Referee #1

I thank the referee for carefully reading the manuscript and for the constructive comments that help improving the paper. The comments are listed in full below (in black font), while the replies are given in blue font; text that has been added to the manuscript is shown in red font.

This manuscript presents a new-ish model of nucleation and growth (modified from a previous model to allow for evaporation of the smallest acid-base clusters), and this model is used to estimate thermodynamic parameters of the small clusters by getting the model to match measurements of nucleation rates from CLOUD measurements. The manuscript is suited for ACP and is mostly ready for publication, but I have some comments that I would like to be addressed before final publication.

(1) How important is the role of coagulation in these simulations? If I understand correctly, one of the motivations for having a model of the broad size distribution is to include coagulational losses of early clusters, but coagulation was not discussed beyond stating that it was part of the model at the end of the introduction.

I agree, that the effects of coagulation should be further highlighted. In the version published in ACPD the effect of coagulation can currently be seen from the increase in the GR in Figure 6 for the low temperature (208 K). At this temperature the relatively small evaporation rates lead to significant cluster concentrations (relative to the monomer of sulfuric acid), which leads to enhanced growth rates. The effect of this “hidden” sulfuric acid (in clusters) on particle growth and nucleation has been described recently (Lehtipalo et al., 2016; Rondo et al., 2016). More information regarding this effect was added to Section 3.4:

“This effect is pronounced at 208 K with some ammonia, which indicates that considering only the condensation of monomers is not sufficient for some conditions. Not only growth can be effected by coagulation but also new particle formation rates; therefore, the implementation of a full coagulation scheme (SI Text S1) is important for the present study.”

(2) L153-156: From context, I’m pretty sure you’re talking about the sulfuric acid / DMA system here, but it be good to be explicit such that the readers know you aren’t talking about the sulfuric acid / ammonia system. “For the reason, the sulfuric acid / dimethylamine system can be. . .”

Agreed, the sentence has been changed to:

“For this reason, the sulfuric acid-dimethylamine system can be treated as quasi-unary and the kinetic approach (all cluster evaporation rates equal zero) yields very good agreement between modeled and measured particle concentrations and formation rates over a wide range of particle diameters.”

(3) L160: Is the upper diameter limit of 295 nm set because the particles in the CLOUD experiments did not grow larger than this? If not, what is the reason for this limit? In the atmosphere, particles larger than this size can contribute a significant amount of the condensation and coagulation sinks.

I agree, that in the atmosphere larger particles can contribute significantly to the condensation/coagulation sink. The model is therefore not restricted to the mentioned size. By increasing the number of bins and/or the width of the bins, larger diameters can be considered. However, as the referee points out, at the given sulfuric acid concentrations and durations of the experiments the particle diameters always stayed below the stated size.

The following sentence was added to the end of the first paragraph of Section 2.2 in order to point this out:

“Choosing a larger number of bins and/or geometric factor would result in a larger upper size limit, which was, however, not necessary in the present study.”

(4) Section 2: Personally, I think about how nucleation impacts the size distribution and how the size distribution feeds back on nucleation. I have a basic qualitative understand about how dS and dH relate to evaporation rates, but not a complete understanding. I certainly expect that some readers will have thought about nucleation thermodynamics a lot and won’t need to see any background; however, I doubt that I’ll be alone in wanting to see a short section describing the mathematical relationship between the thermodynamic parameters and the evaporation rate. At a minimum please reference where we can find this discussion.

In the ACPD version of the manuscript a reference to SI Text S2 is provided in L196/L197. SI Text S2 describes the relationship between the evaporation rate and the thermodynamic parameters (dH and dS). Further explanation on the relationship between evaporation rate and dH/dS is given in Section 2.2 (L196-L200).

However, it is probably good to provide a bit of information (and the reference to the SI) already earlier. Therefore, the following information was added to the end of the first paragraph of Section 2:

“The thermodynamic parameters (enthalpy change dH and entropy change dS due to the addition or removal of a molecule) are required in order to obtain the evaporation rate of a cluster. The mathematical relationship between dH, dS and the evaporation rate are provided in the supplementary information (SI Text S2).”

(5) L408-411: So in the real atmosphere (without walls), the straight line is appropriate? Or I suppose it is then the coagulation sink to determine the non-linearity of the curve?

The referee is correct. The ratio of the arrival rate of the condensing vapor to its loss rate determines whether the relationship between J and vapor concentration is a straight line (on a log-log-plot) or not. When this ratio is high, the relationship is rather linear; at a small ratio it is non-linear. In CLOUD, no pre-existing particles are present; therefore, wall loss is the main sink for the condensing vapor(s); in the atmosphere the loss is determined by the condensation sink on larger (pre-existing) particles.

The sentence in Section 3.2 has been modified to include the information that the shape of the curve can also be influenced by pre-existing particles:

“The curvature is due to the fact that the survival probability of subcritical clusters (i.e., clusters below the nonamer) can be strongly affected by losses to walls or pre-existing particles (Ehrhart and Curtius, 2013).”

(6) L443-450: Does it matter that the model is overpredicting when the overpredicted $J_{1.7}$ values are 1E-4 cm-3 s-1 and slower? There rates are trivial. This may be worth noting, even though it’s good to discuss that it is an overprediction.

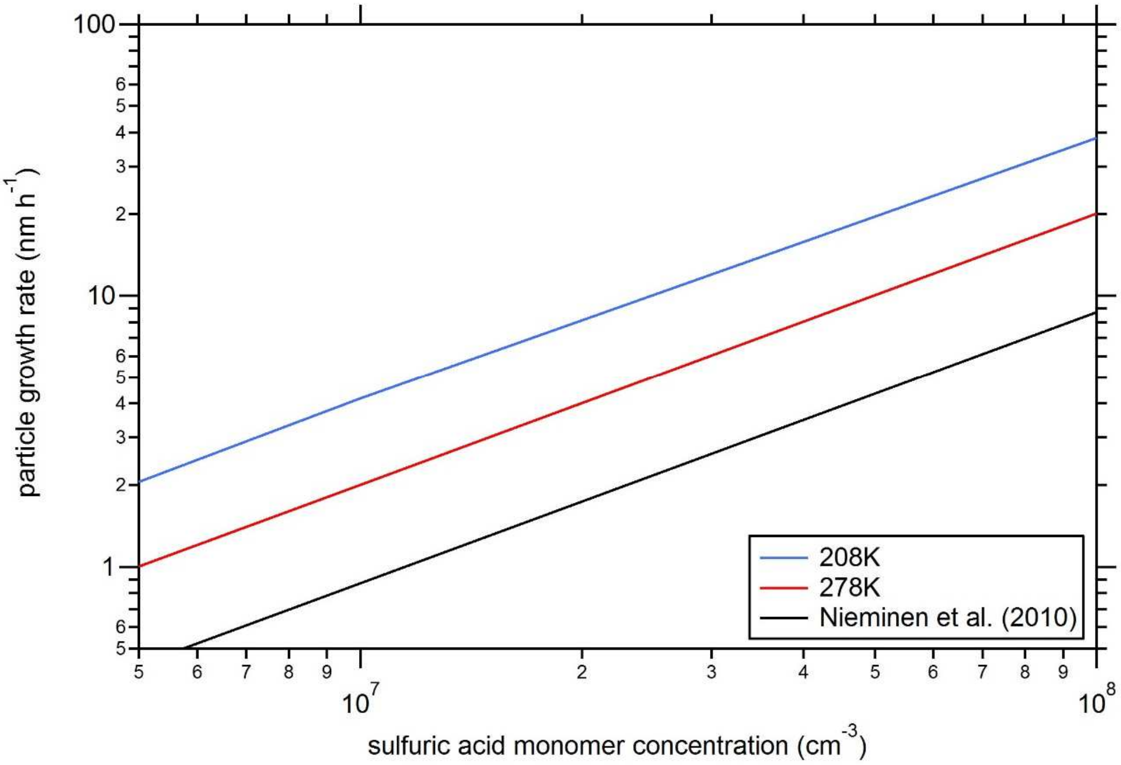
I agree, that a comment should be added that such slow rates (<1e-03 or 1e-04 s-1) are generally not relevant - at least at the high temperatures, i.e., near ground level. The following was added:

“However, the slow rates of $<1\times10^{-3}$ or 1×10^{-4} s^{-1} are not atmospherically relevant near the ground in most cases.”

(7) Figure 6 and associated discussion: These are growth rates for which size of particle? Do the lines converge for larger particle sizes?

In the previous version a particle diameter of 1.7 nm was chosen. In the revised figure (see below, new Figure 6) a particle diameter of 2.4 nm is used, which is more comparable to other studies on sulfuric acid-ammonia nucleation. This information is also added to the revised figure caption:

"The NH_3 concentration was set to 1×10^8 cm^{-3} (blue and red curve); for all calculations a density of 1615 kg m^{-3} and a particle mobility diameter of 2.4 nm was used; the diameter of the particles was calculated assuming a molecular mass of 151 amu (2 water and 1 ammonia molecule per sulfuric acid molecule)."



For larger diameters the lines do not converge, i.e., the model still predicts a significant faster growth rate at 208 K compared with 278 K. In general, the magnitude of the growth rates decreases, however, with increasing size (see also discussion in Nieminen et al., 2010).

(8) L464-465: Why couldn't a parameterization be made for growth rates? Overall, I'm a bit confused to all of the discussions throughout about parameterizations not being able to do various things. Parameterizations can do anything you want so long as you have the data to make them.

The last remark by the referee is exactly the point. A model like SANTIAGO can yield the growth rates (for all different sizes) even though they were not explicitly measured or parameterized. However, the reviewer is correct that growth rates could also be parameterized from existing data. In order to clarify this the end of Section 3.4 was modified as follows:

"The possibility of deriving growth rates with the model is an important feature that is not included in the parameterization for the CLOUD new particle formation rates by Dunne et al. (2016). The modeled growth rates enable further comparison to experimental data and the future study of particle growth to climatically relevant diameters."

(9) L548: When mapping between concentrations and mixing ratios, what pressure (and temperature) are you assuming? For a given mixing ratio, the corresponding concentration is about 5x smaller in the tropical upper troposphere than in the boundary layer.

Whenever a mixing ratio is reported it refers to the present temperature (the pressure in the CLOUD chamber is always 1 bar); this means that 1 pptv at 208 K correspond to 3.5×10^7 cm^{-3} but to 2.5×10^7 cm^{-3} at 292 K. Therefore, in Figure 5 the unit cm^{-3} has been chosen. To make this clear, the following information was added to the caption of Figure 4:

“The color code indicates the ammonia mixing ratio (for the respective temperatures indicated in the figure panels and a pressure of 1 bar); the grey symbols indicate pure binary conditions.”

(10) L553-554: Are the growth rates throughout the dry particle growth rates? RH can greatly impact the wet particle growth rates.

In the cited references and in the CLOUD experiments no attempt has been made to dry the particles. Therefore, the growth includes the effect of water vapor; however, at the present conditions this seems to have only an effect via the condensation of sulfuric acid. Depending on the RH, the sulfuric acid molecules contain a different number of water molecules (Hanson and Eisele, 2000). This can lead to some effect on the growth rate. Nieminen et al. (2010) report that the growth rates differ by a factor of ~2 depending on whether no water is attached to the sulfuric acid molecule or three water molecules are attached. The effect of water on the growth rate was taken into account for the generation of the growth rate curves from Figure 6 (described in the reply to comment (7)).

(11) L640: Is this ratio of 4 representative of the mean error or the mean bias?

The factor of 4 (ratio r for n = 125 experiments) is calculated from the following equation:

$$r = \frac{1}{n} \cdot \sum_{i=1}^{n} 10^{\left|log(J_{model,i}) - log(J_{exp,i})\right|}$$

It is therefore, the average ratio between modeled and measured new particle formation rate. Because the absolute values are used, it is rather the mean error than the mean bias.

“The average ratio between modeled and measured data is found to be as small as a factor of ~4 (mean error) for a wide range of conditions (208 K to 292 K, sulfuric acid at atmospherically relevant concentrations, e.g., $\geq 5\times10^5$ cm^{-3} at 208 K and $\leq 2\times10^9$ at 292 K) when using the best fit parameters.”

References

Dunne, E. M., et al.: Global atmospheric particle formation from CERN CLOUD measurements, *Science*, 354, 1119–1124, doi: 10.1126/science.aaf2649, 2016.

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

Hanson, D. R., and Eisele, F.: Diffusion of H_2SO_4 in Humidified Nitrogen: Hydrated H_2SO_4, *J. Phys. Chem. A*, *104*, 1715–1719, doi: 10.1021/jp993622j, 2000.

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

Nieminen, T., Lehtinen, K. E. J., and Kulmala, M.: Sub-10 nm particle growth by vapor condensation – effects of vapor molecule size and particle thermal speed, *Atmos. Chem. Phys.*, 10, 9773–9779, doi: 10.5194/acp-10-9773-2010, 2010.

Rondo, L., et al.: Effect of dimethylamine on the gas phase sulfuric acid concentration measured by Chemical Ionization Mass Spectrometry, *J. Geophys. Res. Atmos.*, 121, doi: 10.1002/2015JD023868, 2016.

Referee #2

I thank the referee for carefully reading the manuscript and for the constructive comments that help improving the paper. The comments are listed in full below (in black font), while the replies are given in blue font; text that has been added to the manuscript is shown in red font.

Andreas Kürten presents the extension of his previous model for sulfuric acid – dimethylamine nucleation. The model is extended to include evaporation intended for modelling sulfuric acid - ammonia nucleation. The main goal of the work is to derive new thermochemical parameters from CLOUD data. Understanding the mechanisms of sulfuric acid nucleation is of general interest and the presented model provides a great addition to the toolbox.

The manuscript is well written and structured and I can recommend publication in Atmospheric Chemistry and Physics and the following minor comments have been addressed.

(1) Line 161: How computationally heavy are these simulations? It would be beneficial to indicate the runtime that a typical simulation takes.

The simulation using one set of thermodynamic parameters for calculating the error from equation (3) (for 125 CLOUD experiments) takes ~10 seconds on a desktop personal computer (3.4 GHz i7 processor). For the Markov chain 500,000 steps were performed (100,000 per chain); this amounts to a total calculation time of ~60 days. However, as mentioned, a single simulation of a new particle formation event only takes ~0.1 s (10 s / 125) on average.

The following information was added to the end of the first paragraph of Section 2.2:

"Compared with the earlier study by Kürten et al. (2018) the number of bins is reduced in order to reduce computation time; the simulation of one new particle formation event (several hours of nucleation) takes ~0.1 s on a personal computer with a 3.4 GHz processor."

(2) Line 167-169: The maximum amount of ammonia molecules in the simulations are not allowed to exceed the number of acid molecules. How well is this assumption justified? Based on quantum chemical data (Olenius et al 2013, Elm et al 2017) on sulfuric acid - ammonia clusters this assumption seems somewhat reasonable, but it might be worth at least checking that the omission of clusters with one more base molecule than acid molecule present is not a large source of errors.

The dominating evaporation channel of a cluster $A_xB_{y=x+1}$ should be the loss of an ammonia (B) molecule. Further, the evaporation rate of B from $A_xB_{y=x+1}$ should be faster compared with the loss of B from A_xB_x. Therefore, the growth of clusters along the acid axis should occur via A_xB_x rather than $A_xB_{y=x+1}$ (because the concentration of $A_xB_{y=x+1}$ should be lower). From these arguments the error from the omission of $A_xB_{y=x+1}$ clusters should be relatively small. Testing this reasoning with further simulations would require a far-reaching update of the model (further differential equations, see SI Text S1 as well as 8 free parameters more, etc.) which would require significantly more computation time. Most likely the result would be that the effect of the $A_xB_{y=x+1}$ addition is small.

Supporting arguments that the concentrations of $A_xB_{y=x+1}$ clusters are small compared with those of $A_xB_{y\leq x}$ can be found from mass spectrometric measurements. In the study by Kirkby et al. (2011) and Schobesberger et al. (2015) no clusters were identified for the sulfuric acid-ammonia system where more base than acid was detected by a high resolution mass spectrometer, i.e., the measured ion clusters were all of the sort $HSO_4^-(H_2SO_4)_a(NH_3)_{b\leq a-1}$. The observation that they always contained one less ammonia than neutral sulfuric acid can be explained by the fact these were not electrical neutral clusters but ion clusters with one bisulfate ion. This HSO_4^- acts as an electron donor (= Lewis base) and therefore the clusters with equal ammonia and acid seem not to be stable. Of course, these observations apply for charged clusters but qualitatively their chemistry supports the fast evaporation rates for clusters with more B than A found by the quantum chemical calculations.

Further information concerning the justification for the chosen nucleation scheme was added to Section 2.2 (second paragraph):

“The assumption that no clusters are allowed that contain more base than acid is based on fast evaporation rates that have been found for such clusters from quantum chemical calculations (Schobesberger et al., 2015; Elm et al 2017; Yu et al., 2018); the assumption is further supported by mass spectrometric measurements that could not identify such clusters (Kirkby et al., 2011; Schobesberger et al., 2015).”

The reference to Schobesberger et al. (2015) was added to the reference list.

(3) Line 170-172: In the pentamer and larger clusters there is not differentiated regarding the amount of bases. How large a source of errors does this assumption lead to? Surely, the 5 sulfuric acid cluster without any bases or only 1-2 ammonia molecules present are not very stable.

I agree that the pentamers with a low base content are likely not very stable. That is the reason why the binary nucleation is not well represented at elevated temperature and also the ternary nucleation at high temperature and low ammonia concentration (see Figure 5). However, even for relatively low ammonia concentrations nucleation seems to proceed mainly via the tetramer with three ammonia molecules (Figure R1 below). The found d*G* value for this cluster is -16.5 kcal mol^{-1} at 278 K. Therefore, the larger clusters with low ammonia content probably do not play a significant role. For most atmospheric situations where nucleation at warm temperature involves sulfuric acid and ammonia, the ammonia concentration is probably higher than the sulfuric acid concentration. Therefore, for each arriving acid also at least one ammonia molecule can be added. This is supported by an observed ~1:1 ratio between acid and base in clusters (Kirkby et al., 2011; Kürten et al., 2014). For very low ammonia concentrations and high temperatures SANTIAGO should not be used for exactly that reason. The clusters with low ammonia content become more relevant and their negligence beyond the tetramer causes inaccuracies (Figure 5); however, for the stated ranges the truncation error is probably small.

A quantitative analysis of this effect would be very interesting; however, same as for comment (2) a lot of effort would be necessary to perform such a study. The effect of truncation is further discussed in Section 4.2.

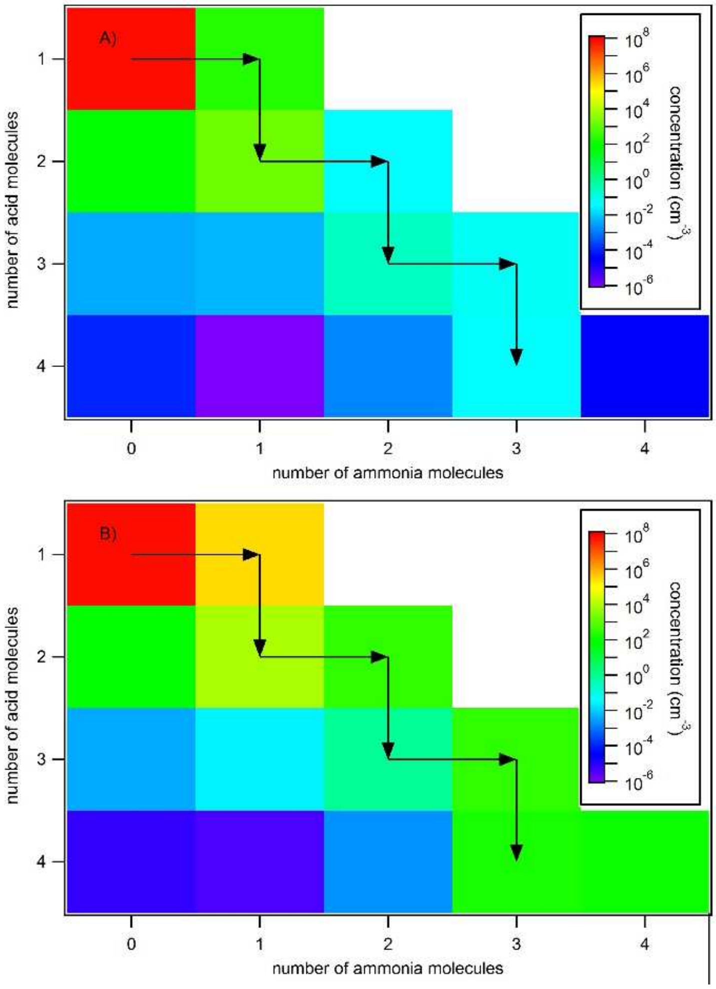


Figure R1: *Cluster concentrations (number of acid molecules on the y-axis and number of ammonia molecules on the x-axis) for two different scenarios. A) Ammonia concentration of* 2.5×10^7 cm^{-3} *and B) ammonia concentration of* 2.5×10^{10} cm^{-3}*. The sulfuric acid concentration is* 6.5×10^7 cm^{-3} *and temperature is 278 K for both simulations.*

(4) Line 182-185: While the results would most likely not be drastically different, the simplification of the evaporation rates, put a very strict constrain on the nucleation mechanism. Can it be quantified how much this simplification influences the results?

I agree that it would be good to compare the results with further model calculations that include all possible evaporation channels. As mentioned in the manuscript this would increase the number of free parameters drastically (from 22 to 40) and due to the non-linearity of the problem the computation time by a big factor. Therefore, this simplification can at the moment not be evaluated quantitatively.

In the manuscript some discussion regarding the simplification is included at the end of Section 4.2.

(5) Line 188-193: It seems like an odd choice to take some of the cluster thermodynamics from a different study and not fitting them like the remaining. Why was this choice made?

This choice was made based on two reasons:

i) The number of free parameters should be as small as possible in order to keep the computation time reasonably small. At the moment 22 free parameters are being used, including the pure acid dimer and trimer would increase this number to 26.

ii) The cluster evaporation rates of the pure acid dimer and trimer were explicitly measured by Hanson and Lovejoy (2006) and it was shown, e.g., by Ehrhart et al. (2016) that they can be used to predict the new particle formation rates in the binary system accurately. In fact, Ehrhart et al. (2016) used a subset of the CLOUD new particle formation rates from the present study (based on the Dunne et al., 2016 and Kürten et al., 2016 data) to test the SAWNUC (Sulfuric Acid Water NUCleation) model for sulfuric acid-water binary nucleation. In my opinion, additional uncertainty would therefore be introduced by fitting/optimizing these evaporation rates in the present study as it can be accepted that they describe the binary nucleation channel quite accurately.

In order to justify the choice made the following was added to Section 2.2 (4th paragraph):

"The thermodynamic parameters for the two smallest pure acid clusters (A_2 and A_3) are taken from a study where the parameters were derived from flow tube measurements (Hanson and Lovejoy, 2006). Ehrhart et al. (2016) showed that a numeric model for sulfuric acid-water binary nucleation using those data can well replicate new particle formation rates measured at CLOUD."

(6) Line 408-411: It should be mentioned that coagulation can also be the cause of the curvature in the line.

I agree, this comment was also made by Reviewer 1 (comment (3)); the relevant sentence was changed to:

"The curvature is due to the fact that the survival probability of subcritical clusters (i.e., clusters below the nonamer) can be strongly affected by wall loss or pre-existing particles (Ehrhart and Curtius, 2013)."

(7) Line 481-482: Looking at Table 1 it appears that the quantum chemical values taken from Ortega et al 2012, fits quite well with the estimated values using the optimization method. This is also evident from comparing Figure 2 with Figure S1. Perhaps it should be further emphasized that the optimization of the values is more or less redundant and that quantum chemically obtained entropy values are quite accurate.

I agree that this comment should be considered. The revised manuscript now includes the following statement in the last sentence of the first paragraph in Section 4.1.1:

"However, no large differences can be found between the initialized and optimized values, which can be interpreted such that the quantum chemical calculations yield accurate results for d*S*."

References

Dunne, E. M., et al.: Global atmospheric particle formation from CERN CLOUD measurements, *Science*, 354, 1119–1124, doi: 10.1126/science.aaf2649, 2016.

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

Ehrhart, S., et al.: Comparison of the SAWNUC model with CLOUD measurements of sulphuric acid-water nucleation, *J. Geophys. Res.-Atmos.*, 121, 12401–12414, doi: 10.1002/2015JD023723, 2016.

Elm, J., and Kristensen, K.: Basis set convergence of the binding energies of strongly hydrogen-bonded atmospheric clusters, *Phys. Chem. Chem. Phys.*, 19, 1122, doi: 10.1039/c6cp06851k, 2017.

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

Kirkby, J., et al.: Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation, *Nature*, 476, 429–435, doi: 10.1038/nature10343, 2011.

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.: 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, 2016.

Kürten, A., et al.: New particle formation in the sulfuric acid–dimethylamine–water system: reevaluation of CLOUD chamber measurements and comparison to an aerosol nucleation and growth model, *Atmos. Chem. Phys.*, 18, 845–863, doi: 10.5194/acp-18-845-2018, 2018.

Olenius, T., et al.: Comparing simulated and experimental molecular cluster distributions, *Faraday Discuss.*, 165, 75–89, doi: 10.1039/C3FD00031A, 2013.

Ortega, I. K., et al.: From quantum chemical formation free energies to evaporation rates, *Atmos. Chem. Phys.*, 12, 225–235, doi: 10.5194/acp-12-225-2012, 2012.

Schobesberger, S., et al.: On the composition of ammonia–sulfuric-acid ion clusters during aerosol particle formation, Atmos. Chem. Phys., 15, 55–78, doi: 10.5194/acp-15-55-2015, 2015.

Yu, F., et al.: H_2SO_4–H_2O–NH_3 ternary ion-mediated nucleation (TIMN): kinetic-based model and comparison with CLOUD measurements, *Atmos. Chem. Phys.*, 18, 17451–17474, doi: 10.5194/acp-18-17451-2018, 2018.