al.: The effect of acid–base clustering and ions on the growth of atmospheric nano-particles, *Nature Commun.*, 7, 11594, doi: 10.1038/ncomms11594, 2016.

McMurry, P. H., and Li, C.: The dynamic behavior of nucleating aerosols in constant reaction rate systems: Dimensional analysis and generic numerical solutions, *Aerosol Sci. Technol.*, 51, 1057–1070, doi: 10.1080/02786826.2017.1331292, 2017.

Qiu, C., and Zhang, R.: Physicochemical properties of alkylaminium sulfates: hygroscopicity, thermostability, and density, *Environ. Sci. Technol.*, 46, 4474–4480, doi: 10.1021/es3004377, 2012.

Yao, L., et al.: Detection of atmospheric gaseous amines and amides by a high-resolution time-of-flight chemical ionization mass spectrometer with protonated ethanol reagent ions, *Atmos. Chem. Phys.*, 16, 14527–14543, doi: 10.5194/acp-16-14527-2016, 2016.

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  $\text{Kr}^{85}$  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  $\sim 50$ , while the second correction (transmission efficiency) requires a factor of  $\sim 3.6$  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  $\text{Kr}^{85}$  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 on 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  $\text{H}_2\text{SO}_4$  reliably during many CLOUD experiments.

## References

- Ahlm, L., et al.: Modeling the thermodynamics and kinetics of sulfuric acid-dimethylamine-water nanoparticle growth in the CLOUD chamber, *Aerosol Sci. Technol.*, 50, 1017–1032, doi: 10.1080/02786826.2016.1223268, 2016.
- Almeida, J., et al.: Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere, *Nature*, 502, 359–363, doi: 10.1038/nature12663, 2013.
- Atkinson, R., et al.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I – Gas phase reactions of  $\text{O}_x$ ,  $\text{HO}_x$ ,  $\text{NO}_x$  and  $\text{SO}_x$  species, *Atmos. Chem. Phys.*, 4, 1461–1738, doi: 10.1002/2015JD023868, 2004.
- Bianchi, F., et al.: Insight into acid-base nucleation experiments by comparison of the chemical composition of positive, negative, and neutral clusters, *Environ. Sci. Technol.*, 48, 13675–13684, doi: 10.1021/es502380b, 2014.
- Carl, S. A., and Crowley, J. N.: Sequential two (blue) photon absorption by  $\text{NO}_2$  in the presence of  $\text{H}_2$  as a source of OH in pulsed photolysis kinetic studies: rate constants for reaction of OH with  $\text{CH}_3\text{NH}_2$ ,  $(\text{CH}_3)_2\text{NH}$ ,  $(\text{CH}_3)_3\text{N}$ , and  $\text{C}_2\text{H}_5\text{NH}_2$  at 295 K, *J. Phys. Chem. A*, 102, 8131–8141, 1998.
- Karlsson, M. N. A., and Martinsson, B. G.: Methods to measure and predict the transfer function size dependence of individual DMAs, *J. Aerosol Sci.*, 34, 603–625, doi: 10.1016/S0021-8502(03)00020-X, 2003.

Kerminen, V.-M., and Kulmala, M.: Analytical formulae connecting the “real” and the “apparent” nucleation rate and the nuclei number concentration for atmospheric nucleation events, *J. Aerosol Sci.*, 33, 609–622, doi: 10.1016/S0021-8502(01)00194-X, 2002.

Kürten, A., et al.: On the derivation of particle nucleation rates from experimental formation rates, *Atmos. Chem. Phys.*, 15, 4063–4075, doi: 10.5194/acp-15-4063-2015, 2015a.

McGrath, M. J., et al.: Atmospheric Cluster Dynamics Code: a flexible method for solution of the birth-death equations, *Atmos. Chem. Phys.*, 12, 2345–2355, doi: 10.5194/acp-12-2345-2012, 2012.

Wiedensohler, A., and Fissan, H. J.: Aerosol charging in high purity gases, *J. Aerosol Sci.*, 19, 867–870, doi: 10.1016/0021-8502(88)90054-7, 1988.

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**

4  
5  
6 Andreas Kürten<sup>1</sup>, Chenxi Li<sup>2</sup>, Federico Bianchi<sup>3</sup>, Joachim Curtius<sup>1</sup>, António Dias<sup>4</sup>, Neil M.  
7 Donahue<sup>5</sup>, Jonathan Duplissy<sup>3</sup>, Richard C. Flagan<sup>6</sup>, Jani Hakala<sup>3</sup>, Tuija Jokinen<sup>3</sup>, Jasper  
8 Kirkby<sup>1,7</sup>, Markku Kulmala<sup>3</sup>, Ari Laaksonen<sup>8</sup>, Katrianne Lehtipalo<sup>3,9</sup>, Vladimir Makhmutov<sup>10</sup>,  
9 Antti Onnela<sup>7</sup>, Matti P. Rissanen<sup>3</sup>, Mario Simon<sup>1</sup>, Mikko Sipilä<sup>3</sup>, Yuri Stozhkov<sup>10</sup>, Jasmin  
10 Tröstl<sup>9</sup>, Penglin Ye<sup>5,11</sup>, and Peter H. McMurry<sup>2</sup>

11  
12 <sup>1</sup>Institute for Atmospheric and Environmental Sciences, Goethe University Frankfurt, 60438  
13 Frankfurt am Main, Germany.

14 <sup>2</sup>Department of Mechanical Engineering, University of Minnesota, 111 Church St. SE,  
15 Minneapolis, MN 55455, USA.

16 <sup>3</sup>Department of Physics, University of Helsinki, FI-00014 Helsinki, Finland.

17 <sup>4</sup>SIM, University of Lisbon, 1849-016 Lisbon, Portugal.

18 <sup>5</sup>Center for Atmospheric Particle Studies, Carnegie Mellon University, Pittsburgh,  
19 Pennsylvania 15213, USA.

20 <sup>6</sup>Division of Chemistry and Chemical Engineering, California Institute of Technology,  
21 Pasadena, California 91125, USA.

22 <sup>7</sup>CERN, CH-1211 Geneva, Switzerland.

23 <sup>8</sup>Finnish Meteorological Institute, FI-00101 Helsinki, Finland.

24 <sup>9</sup>Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland.

25 <sup>10</sup>Solar and Cosmic Ray Research Laboratory, Lebedev Physical Institute, 119991 Moscow,  
26 Russia.

27 <sup>11</sup>Aerodyne Research Inc., Billerica, Massachusetts 01821, USA.

28  
29 Correspondence to: Andreas Kürten ([kuerten@iau.uni-frankfurt.de](mailto:kuerten@iau.uni-frankfurt.de))

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  $1 \times 10^6$  and  $3 \times 10^7$   $\text{cm}^{-3}$  and  
48 dimethylamine mixing ratio of ~40 pptv, i.e.,  $1 \times 10^9$   $\text{cm}^{-3}$ ).

## 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 ( $\text{H}_2\text{SO}_4$ ) 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  $\text{H}_2\text{SO}_4$  and  $\text{NH}_3$  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  $\sim 20$  pptv ( $5 \times 10^8$   
71  $\text{cm}^{-3}$ ), 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  $\alpha$ -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.  $1 \times 10^6$  to  $3 \times 10^7$   $\text{cm}^{-3}$ , 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  $\sim 40$  pptv ( $1 \times 10^9$   $\text{cm}^{-3}$ ), which is within the rather wide range of observations  
108 (0.1 to 157 pptv, i.e.,  $2.5 \times 10^6$  to  $4 \times 10^9$   $\text{cm}^{-3}$ ) 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  $\text{m}^3$  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 ( $\text{H}_2\text{SO}_4$ ) photolytically from reactions involving  $\text{O}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{SO}_2$  and  $\text{O}_2$ . 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.,  $\text{O}_2$  and  $\text{N}_2$  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 Kr<sup>85</sup> 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 ( $5 \times 10^6$  to  $2.5 \times 10^7$  cm<sup>-3</sup>) 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<sup>-3</sup> s<sup>-1</sup>) 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  $k_b$ ,  $T$ ,  $\eta$ , 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  $\lambda$  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  $0.00181 \text{ s}^{-1}$ ), 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  $1470 \text{ kg m}^{-3}$  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  $\sim 2.3$  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  $GR$  ( $\text{nm s}^{-1}$ ) 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  $4.3 \text{ nm}$ ; 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 SO<sub>2</sub> 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<sup>-1</sup> (sum of sulfuric acid  
 247 with 0.098 kg mol<sup>-1</sup> and dimethylamine with 0.045 kg mol<sup>-1</sup>), and the density as 1470 kg m<sup>-3</sup>  
 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 SO<sub>2</sub> 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 ( $\leq 20$  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  $\sim 1$ . Therefore, the high dimethylamine to acid ratio used in the  
326 CLOUD7 experiment ( $\sim 100$ ) 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  $1470 \text{ kg m}^{-3}$   
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  $\sim 3.7$  (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  $\sim 1.4$  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).

459

### 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 ( $\geq 4$ 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  $6.4 \times 10^{-20}$  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  $\geq 15$  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  $1470 \text{ kg m}^{-3}$  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  $2.5 \times 10^7 \text{ cm}^{-3}$  ( $\sim 1$  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  $1 \times 10^6$  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  $\sim 100$ ).  
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, ( $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$ ) 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  $\sim 6$  pptv ( $1.5 \times 10^8$   
653  $\text{cm}^{-3}$ ) 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  $2 \times 10^{-3}$  to  $4 \times 10^{-2}$  ( $M$ ) for the experiments shown in this study  
666 (Fig. 1). The monomer production rate ( $P_1$ ) ranges from  $7 \times 10^3$  to  $2 \times 10^6$   $\text{cm}^{-3} \text{s}^{-1}$ .

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  $\sim 50$  at high acid  
674 concentrations ( $\sim 1 \times 10^7$   $\text{cm}^{-3}$ ). 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  $\sim 30$  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  $\sim 100$ ).**

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  $\text{s}^{-1}$  (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.,  $0.143 \text{ kg mol}^{-1}$ ,  $\rho$  is the density of  $1470 \text{ kg}$   
796  $\text{m}^{-3}$  (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  $0.3 \text{ nm}$  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

804 **ACKNOWLEDGEMENTS**

805

806 Funding from the German Federal Ministry of Education and Research (grant no. 01LK1222A)  
807 and the Marie Curie Initial Training Network “CLOUD-TRAIN” (grant no. 316662) is  
808 gratefully acknowledged. PHM's and CL's contributions to this work were supported by the US  
809 Department of Energy’s Atmospheric System Research program, an Office of Science, Office  
810 of Biological and Environmental Research, under grant number DE-SC0011780. RCF  
811 acknowledges funding from the NSF Grants 1439551 and 1602086. MRP appreciates funding  
812 from the Academy of Finland (project no. 299574). KL thanks the European Union’s Horizon  
813 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement  
814 no. 656994 (nano-CAVa).



815 **References**

- 816
- 817 Ahlm, L., Yli-Juuti, T., Schobesberger, S., Praplan, A. P., Kim, J., Tikkanen, O. -P., Lawler,  
 818 M. J., Smith, J. N., Tröstl, J., Acosta Navarro, J. C., Baltensperger, U., Bianchi, F., Donahue,  
 819 N. M., Duplissy, J., Franchin, A., Jokinen, T., Keskinen, H., Kirkby, J., Kürten, A., Laaksonen,  
 820 A., Lehtipalo, K., Petäjä, T., Riccobono, F., Rissanen, M. P., Rondo, L., Schallhart, S., Simon,  
 821 M., Winkler, P. M., Worsnop, D. R., Virtanen, A., and Riipinen, I.: Modeling the  
 822 thermodynamics and kinetics of sulfuric acid-dimethylamine-water nanoparticle growth in the  
 823 CLOUD chamber, *Aerosol Sci. Technol.*, 50, 1017–1032, doi:  
 824 10.1080/02786826.2016.1223268, 2016.
- 825
- 826 Almeida, J., Schobesberger, S., Kürten, A., Ortega, I. K., Kupiainen-Määttä, O., Praplan, A. P.,  
 827 Adamov, A., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Donahue,  
 828 N. M., Downard, A., Dunne, E. M., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Guida,  
 829 R., Hakala, J., Hansel, A., Heinritzi, M., Henschel, H., Jokinen, T., Junninen, H., Kajos, M.,  
 830 Kangasluoma, J., Keskinen, H., Kupc, A., Kurtén, T., Kvashin, A. N., Laaksonen, A., Lehtipalo,  
 831 K., Leiminger, M., Leppä, J., Loukonen, V., Makhmutov, V., Mathot, S., McGrath, M. J.,  
 832 Nieminen, T., Olenius, T., Onnela, A., Petäjä, T., Riccobono, F., Riipinen, I., Rissanen, M.,  
 833 Rondo, L., Ruuskanen, T., Santos, F. D., Sarnela, N., Schallhart, S., Schnitzhofer, R., Seinfeld,  
 834 J. H., Simon, M., Sipilä, M., Stozhkov, Y., Stratmann, F., Tomé, A., Tröstl, J., Tsagkogeorgas,  
 835 G., Vaattovaara, P., Viisanen, Y., Virtanen, A., Vrtala, A., Wagner, P. E., Weingartner, E.,  
 836 Wex, H., Williamson, C., Wimmer, D., Ye, P., Yli-Juuti, T., Carslaw, K. S., Kulmala, M.,  
 837 Curtius, J., Baltensperger, U., Worsnop, D. R., Vehkamäki, H., and Kirkby, J.: Molecular  
 838 understanding of sulphuric acid-amine particle nucleation in the atmosphere, *Nature*, 502, 359–  
 839 363, doi: 10.1038/nature12663, 2013.
- 840
- 841 Ball, S. M., Hanson, D. R., Eisele, F. L., and McMurry, P. H.: Laboratory studies of particle  
 842 nucleation: Initial results for H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O, and NH<sub>3</sub> vapors, *J. Geophys. Res.-Atmos.*, 104, D19,  
 843 23709–23718, doi: 10.1029/1999JD900411, 1999.
- 844
- 845 Bergman, T., Laaksonen, A., Korhonen, H., Malila, J., Dunne, E. M., Mielonen, T., Lehtinen,  
 846 K. E. J., Kühn, T., Arola, A., and Kokkola, H.: Geographical and diurnal features of amine-  
 847 enhanced boundary layer nucleation, *J. Geophys. Res.-Atmos.*, 120, 9606–9624, doi:  
 848 10.1002/2015JD023181, 2015.
- 849
- 850 Berndt, T., Sipilä, M., Stratmann, F., Petäjä, T., Vanhanen, J., Mikkilä, J., Patokoski, J., Taipale,  
 851 R., Mauldin III, R. L., and Kulmala, M.: Enhancement of atmospheric H<sub>2</sub>SO<sub>4</sub> / H<sub>2</sub>O nucleation:  
 852 organic oxidation products versus amines, *Atmos. Chem. Phys.*, 14, 751–764, doi: 10.5194/acp-  
 853 14-751-2014, 2014.
- 854
- 855 Bianchi, F., Praplan, A. P., Sarnela, N., Dommen, J., Kürten, A., Ortega, I. K., Schobesberger,  
 856 S., Junninen, H., Simon, M., Tröstl, J., Jokinen, T., Sipilä, M., Adamov, A., Amorim, A.,  
 857 Almeida, J., Breitenlechner, M., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Hakala,  
 858 J., Hansel, A., Heinritzi, M., Kangasluoma, J., Keskinen, H., Kim, J., Kirkby, J., Laaksonen,

859 A., Lawler, M. J., Lehtipalo, K., Leiminger, M., Makhmutov, V., Mathot, S., Onnela, A., Petäjä,  
860 T., Riccobono, F., Rissanen, M. P., Rondo, L., Tomé, A., Virtanen, A., Viisanen, Y.,  
861 Williamson, C., Wimmer, D., Winkler, P. M., Ye, P., Curtius, J., Kulmala, M., Worsnop, D. R.,  
862 Donahue, N. M., and Baltensperger, U.: Insight into acid-base nucleation experiments by  
863 comparison of the chemical composition of positive, negative, and neutral clusters, *Environ.*  
864 *Sci. Technol.*, 48, 13675–13684, doi: 10.1021/es502380b, 2014.

865

866 Chan, T. W., and Mozurkewich, M.: Measurement of the coagulation rate constant for sulfuric  
867 acid particles as a function of particle size using tandem differential mobility analysis, *J.*  
868 *Aerosol Sci.*, 32, 321–339, doi: 10.1016/S0021-8502(00)00081-1, 2001.

869

870 Chen, M., Titcombe, M., Jiang, J., Jen, C., Kuang, C., Fischer, M. L., Eisele, F. L., Siepmann,  
871 J. I., Hanson, D. R., Zhao, J., and McMurry, P. H.: Acid–base chemical reaction model for  
872 nucleation rates in the polluted atmospheric boundary layer, *P. Natl. Acad. Sci. USA*, 109,  
873 18713–18718, doi: 10.1073/pnas.1210285109, 2012.

874

875 Clark, W. E., and Whitby, K. T.: Measurements of aerosols produced by the photochemical  
876 oxidation of SO<sub>2</sub> in air, *J. Colloid Interface Sci.*, 51, 477–490, doi: 10.1016/0021-  
877 9797(75)90144-7, 1975.

878

879 Crounse, J. D., Nielsen, L. B., Jørgensen, S., Kjaergaard, H. G., and Wennberg, P. O.:  
880 Autooxidation of organic compounds in the atmosphere, *J. Phys. Chem. Lett.*, 4, 3513–3520,  
881 doi: 10.1021/jz4019207, 2013.

882

883 Crump, J. G., and Seinfeld, J. H.: Turbulent deposition and gravitational sedimentation of an  
884 aerosol in a vessel of arbitrary shape, *J. Aerosol Sci.*, 12, 405–415, doi: 10.1016/0021-  
885 8502(81)90036-7, 1981.

886

887 Dunne, E. M., Gordon, H., Kürten, A., Almeida, J., Duplissy, J., Williamson, C., Ortega, I. K.,  
888 Pringle, K. J., Adamov, A., Baltensperger, U., Barmet, P., Benduhn, F., Bianchi, F.,  
889 Breitenlechner, M., Clarke, A., Curtius, J., Dommen, J., Donahue, N. M., Ehrhart, S., Flagan,  
890 R. C., Franchin, A., Guida, R., Hakala, J., Hansel, A., Heinritzi, M., Jokinen, T., Kangasluoma,  
891 J., Kirkby, J., Kulmala, M., Kupc, A., Lawler, M. J., Lehtipalo, K., Makhmutov, V., Mann, G.,  
892 Mathot, S., Merikanto, J., Miettinen, P., Nenes, A., Onnela, A., Rap, A., Reddington, C. L. S.,  
893 Riccobono, F., Richards, N. A. D., Rissanen, M. P., Rondo, L., Sarnela, N., Schobesberger, S.,  
894 Sengupta, K., Simon, M., Sipilä, M., Smith, J. N., Stozkhov, Y., Tomé, A., Tröstl, J., Wagner,  
895 P. E., Wimmer, D., Winkler, P. M., Worsnop, D. R., and Carslaw, K. S.: Global atmospheric  
896 particle formation from CERN CLOUD measurements, *Science*, 354, 1119–1124, doi:  
897 10.1126/science.aaf2649, 2016.

898

899 Duplissy, J., Merikanto, J., Franchin, A., Tsagkogeorgas, G., Kangasluoma, J., Wimmer, D.,  
900 Vuollekoski, H., Schobesberger, S., Lehtipalo, K., Flagan, R. C., Brus, D., Donahue, N. M.,  
901 Vehkämäki, H., Almeida, J., Amorim, A., Barmet, P., Bianchi, F., Breitenlechner, M., Dunne,  
902 E. M., Guida, R., Henschel, H., Junninen, H., Kirkby, J., Kürten, A., Kupc, A., Määttänen, A.,

903 Makhmutov, V., Mathot, S., Nieminen, T., Onnela, A., Praplan, A. P., Riccobono, F., Rondo,  
904 L., Steiner, G., Tome, A., Walther, H., Baltensperger, U., Carslaw, K. S., Dommen, J., Hansel,  
905 A., Petäjä, T., Sipilä, M., Stratmann, F., Vrtala, A., Wagner, P. E., Worsnop, D. R., Curtius, J.,  
906 and Kulmala, M.: Effect of ions on sulfuric acid-water binary particle formation II:  
907 Experimental data and comparison with QC-normalized classical nucleation theory, *J.*  
908 *Geophys. Res.-Atmos.*, 121, 1752–1775, doi: 10.1002/2015JD023539, 2016.

909

910 Ehrhart, S. and Curtius, J.: Influence of aerosol lifetime on the interpretation of nucleation  
911 experiments with respect to the first nucleation theorem, *Atmos. Chem. Phys.*, 13, 11465–  
912 11471, doi: 10.5194/acp-13-11465-2013, 2013.

913

914 Ehrhart, S., Ickes, L., Almeida, J., Amorim, A., Barmet, P., Bianchi, F., Dommen, J., Dunne,  
915 E. M., Duplissy, J., Franchin, A., Kangasluoma, J., Kirkby, J., Kürten, A., Kupc, A., Lehtipalo,  
916 K., Nieminen, T., Riccobono, F., Rondo, L., Schobesberger, S., Steiner, G., Tomé, A., Wimmer,  
917 D., Baltensperger, U., Wagner, P. E., and Curtius, J.: Comparison of the SAWNUC model with  
918 CLOUD measurements of sulphuric acid-water nucleation, *J. Geophys. Res.-Atmos.*, 121,  
919 12401–12414, doi: 10.1002/2015JD023723, 2016.

920

921 Ehn, M., Thornton, J. A., Kleist, E., Sipilä, M., Junninen, H., Pullinen, I., Springer, M., Rubach,  
922 F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I.-H., Rissanen, M., Jokinen, T.,  
923 Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurtén, T., Nielsen, L. B.,  
924 Jørgensen, S., Kjaergaard, H. G., Canagaratna, M., Dal Maso, M., Berndt, T., Petäjä, T.,  
925 Wahner, A., Kerminen, V.-M., Kulmala, M., Worsnop, D. R., Wildt, J., and Mentel, T. F.: A  
926 large source of low-volatility secondary organic aerosol, *Nature*, 506, 476–479, doi:  
927 10.1038/nature13032, 2014.

928

929 Fiedler, V., Dal Maso, M., Boy, M., Aufmhoff, H., Hoffmann, J., Schuck, T., Birmili, W.,  
930 Hanke, M., Uecker, J., Arnold, F., and Kulmala, M.: The contribution of sulphuric acid to  
931 atmospheric particle formation and growth: a comparison between boundary layers in Northern  
932 and Central Europe, *Atmos. Chem. Phys.*, 5, 1773–1785, doi: 10.5194/acp-5-1773-2005, 2005.

933

934 Freshour, N. A., Carlson, K. K., Melka, Y. A., Hinz, S., Panta, B., and Hanson, D. R.: Amine  
935 permeation sources characterized with acid neutralization and sensitivities of an amine mass  
936 spectrometer, *Atmos. Meas. Tech.*, 7, 3611–3621, doi: 10.5194/amt-7-3611-2014, 2014.

937

938 Glasoe, W. A., Volz, K., Panta, B., Freshour, N., Bachman, R., Hanson, D. R., McMurry, P.  
939 H., and Jen, C.: Sulfuric acid nucleation: An experimental study of the effect of seven bases, *J.*  
940 *Geophys. Res.-Atmos.*, 120, 1933–1950, doi: 10.1002/2014JD022730, 2015.

941

942 Gordon, H., Sengupta, K., Rap, A., Duplissy, J., Frege, C., Williamson, C., Heinritzi, M.,  
943 Simon, M., Yan, C., Almeida, J., Tröstl, J., Nieminen, T., Ortega, I. K., Wagner, R., Dunne, E.  
944 M., Adamov, A., Amorim, A., Bernhammer, A. K., Bianchi, F., Breitenlechner, M., Brilke, S.,  
945 Chen, X., Craven, J. S., Dias, A., Ehrhart, S., Fischer, L., Flagan, R. C., Franchin, A., Fuchs,  
946 C., Guida, R., Hakala, J., Hoyle, C. R., Jokinen, T., Junninen, H., Kangasluoma, J., Kim, J.,

947 Kirkby, J., Krapf, M., Kürten, A., Laaksonen, A., Lehtipalo, K., Makhmutov, V., Mathot, S.,  
948 Molteni, U., Monks, S. A., Onnela, A., Peräkylä, O., Piel, F., Petäjä, T., Praplan, A. P., Pringle,  
949 K. J., Richards, N. A. D., Rissanen, M. P., Rondo, L., Sarnela, N., Schobesberger, S., Scott, C.  
950 E., Seinfeld, J. H., Sharma, S., Sipilä, M., Steiner, G., Stozhkov, Y., Stratmann, F., Tomé, A.,  
951 Virtanen, A., Vogel, A. L., Wagner, A. C., Wagner, P. E., Weingartner, E., Wimmer, D.,  
952 Winkler, P. M., Ye, P., Zhang, X., Hansel, A., Dommen, J., Donahue, N. M., Worsnop, D. R.,  
953 Baltensperger, U., Kulmala, M., Curtius, J., and Carslaw, K. S.: Reduced anthropogenic aerosol  
954 radiative forcing caused by biogenic new particle formation, *Proc. Natl. Acad. Sci. USA*, 113,  
955 12053–12058, doi: 10.1073/pnas.1602360113, 2016.

956

957 Hamaker, H. C.: The London–van der Waals attraction between spherical particles, *Physica*, 4,  
958 1058–1072, doi: 10.1016/S0031-8914(37)80203-7, 1937.

959

960 Hanson, D. R., and Eisele, F.: Diffusion of H<sub>2</sub>SO<sub>4</sub> in humidified nitrogen: Hydrated H<sub>2</sub>SO<sub>4</sub>, *J.*  
961 *Phys. Chem. A*, 104, 1715–1719, doi: 10.1021/jp993622j, 2000.

962

963 Hanson, D. R., and Lovejoy, E. R.: Measurement of the thermodynamics of the hydrated dimer  
964 and trimer of sulfuric acid, *J. Phys. Chem. A*, 110, 9525–9528, doi: 10.1021/jp062844w, 2006.

965

966 Hanson, D. R., Bier, I., Panta, B., Jen, C. N., and McMurry, P. H.: Computational Fluid  
967 Dynamics Studies of a Flow Reactor: Free Energies of Clusters of Sulfuric Acid with NH<sub>3</sub> or  
968 Dimethyl Amine, *J. Phys. Chem. A*, 121, 3976–3990, doi: 10.1021/acs.jpca.7b00252, 2017.

969

970 Hinds, W. C.: Aerosol technology: Properties, behavior, and measurement of airborne particles,  
971 second edition, John Wiley & Sons, Inc., 150–153, 1999.

972

973 Hirsikko, A., Laakso, L., Hörrak, U., Aalto, P. P., Kerminen, V.-M., and Kulmala, M.: Annual  
974 and size dependent variation of growth rates and ion concentrations in boreal forest, *Boreal*  
975 *Environ. Res.*, 10, 357–369, 2005.

976

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

980

981 Jen, C. N., Zhao, J., McMurry, P. H., and Hanson, D. R.: Chemical ionization of clusters formed  
982 from sulfuric acid and dimethylamine or diamines, *Atmos. Chem. Phys.*, 16, 12513–12529, doi:  
983 10.5194/acp-16-12513-2016, 2016a.

984

985 Jen, C. N., Bachman, R., Zhao, J., McMurry, P. H., and Hanson, D. R.: Diamine-sulfuric acid  
986 reactions are a potent source of new particle formation, *Geophys. Res. Lett.*, 43, 867–873, doi:  
987 10.1002/2015GL066958, 2016b.

988

989 Jokinen, T., Sipilä, M., Junninen, H., Ehn, M., Lönn, G., Hakala, J., Petäjä, T., Mauldin III, R.  
990 L., Kulmala, M., and Worsnop, D. R.: Atmospheric sulphuric acid and neutral cluster

991 measurements using CI-API-TOF, *Atmos. Chem. Phys.*, 12, 4117–4125, doi: 10.5194/acp-12-  
992 4117-2012, 2012.

993

994 Jokinen, T., Berndt, T., Makkonen, R., Kerminen, V.-M., Junninen, H., Paasonen, P.,  
995 Stratmann, F., Herrmann, H., Guenther, A. B., Worsnop, D. R., Kulmala, M., Ehn, M., and  
996 Sipilä, M.: Production of extremely low volatile organic compounds from biogenic emissions:  
997 Measured yields and atmospheric implications, *P. Natl. Acad. Sci. USA*, 112, 7123–7128, doi:  
998 10.1073/pnas.1423977112, 2015.

999

1000 Karlsson, M. N. A., and Martinsson, B. G.: Methods to measure and predict the transfer function  
1001 size dependence of individual DMAs, *J. Aerosol Sci.*, 34, 603–625, doi: 10.1016/S0021-  
1002 8502(03)00020-X, 2003.

1003

1004 Kerminen, V.-M., and Kulmala, M.: Analytical formulae connecting the “real” and the  
1005 “apparent” nucleation rate and the nuclei number concentration for atmospheric nucleation  
1006 events, *J. Aerosol Sci.*, 33, 609–622, doi: 10.1016/S0021-8502(01)00194-X, 2002.

1007

1008 Kirkby, J., Curtius, J., Almeida, J., Dunne, E., Duplissy, J., Ehrhart, S., Franchin, A., Gagné,  
1009 S., Ickes, L., Kürten, A., Kupc, A., Metzger, A., Riccobono, F., Rondo, L., Schobesberger, S.,  
1010 Tsagkogeorgas, G., Wimmer, D., Amorim, A., Bianchi, F., Breitenlechner, M., David, A.,  
1011 Dommen, J., Downard, A., Ehn, M., Flagan, R.C., Haider, S., Hansel, A., Hauser, D., Jud, W.,  
1012 Junninen, H., Kreissl, F., Kvashin, A., Laaksonen, A., Lehtipalo, K., Lima, J., Lovejoy, E. R.,  
1013 Makhmutov, V., Mathot, S., Mikkilä, J., Minginette, P., Mogo, S., Nieminen, T., Onnela, A.,  
1014 Pereira, P., Petäjä, T., Schnitzhofer, R., Seinfeld, J. H., Sipilä, M., Stozhkov, Y., Stratmann, F.,  
1015 Tomé, A., Vanhanen, J., Viisanen, Y., Vrtala, A., Wagner, P. E., Walther, H., Weingartner, E.,  
1016 Wex, H., Winkler, P. M., Carslaw, K. S., Worsnop, D. R., Baltensperger, U., and Kulmala, M.:  
1017 Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation,  
1018 *Nature*, 476, 429–435, doi: 10.1038/nature10343, 2011.

1019

1020 Kirkby, J., Duplissy, J., Sengupta, K., Frege, C., Gordon, H., Williamson, C., Heinritzi, M.,  
1021 Simon, M., Yan, C., Almeida, J., Tröstl, J., Nieminen, T., Ortega, I. K., Wagner, R., Adamov,  
1022 A., Amorim, A., Bernhammer, A.-K., Bianchi, F., Breitenlechner, M., Brilke, S., Chen, X.,  
1023 Craven, J., Dias, A., Ehrhart, S., Flagan, R. C., Franchin, A., Fuchs, C., Guida, R., Hakala, J.,  
1024 Hoyle, C. R., Jokinen, T., Junninen, H., Kangasluoma, J., Kim, J., Krapf, M., Kürten, A.,  
1025 Laaksonen, A., Lehtipalo, K., Makhmutov, V., Mathot, S., Molteni, U., Onnela, A., Peräkylä,  
1026 O., Piel, F., Petäjä, T., Praplan, A. P., Pringle, K., Rap, A., Richards, N. A. D., Riipinen, I.,  
1027 Rissanen, M. P., Rondo, L., Sarnela, N., Schobesberger, S., Scott, C. E., Seinfeld, J. H., Sipilä,  
1028 M., Steiner, G., Stozhkov, Y., Stratmann, F., Tomé, A., Virtanen, A., Vogel, A. L., Wagner, A.,  
1029 Wagner, P. E., Weingartner, E., Wimmer, D., Winkler, P. M., Ye, P., Zhang, X., Hansel, A.,  
1030 Dommen, J., Donahue, N. M., Worsnop, D. R., Baltensperger, U., Kulmala, M., Carslaw, K.  
1031 S., and Curtius, J.: Ion-induced nucleation of pure biogenic particles, *Nature*, 533, 521–526,  
1032 doi: 10.1038/nature17953, 2016.

1033

1034 Ku, B. K., and Fernandez de la Mora, J.: Relation between electrical mobility, mass, and size  
1035 for nanodrops 1–6.5 nm in diameter in air, *Aerosol Sci. Technol.*, 43, 241–249, doi:  
1036 10.1080/02786820802590510, 2009.  
1037  
1038 Kuang, C., McMurry, P. H., McCormick, A. V., and Eisele, F. L.: Dependence of nucleation  
1039 rates on sulfuric acid vapor concentration in diverse atmospheric locations, *J. Geophys. Res.-*  
1040 *Atmos.*, 113, D10209, doi: 10.1029/2007JD009253, 2008.  
1041  
1042 Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili,  
1043 W., and McMurry, V.-M.: Formation and growth rates of ultrafine atmospheric particles: a  
1044 review of observations, *J. Aerosol Sci.*, 35, 143–176, doi: 10.1016/j.jaerosci.2003.10.003, 2004.  
1045  
1046 Kulmala, M., Kontkanen, J., Junninen, H., Lehtipalo, K., Manninen, H. E., Nieminen, T.,  
1047 Petäjä, T., Sipilä, M., Schobesberger, S., Rantala, P., Franchin, A., Jokinen, T., Järvinen, E.,  
1048 Äijälä, M., Kangasluoma, J., Hakala, J., Aalto, P. P., Paasonen, P., Mikkilä, J., Vanhanen, J.,  
1049 Aalto, J., Hakola, H., Makkonen, U., Ruuskanen, T., Mauldin III, R. L., Duplissy, J.,  
1050 Vehkamäki, H., Bäck, J., Kortelainen, A., Riipinen, I., Kurtén, T., Johnston, M. V., Smith, J.  
1051 N., Ehn, M., Mentel, T. F., Lehtinen, K. E. J., Laaksonen, A., Kerminen, V.-M., and Worsnop,  
1052 D. R.: Direct observations of atmospheric aerosol nucleation, *Science*, 339, 943–946, doi:  
1053 10.1126/science.1227385, 2013.  
1054  
1055 Kupc, A., Amorim, A., Curtius, J., Danielczok, A., Duplissy, J., Ehrhart, S., Walther, H., Ickes,  
1056 L., Kirkby, J., Kürten, A., Lima, J. M., Mathot, S., Minginette, P., Onnela, A., Rondo, L., and  
1057 Wagner, P. E.: A fibre-optic UV system for H<sub>2</sub>SO<sub>4</sub> production in aerosol chambers causing  
1058 minimal thermal effects, *J. Aerosol Sci.*, 42, 532–543, doi: 10.1016/j.jaerosci.2011.05.001,  
1059 2011.  
1060  
1061 Kürten, A., Rondo, L., Ehrhart, S., and Curtius, J.: Performance of a corona ion source for  
1062 measurement of sulfuric acid by chemical ionization mass spectrometry, *Atmos. Meas. Tech.*,  
1063 4, 437–443, doi: 10.5194/amt-4-437-2011, 2011.  
1064  
1065 Kürten, A., Jokinen, T., Simon, M., Sipilä, M., Sarnela, N., Junninen, H., Adamov, A., Almeida,  
1066 J., Amorim, A., Bianchi, F., Breitenlechner, M., Dommen, J., Donahue, N. M., Duplissy, J.,  
1067 Ehrhart, S., Flagan, R. C., Franchin, A., Hakala, J., Hansel, A., Heinritzi, M., Hutterli, M.,  
1068 Kangasluoma, J., Kirkby, J., Laaksonen, A., Lehtipalo, K., Leiminger, M., Makhmutov, V.,  
1069 Mathot, S., Onnela, A., Petäjä, T., Praplan, A. P., Riccobono, F., Rissanen, M. P., Rondo, L.,  
1070 Schobesberger, S., Seinfeld, J. H., Steiner, G., Tomé, A., Tröstl, J., Winkler, P. M., Williamson,  
1071 C., Wimmer, D., Ye, P., Baltensperger, U., Carslaw, K. S., Kulmala, M., Worsnop, D. R., and  
1072 Curtius, J.: Neutral molecular cluster formation of sulfuric acid-dimethylamine observed in  
1073 real-time under atmospheric conditions, *P. Natl. Acad. Sci. USA*, 111, 15019–15024, doi:  
1074 10.1073/pnas.1404853111, 2014.  
1075

1076 Kürten, A., Williamson, C., Almeida, J., Kirkby, J., and Curtius, J.: On the derivation of particle  
1077 nucleation rates from experimental formation rates, *Atmos. Chem. Phys.*, 15, 4063–4075, doi:  
1078 10.5194/acp-15-4063-2015, 2015a.  
1079

1080 Kürten, A., Münch, S., Rondo, L., Bianchi, F., Duplissy, J., Jokinen, T., Junninen, H., Sarnela,  
1081 N. Schobesberger, S., Simon, M., Sipilä, M., Almeida, J., Amorim, A., Dommen, J., Donahue,  
1082 N. M., Dunne, M., Flagan, R. C., Franchin, A., Kirkby, J., Kupc, A., Makhmutov, V., Petäjä,  
1083 T. Praplan, A. P., Riccobono, F., Steiner, G., Tomé, A., Tsagkogeorgas, G., Wagner, P. E.,  
1084 Wimmer, D., Baltensperger, U., Kulmala, M., Worsnop, D. R., and Curtius, J.:  
1085 Thermodynamics of the formation of sulfuric acid dimers in the binary (H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O) and  
1086 ternary (H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O-NH<sub>3</sub>) system, *Atmos. Chem. Phys.*, 15, 10701–10721, doi: 10.5194/acp-  
1087 15-10701-2015, 2015b.  
1088

1089 Kürten, A., Bianchi, F., Almeida, J., Kupiainen-Määttä, O., Dunne, E. M., Duplissy, J.,  
1090 Williamson, C., Barmet, P., Breitenlechner, M., Dommen, J., Donahue, N. M., Flagan, R. C.,  
1091 Franchin, A., Gordon, H., Hakala, J., Hansel, A., Heinritzi, M., Ickes, L., Jokinen, T.,  
1092 Kangasluoma, J., Kim, J., Kirkby, J., Kupc, A., Lehtipalo, K., Leiminger, M., Makhmutov, V.,  
1093 Onnela, A., Ortega, I. K., Petäjä, T., Praplan, A. P., Riccobono, F., Rissanen, M. P., Rondo, L.,  
1094 Schnitzhofer, R., Schobesberger, S., Smith, J. N., Steiner, G., Stozhkov, Y., Tomé, A., Tröstl,  
1095 J., Tsagkogeorgas, G., Wagner, P. E., Wimmer, D., Ye, P., Baltensperger, U., Carslaw, K.,  
1096 Kulmala, M., and Curtius, J.: Experimental particle formation rates spanning tropospheric  
1097 sulfuric acid and ammonia abundances, ion production rates and temperatures, *J. Geophys.*  
1098 *Res.-Atmos.*, 121, 12377–12400, doi: 10.1002/2015JD023908, 2016a.  
1099

1100 Kürten, A., Bergen, A., Heinritzi, M., Leiminger, M., Lorenz, V., Piel, F., Simon, M., Sitals,  
1101 R., Wagner, A. C., and Curtius, J.: Observation of new particle formation and measurement of  
1102 sulfuric acid, ammonia, amines and highly oxidized organic molecules at a rural site in central  
1103 Germany, *Atmos. Chem. Phys.*, 16, 12793–12813, doi: 10.5194/acp-16-12793-2016, 2016b.  
1104

1105 Kurtén, T., Loukonen, V., Vehkamäki, H., and Kulmala, M.: Amines are likely to enhance  
1106 neutral and ion-induced sulfuric acid-water nucleation in the atmosphere more effectively than  
1107 ammonia, *Atmos. Chem. Phys.*, 8, 4095–4103, doi: 10.5194/acp-8-4095-2008, 2008.  
1108

1109 Lee, S.-H., Reeves, J. M., Wilson, J. C., Hunton, D. E., Viggiano, A. A., Miller, T. M.,  
1110 Ballenthin, J. O., and Lait, L. R.: Particle formation by ion nucleation in the upper troposphere  
1111 and lower stratosphere, *Science*, 301, 1886–1889, doi: 10.1126/science.1087236, 2003.  
1112

1113 Lehtipalo, K., Rondo, L., Kontkanen, J., Schobesberger, S., Jokinen, T., Sarnela, N., Kürten,  
1114 A., Ehrhart, S., Franchin, A., Nieminen, T., Riccobono, F., Sipilä, M., Yli-Juuti, T., Duplissy,  
1115 J., Adamov, A., Ahlm, L., Almeida, J., Amorim, A., Bianchi, F., Breitenlechner, M., Dommen,  
1116 J., Downard, A. J., Dunne, E. M., Flagan, R. C., Guida, R., Hakala, J., Hansel, A., Jud, W.,  
1117 Kangasluoma, J., Kerminen, V.-M., Keskinen, H., Kim, J., Kirkby, J., Kupc, A., Kupiainen-  
1118 Määttä, O., Laaksonen, A., Lawler, M. J., Leiminger, M., Mathot, S., Olenius, T., Ortega, I. K.,  
1119 Onnela, A., Petäjä, T., Praplan, A., Rissanen, M. P., Ruuskanen, T., Santos, F. D., Schallhart,

1120 S., Schnitzhofer, R., Simon, M., Smith, J. N., Tröstl, J., Tsagkogeorgas, G., Tomé, A.,  
1121 Vaattovaara, P., Vehkamäki, H., Vrtala, A. E., Wagner, P. E., Williamson, C., Wimmer, D.,  
1122 Winkler, P. M., Virtanen, A., Donahue, N. M., Carslaw, K. S., Baltensperger, U., Riipinen, I.,  
1123 Curtius, J., Worsnop, D. R., and Kulmala, M.: The effect of acid–base clustering and ions on  
1124 the growth of atmospheric nano-particles, *Nature Commun.*, 7, 11594, doi:  
1125 10.1038/ncomms11594, 2016.  
1126  
1127 Lovejoy, E. R., Curtius, J., and Froyd, K. D.: Atmospheric ion-induced nucleation of sulfuric  
1128 acid and water, *J. Geophys. Res.-Atmos.*, 109, D08204, doi: 10.1029/2003JD004460, 2004.  
1129  
1130 McGrath, M. J., Olenius, T., Ortega, I. K., Loukonen, V., Paasonen, P., Kurtén, T., Kulmala,  
1131 M., and Vehkamäki, H.: Atmospheric Cluster Dynamics Code: a flexible method for solution  
1132 of the birth-death equations, *Atmos. Chem. Phys.*, 12, 2345–2355, doi: 10.5194/acp-12-2345-  
1133 2012, 2012.  
1134  
1135 McMurry, P. H.: Photochemical Aerosol Formation from SO<sub>2</sub>: A theoretical analysis of smog  
1136 chamber data, *J. Colloid Interf. Sci.*, 78, 513–527, doi: 10.1016/0021-9797(80)90589-5, 1980.  
1137  
1138 McMurry, P. H., and Li, C.: The dynamic behavior of nucleating aerosols in constant reaction  
1139 rate systems: Dimensional analysis and generic numerical solutions, *Aerosol Sci. Technol.*, 51,  
1140 1057–1070, doi: 10.1080/02786826.2017.1331292, 2017.  
1141  
1142 Nadykto, A. B., Yu, F., Jakovleva, M. V., Herb, J., and Xu, Y.: Amines in the Earth’s  
1143 atmosphere: A density functional theory study of the thermochemistry of pre-nucleation  
1144 clusters, *Entropy*, 13, 554–569; doi: 10.3390/e13020554, 2011.  
1145  
1146 Olenius, T., Halonen, R., Kurtén, T., Henschel, H., Kupiainen-Määttä, O., Ortega, I. K., Jen, C.  
1147 N., Vehkamäki, H., and Riipinen, I.: New particle formation from sulfuric acid and amines:  
1148 Comparison of monomethylamine, dimethylamine, and trimethylamine, *J. Geophys. Res.*  
1149 *Atmos.*, 122, 7103–7118, doi: 10.1002/2017JD026501, 2017.  
1150  
1151 Ortega, I. K., Kupiainen, O., Kurtén, T., Olenius, T., Wilkman, O., McGrath, M. J., Loukonen,  
1152 V., and Vehkamäki, H.: From quantum chemical formation free energies to evaporation rates,  
1153 *Atmos. Chem. Phys.*, 12, 225–235, doi: 10.5194/acp-12-225-2012, 2012.  
1154  
1155 Park, S. H., Kim, H. O., Han, Y. T., Kwon, S. B., and Lee, K. W.: Wall loss rate of polydispersed  
1156 aerosols, *Aerosol Sci. Technol.*, 35, 710–717, doi: 10.1080/02786820152546752, 2001.  
1157  
1158 Place, B. K., Quilty, A. T., Di Lorenzo, R. A., Ziegler, S. E., and VandenBoer, T. C.:  
1159 Quantitation of 11 alkylamines in atmospheric samples: separating structural isomers by ion  
1160 chromatography, *Atmos. Meas. Tech.*, 10, 1061–1078, doi: 10.5194/amt-10-1061-2017, 2017.  
1161



1162 Praplan, A. P., Bianchi, F., Dommen, J., and Baltensperger, U.: Dimethylamine and ammonia  
1163 measurements with ion chromatography during the CLOUD4 campaign, *Atmos. Meas. Tech.*,  
1164 5, 2161–2167, doi: 10.5194/amt-5-2161-2012, 2012.  
1165

1166 Rao, N. P., and McMurry, P. H.: Nucleation and Growth of Aerosol in Chemically Reacting  
1167 Systems: A Theoretical Study of the Near-Collision-Controlled Regime, *Aerosol Sci. Technol.*,  
1168 11, 120–132, doi: 10.1080/02786828908959305, 1989.  
1169

1170 Qiu, C., and Zhang, R.: Physiochemical properties of alkylammonium sulfates: hygroscopicity,  
1171 thermostability, and density, *Environ. Sci. Technol.*, 46, 4474–4480, doi: 10.1021/es3004377,  
1172 2012.  
1173

1174 Riccobono, F., Schobesberger, S., Scott, C. E., Dommen, J., Ortega, I. K., Rondo, L., Almeida,  
1175 J., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Downard, A., Dunne, E. M.,  
1176 Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Hansel, A., Junninen, H., Kajos, M.,  
1177 Keskinen, H., Kupc, A., Kürten, A., Kvashin, A. N., Laaksonen, A., Lehtipalo, K., Makhmutov,  
1178 V., Mathot, S., Nieminen, T., Onnela, A., Petäjä, T., Praplan, A. P., Santos, F. D., Schallhart,  
1179 S., Seinfeld, J. H., Sipilä, M., Spracklen, D. V., Stozhkov, Y., Stratmann, F., Tomé, A.,  
1180 Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Vrtala, A., Wagner, P. E., Weingartner, E.,  
1181 Wex, H., Wimmer, D., Carslaw, K. S., Curtius, J., Donahue, N. M., Kirkby, J., Kulmala, M.,  
1182 Worsnop, D. R., and Baltensperger, U.: Oxidation products of biogenic emissions contribute to  
1183 nucleation of atmospheric particles, *Science*, 344, 717–721, doi: 10.1126/science.1243527,  
1184 2014.  
1185

1186 Simon, M., Heinritzi, M., Herzog, S., Leiminger, M., Bianchi, F., Praplan, A., Dommen, J.,  
1187 Curtius, J., and Kürten, A.: Detection of dimethylamine in the low pptv range using nitrate  
1188 chemical ionization atmospheric pressure interface time-of-flight (CI-API-TOF) mass  
1189 spectrometry, *Atmos. Meas. Tech.*, 9, 2135–2145, doi: 10.5194/amt-9-2135-2016, 2016.  
1190

1191 Voigtländer, J., Duplissy, J., Rondo, L., Kürten, A., and Stratmann, F.: Numerical simulations  
1192 of mixing conditions and aerosol dynamics in the CERN CLOUD chamber, *Atmos. Chem.*  
1193 *Phys.*, 12, 2205–2214, doi: 10.5194/acp-12-2205-2012, 2012.  
1194

1195 Wang, S. C., and Flagan, R. C.: Scanning electrical mobility spectrometer, *Aerosol Sci.*  
1196 *Technol.*, 13, 230–240, doi: 10.1080/02786829008959441, 1990.  
1197

1198 Weber, R. J., Marti, J., McMurry, P. H., Eisele, F. L., Tanner, D. J., and Jefferson, A.: Measured  
1199 atmospheric new particle formation rates: implications for nucleation mechanisms, *Chem. Eng.*  
1200 *Comm.*, 151, 53–64, doi: 10.1080/00986449608936541, 1996.  
1201

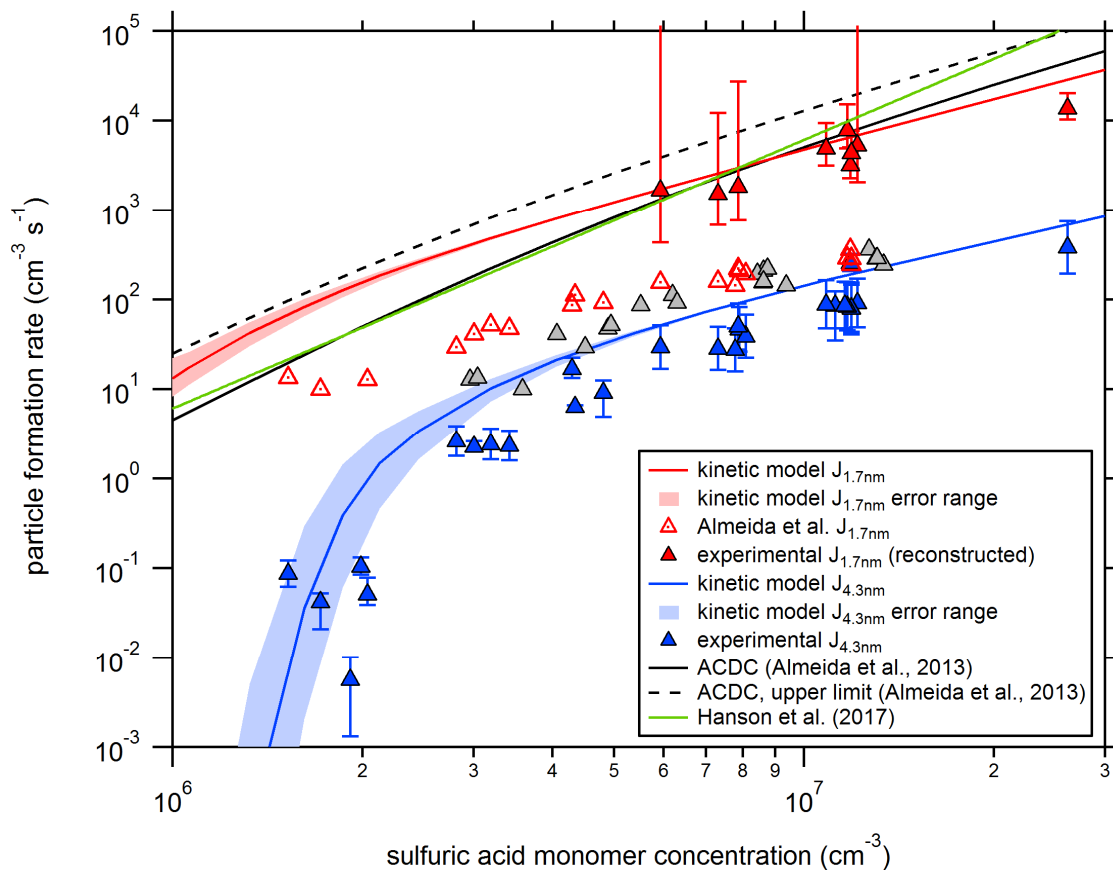
1202 Weber, R. J., Marti, J. J., McMurry, P. H., Eisele, F. L., Tanner, D. J., and Jefferson, A.:  
1203 Measurements of new particle formation and ultrafine particle growth rates at a clean  
1204 continental site, *J. Geophys. Res.-Atmos.*, 102, D4, 4375–4385, doi: 10.1029/96JD03656, 1997.  
1205

1206 Weber, R. J., McMurry, P. H., Mauldin, L., Tanner, D. J., Eisele, F. L., Brechtel, F. J.,  
1207 Kreidenweis, S. M., Kok, G. L., Schillawski, R. D., and Baumgardner, D.: A study of new  
1208 particle formation and growth involving biogenic and trace gas species measured during ACE  
1209 1, *J. Geophys. Res.-Atmos.*, 103, D13, 16385–16396, doi: 10.1029/97JD02465, 1998.  
1210  
1211 Wiedensohler, A., and Fissan, H. J.: Aerosol charging in high purity gases, *J. Aerosol Sci.*, 19,  
1212 867–870, doi: 10.1016/0021-8502(88)90054-7, 1988.  
1213  
1214 Yao, L., Wang, M.-Y., Wang, X.-K., Liu, Y.-J., Chen, H.-F., Zheng, J., Nie, W., Ding, A.-J.,  
1215 Geng, F.-H., Wang, D.-F., Chen, J.-M., Worsnop, D. R., and Wang, L.: Detection of  
1216 atmospheric gaseous amines and amides by a high-resolution time-of-flight chemical ionization  
1217 mass spectrometer with protonated ethanol reagent ions, *Atmos. Chem. Phys.*, 16, 14527–  
1218 14543, doi: 10.5194/acp-16-14527-2016, 2016.  
1219  
1220 You, Y., Kanawade, V. P., de Gouw, J. A., Guenther, A. B., Madronich, S., Sierra-Hernández,  
1221 M. R., Lawler, M., Smith, J. N., Takahama, S., Ruggeri, G., Koss, A., Olson, K., Baumann, K.,  
1222 Weber, R. J., Nenes, A., Guo, H., Edgerton, E. S., Porcelli, L., Brune, W. H., Goldstein, A. H.,  
1223 and Lee, S.-H.: Atmospheric amines and ammonia measured with a chemical ionization mass  
1224 spectrometer (CIMS), *Atmos. Chem. Phys.*, 14, 12181–12194, doi: 10.5194/acp-14-12181-  
1225 2014, 2014.  
1226  
1227 Yu, H., and Lee, S.-H.: Chemical ionisation mass spectrometry for the measurement of  
1228 atmospheric amines, *Environ. Chem.*, 9, 190–201, doi: 10.1071/EN12020, 2012.  
1229  
1230 Yu, H., Dai, L., Zhao, Y., Kanawade, V. P., Tripathi, S. N., Ge, X., Chen, M., and Lee, S. N.:  
1231 Laboratory observations of temperature and humidity dependencies of nucleation and growth  
1232 rates of sub-3 nm particles, *J. Geophys. Res. Atmos.*, 122, 1919–1929, doi:  
1233 10.1002/2016JD025619, 2017.  
1234  
1235 Zhao, J., Smith, J. N., Eisele, F. L., Chen, M., Kuang, C., and McMurry, P. H.: Observation of  
1236 neutral sulfuric acid-amine containing clusters in laboratory and ambient measurements, *Atmos.*  
1237 *Chem. Phys.*, 11, 10823–10836, doi: 10.5194/acp-11-10823-2011, 2011.  
1238  
1239 Zollner, J. H., Glasoe, W. A., Panta, B., Carlson, K. K., McMurry, P. H., and Hanson, D. R.:  
1240 Sulfuric acid nucleation: power dependencies, variation with relative humidity, and effect of  
1241 bases, *Atmos. Chem. Phys.*, 12, 4399–4411, doi: 10.5194/acp-12-4399-2012, 2012.

1242 **Table 1.** Overview of the two different model versions used to generate the data in the figures.  
 1243

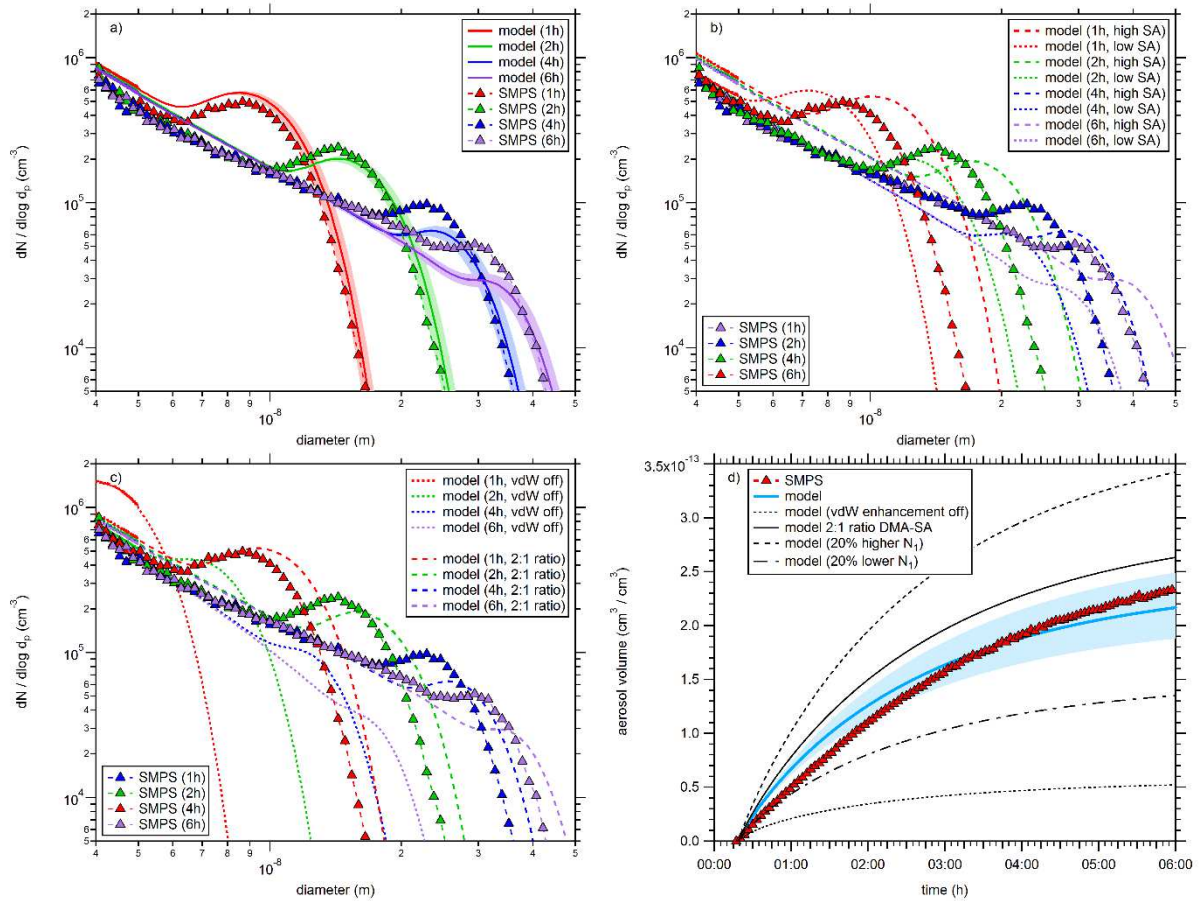
	kinetic model	model with evaporation rates
used for	Fig. 1, Fig. 2, Fig. 3 upper panel (black lines)	Fig. 3 upper panel (colored lines), Fig. 3 lower panel
described in	section 2.4	section 2.5, Appendix A
evaporation rates	all zero	$k_{e,A1B1} = 0.1 \text{ s}^{-1}$ $k_{e,A3B1} = 1 \text{ s}^{-1}$ $k_{e,A3B2} = 1 \text{ s}^{-1}$ $(k_{e,A4B1} = \infty \text{ s}^{-1})$ all others zero

1244



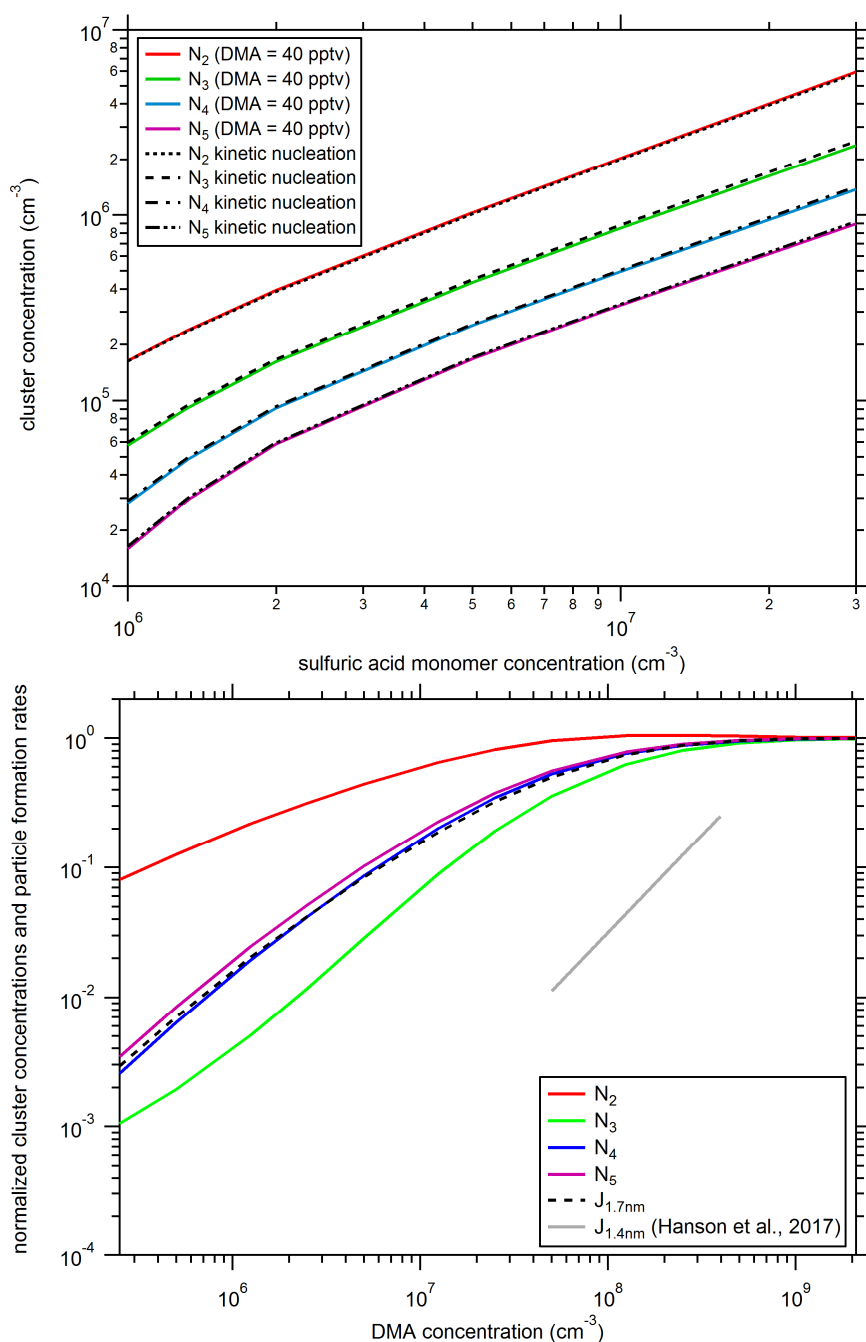
1245  
 1246  
 1247  
 1248  
 1249  
 1250  
 1251  
 1252  
 1253  
 1254  
 1255  
 1256  
 1257  
 1258

**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.



1259  
 1260  
 1261  
 1262  
 1263  
 1264  
 1265  
 1266  
 1267  
 1268  
 1269  
 1270

**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.



1271  
 1272  
 1273  
 1274  
 1275  
 1276  
 1277  
 1278  
 1279  
 1280  
 1281  
 1282  
 1283

**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.