Atmospheric
Chemistry
and Physics
Discussions

Open Access

ACPD

Interactive
comment

Interactive comment on "H$_2$SO$_4$-H$_2$O-NH$_3$ ternary ion-mediated nucleation (TIMN): Kinetic-based model and comparison with CLOUD measurements" *by* Fangqun Yu et al.

Anonymous Referee #1

Received and published: 20 June 2018

Review of "H$_2$SO$_4$-H$_2$O-NH$_3$ ternary ion-mediated nucleation (TIMN): Kinetic-based model and comparison with CLOUD measurements" by F. Yu et al.

The manuscript presents a kinetic, quasi-unary molecular cluster and aerosol particle model to simulate ternary ion-mediated nucleation (TIMN) from sulfuric acid (H$_2$SO$_4$), water (H$_2$O) and ammonia (NH$_3$). This work extends the previously developed binary H$_2$SO$_4$-H$_2$O (BIMN) model (Yu, 2006b) to include also ammonia. This is done by using quantum chemical data for some H$_2$SO$_4$-H$_2$O-NH$_3$ molecular clusters (some of which have been previously published by the authors, and some of which are new

but not yet published) and previously measured experimental thermodynamic data for bulk solutions, and implementing them in the model. Model results for the formation rate $J_{1.7}$ of nanoparticles of 1.7 nm are compared to rates derived from particle measurements at the CLOUD aerosol chamber.

The manuscript is fairly clearly written and suits in the scope of ACP. However, the model details need further clarification, and some assumptions and approximations made in the model require justification and/or more discussion. Also, discussion of the results with respect to experiments and other nucleation parameterizations or models needs to be more balanced. After the authors have addressed these issues (as listed in detail below), the study can be considered for publication in ACP.

Specific comments:

The most important issues regarding the model can be summarized as follows:

The authors claim to present "the first comprehensive kinetically-based H_2SO_4-H_2O-NH_3 ternary ion-mediated nucleation (TIMN) model that is based on the thermodynamic data derived from both quantum-chemical calculations and laboratory measurements."

However, it turns out that the model is in fact quasi-unary, i.e. approximates the multi-compound chemical system as a one-compound system. Also, the quantum-chemical data is rather sparse, liquid thermodynamic data is used from quite small nanoparticle sizes onward, and the rest of the thermodynamics is in practice guessed by connecting quantum chemical and bulk data by an exponential function.

These facts and the related uncertainties should be clearly brought up and discussed. Considering the roughness of some approximations, the suggestion that the model is in excellent agreement with CLOUD data needs much more comparisons and more than a few data points from CLOUD.

Thermodynamic data

The thermodynamic input data includes quantum chemical (QC) data for the very smallest clusters of a few molecules. Particles containing more than at least ten sulfuric acid molecules are assumed to behave according to the electrically neutral macroscopic liquid droplet model. For the intermediate sizes below ten H_2SO_4 molecules, QC data and liquid data are connected together by a type of exponential function.

(1) In general, it would be extremely helpful to explain the thermodynamic data in the form of a table which lists the different cluster / particle compositions and sizes, and the approaches used for their Gibbs free energies. It's much easier and faster for the reader than finding the information in the text.

Quantum chemical (QC) data for small molecular clusters

The QC data has been obtained using the PW91PW91/6-311++G(3df,3pd) density functional theory (DFT) method. PW91 is a commonly used DFT method in atmospheric cluster calculations, and it has been shown to yield mean errors similar to (although somewhat higher than) other common DFT methods in QC benchmarking studies (e.g. Elm and Kristensen, 2017).
In terms of the number of sulfuric acid molecules, which is the principal building block of the clusters and particles in the presented kinetic model, the used QC data covers cluster sizes up to (a) 1 sulfuric acid molecule for positively charged, (b) 4 for negatively charged (5 if the bisulfate ion is counted in), and (c) 4 for electrically neutral clusters.

C3

(2) Page 5, line 152: "The thermodynamic data sets used for binary clusters were also updated."
For which clusters were the data updated: All or just some of them? What kind of differences are there compared to the previously published data for these clusters?

(3) Page 9, line 250: "We have extended the earlier QC studies of binary and ternary clusters to larger sizes."
Which sizes? Please indicate clearly which clusters are new, and which have been studied in previous publications. Also, list clearly the clusters for which QC data is applied (instead of other type of thermodynamic data). Are these the clusters listed in Tables 2-4?

(4) Page 9, lines 254-255: The authors have used also a "locally developed sampling code, which creates a 'mesh' around the cluster, in which molecules being attached to the cluster are the mesh nodes", but this sentence is all that is said about the code. Please elaborate what this code exactly does, and give a reference, if possible.

(5) Page 10, lines 289-292: "Both the absolute values and trends in ΔG^0_{+W} derived from calculations are in agreement with the laboratory measurements within the uncertainty range of $\sim$1-2 kcal mol^{-1} for both QC calculations and measurements. This confirms the efficiency and precision of QC methods in calculating thermodynamic data needed for the development of nucleation models."
$\sim$1-2 kcal mol^{-1} can be expected to be the general uncertainty of quantum chemical methods. However, as the Gibbs free energies are incorporated in the exponential factor of the evaporation rate (Eq. (7)), this uncertainty may propagate to an uncertainty of up to orders of magnitude in the particle formation rates and concentrations. This is discussed and demonstrated e.g. by Kürten at al. (2016), who estimated the uncertainties in the modeled particle formation rates by increasing or decreasing all

Gibbs free energies by 1 kcal mol^{-1}. Depending on the conditions, this changes the formation rate by less than an order of magnitude, or even by up to several orders of magnitude.

Please discuss also the sensitivity of the particle kinetics to the evaporation rates, and the impact of the uncertainties in ΔG on the formation rate.

(6) Page 11, lines 321-322: "Since positively charged H_2SO_4 dimers are expected to contain large number of water molecules, no quantum chemical data for these clusters are available."

What does this mean? Does it mean that the data cannot be computed at all, or that the authors haven't computed such data in these studies?

(7) Page 12, lines 348-351: "Table 3 shows that the presence of NH_3 in H_2SO_4 clusters suppress hydration and that ΔG^0_{+W} for S_2A_2 falls below -2.0 kcal mol^{-1}. This is consistent with earlier studies by our group and others showing that large S_nA_n clusters (n>2) are not hydrated under typical atmospheric conditions."

Please give references for these studies, especially for those conducted by other groups. Does this mean that all clusters and nanoparticles larger than $(H_2SO_4)_2(NH_3)_2$ are generally not hydrated, or do the particles become hydrated again at some larger size? At which size? What is assumed about the hydration of electrically neutral H_2SO_4-NH_3 clusters beyond the quantum chemistry data set, i.e. larger than $(H_2SO_4)_4(NH_3)_5$?

Generally, the hydration of a specific cluster (S_2A_2) tells nothing about the hydration of other clusters with different numbers of acid and base molecules. Therefore, it should be stated here that neglecting water in the larger clusters is just an assumption that has to be made due to the lack of thermodynamic data (as the authors have actually done later on line 454).

(8) Page 12, lines 365-367: "This finding is fully consistent with the laboratory measurements showing that growth of neutral S_sA_a clusters follows $s = a$ pathway (Schobesberger et al., 2015)."
The study by Schobesberger et al. (2015) does not present any measurement data for neutral clusters. (Instead, they are modeled by the ACDC program in that study.) Please correct the sentence.

(9) Page 13, lines 389-393: "ΔG^0_{+S} values for $S^-S_{3-4}W_w$ are consistently $\sim$1.5-3 kcal mol^{-1} less negative than the corresponding semi-experimental estimates (Table 4). The possible reasons behind the observed systematic difference are yet to be identified and include the use of low-level ab initio HF method to compute reaction enthalpies and uncertainties in experimental enthalpies in studies by Froyd and Lovejoy (2003)."
The computed values for ΔG^0_{+W} (as well as for ΔG^0_{+W} for some positive clusters), on the other hand, are *more* negative than those determined by Froyd and Lovejoy (2003). Why doesn't the discussed systematic difference apply to these values?

(10) Page 15, lines 471-472: "In the TIMN model, the equilibrium distributions are used to calculate number concentrations weighted stepwise Gibbs free energy change"
Where is this averaged ΔG used in the model? Doesn't the model use averaged evaporation frequencies (Eq. (10)), which are calculated over the individual evaporation rates and thus do not correspond to the averaged ΔG?

(11) Page 15, lines 477-479: "In the atmosphere, where substantial nucleation is observed, the sizes of critical clusters are generally small ($s < \sim 5 - 10$) and nucleation rates are largely controlled by the stability (or γ) of small clusters with $s < \sim 5 - 10$."
Please give references for this.

C6

(12) Table 2 and discussion on pages 17-19: For positively charged clusters, there is QC data only up to clusters containing one H_2SO_4 molecule and two NH_3 molecules. That is, not even the first growth step with respect to H_2SO_4 clustering (i.e. the formation of a H_2SO_4 dimer) is covered, and in practice all the data for positive clusters is guessed by using Eq. (11) (except for clusters containing more than 10 acid molecules, starting from which data for electrically neutral bulk solutions is used also for the positive clusters).

This is an extremely crude approximation. Please bring up this fact, and explain what new "insights" we can learn about the thermodynamics of these clusters by using these type of data.

(13) Page 17, lines 536-538: Similarly to positive clusters, the results for the thermodynamics of negative clusters raise some questions: "The effect of NH_3 on negative ions becomes important at $s \geq\sim 4$, when bonding between the clusters and NH_3 becomes strong enough to contaminate a large fraction of binary clusters with ammonia (Fig. 3)."

No QC data or experimental bulk data is used for the clusters around sizes $s \approx 4 - 9$. Considering that this behavior is deduced by interpolating between QC data for small clusters that take up ammonia rather weakly, and macroscopic solution data for an electrically neutral H_2SO_4-H_2O-NH_3 liquid, it is difficult to see this result as very reliable. Please state that the thermodynamics of these clusters are highly uncertain (or explain why they would not be).

(14) Table 4: The hydrate data for the negatively charged clusters is quite sparse for some clusters. Why are not hydrates with more water molecules considered for, for example, S^-S_1 or S^-S_2?

(15) Tables 2-4: Why isn't all QC data that is used in the model given in the tables?

For example, binary electrically neutral clusters are not included in Table 3. Please indicate clearly where these data can be found.

(16) Figure 3: Why are some hydrates with different numbers of water molecules grouped together? For instance, $(H_2SO_4)_2(H_2O)_{1-7}$ is presented as one bar; this doesn't tell much about the hydration as 1 and 7 are quite different numbers.
Also, in panel (d), please clarify that there is no hydrate data for these clusters; otherwise the figure panel might be understood so that the clusters don't take up water at all.

(17) Figure 4: Why is the cumulative Gibbs free energy zero for the first growth steps of the negative clusters in panel (b)? In panel (a), it does not look like these values add up to zero, but should be negative instead.

(18) Caption of Figure 4: "Calculations were carried out at T=292 K, RH=38%, $[H_2SO_4]=3x10^8$ cm^{-3} and $[NH_3]$= 0.3 ppb."
How were the vapor concentrations, e.g. $[H_2SO_4]$, used in the calculations?

Experimental bulk data for larger nanoparticles

Bulk thermodynamic data is assumed for particles of all charging states containing at least ten H_2SO_4 molecules. While this is in practice the only available option due to the lack of other type of data, the approximation calls for some discussion about the related uncertainties.

(19) At which conditions (temperature, partial pressures of the H_2SO_4, NH_3, H_2O vapors) were the measurements (Marti et al., 1997; Hyvärinen et al., 2005) performed?

How reliably can it be extrapolated to different conditions outside the measurement range?

(20) Page 16, lines 487-491: "Based on experimental data (Kebarle et al., 1967; Davidson et al., 1977; Wlodek et al., 1980; Holland and Castleman, 1982; Froyd and Lovejoy, 2003), the stepwise ΔG values for clusters decreases exponentially as the cluster sizes increase and approaches to the bulk values when clusters containing more than ~8-10 molecules (Yu, 2005)."
Is possible size-dependent chemical composition, i.e. acid:base molar ratio, considered here (e.g. Chen et al., 2018)? How does it affect the model results?

(21) Page 16, lines 491-494: "Cluster compositions measured with an atmospheric pressure interface time-of-flight (APi-TOF) mass spectrometer during CLOUD experiments also show that the chemical effect of charge-carrying becomes unimportant when the cluster contains more than 9 H_2SO_4 molecules (Schobesberger et al., 2015)."
In the study by Schobesberger et al. (2015), it looks like the different charges approach similar composition somewhere in the size range where the H_2SO_4 content is ~20-100 molecules (Figure 9 in the study). At 10 H_2SO_4 molecules, the composition of negative and positive particles is still different. Please comment.

(22) Page 17, line 524: "consistent with the laboratory measurements (Marti et al., 1997)"
Isn't the discussed ΔG data derived from these measurements (i.e. naturally, it is consistent)? Please clarify.

Page 24, lines 774-776: Is this the correct reference?

Approximated values for intermediate sizes with < 10 H$_2$SO$_4$ molecules

(23) Eq. (11): What is this "extrapolation" formula based on? It is not clear why this functional form would be suitable for connecting QC and bulk measurements. Please explain clearly how the formula is derived, and discuss the related uncertainties.

(24) Page 16, lines 503-506: "c in Eq. (11) is the exponential coefficient that determines how fast $\Delta G_{s-1,s}$ approaches to bulk values as s increases. In the present study, c is estimated from $\Delta G_{s-1,s}$ at s=2 and s=3 for neutral binary and ternary cluster for which experimental (Hanson and Lovejoy, 2006; Kazil et al., 2007) or quantum-chemical data (Table 3) are available."
What can the data for clusters that contain 2 or 3 H$_2$SO$_4$ molecules possibly tell about how fast ΔG approaches bulk values?
Is c estimated based on QC data, experimental data, or both? How is this done exactly? Is it only for neutral clusters, or also for charged clusters?

(25) Finally, the most important issue regarding the thermodynamics is the fact that the "critical sizes", i.e. the barriers for nucleation, are located around cluster sizes for which there is no reliable thermodynamic data (Figure 4). For all different types of clusters (binary, ternary, all charging states), the maximum of the free energy curve is beyond the QC data (or just at the upper limit of the QC data in the case of negative ternary clusters). That is, the critical stage of nucleation is based on Eq. (11), which in turn does not seem to be based on an actual physical model.
Considering this, can the model really give important new information on H$_2$SO$_4$-H$_2$O-NH$_3$ particle formation mechanisms?

Kinetic model

(26) In the kinetic model, the clusters are assumed to be in equilibrium with respect to both water and ammonia. Such equilibriation assumption can be made if the time scales of the attachment and evaporation processes of some compound are substantially shorter than those of other compounds. This is the case for water, as (a) its concentration (to which the attachment, i.e. molecular collision, frequency is directly proportional) is around $\sim$10 orders of magnitude higher than that of H_2SO_4 or NH_3, and (b) its binding to the clusters is so much weaker that its evaporation rate is $\sim$ several orders of magnitude higher than that of other compounds (except for some charged clusters in e.g. Table 2).

This is, however, generally not the case for ammonia. The binding of NH_3 depends strongly on the cluster composition: Depending on the acid:base ratio, either NH_3 or H_2SO_4 evaporates much faster than the other. Within the set of small clusters, the weakest and strongest bindings of NH_3 are of the same order as those of H_2SO_4 (e.g. Table 3). The collision rates of NH_3 are not necessarily multiple times higher than those of H_2SO_4, either: While ammonia is generally more abundant than H_2SO_4 in the atmosphere, there are environments where $[H_2SO_4]$ and $[NH_3]$ are around the same order (such as some of those simulated in this study).

Due to these reasons, the explanation for assuming equilibrium with respect to NH_3 is not justifiable (pages 13-14, lines 414-418): "In the lower troposphere, where most of the nucleation events were observed, $[H_2SO_4]$ is typically at sub-ppt to ppt level, while $[NH_3]$ is in the range of sub-ppb to ppb levels. This means that small ternary clusters can be considered to be in equilibrium with H_2O and NH_3 vapors."

(a) Doesn't ammonia need to also evaporate much faster from the clusters for the equilibrium assumption to be justified? (b) At the simulated conditions, $[H_2SO_4]$ and $[NH_3]$ are in many cases of the same order. For instance, in Figure 6 at the lower end of the $[NH_3]$ axis, $[NH_3]$ is of the same order or even lower than $[H_2SO_4]$. In Figure 7a, $[NH_3]$ is around 10 ppt, i.e. $\sim 10^8$ cm-3, and $[H_2SO_4]$ is around $10^7 \ldots 10^9$ cm^{-3}.

C11

Please show that the equilibrium with respect to NH$_3$ really is a valid assumption for these simulation systems.

(27) Some other aspects of the model also need clarification. The kinetic equations (Eqs.(1-6)) seem to include also collisions between charged clusters / particles of the same polarity. How high are the rate constants for such processes? Doesn't electrostatic repulsion prevent these attachments?
Further, if multiply charged particles can form in these collisions, how are these different charge numbers treated in the model? Shouldn't there be separate equations for particles that contain a single charge, two charges, three, and so on?

(28) Page 5, lines 162-166: "The initial negative ions, which are normally assumed to be NO$_3^-$, are converted into HSO$_4^-$ core ions (i.e., S$^-$) and, then, to larger H$_2$SO$_4$ clusters in the presence of gaseous H$_2$SO$_4$. The initial positive ions H$^+$W$_w$ are converted into H$^+$A$_{1-2}$W$_w$ in the presence of NH$_3$, H$^+$S$_s$W$_w$ in the presence of H$_2$SO$_4$, or H$^+$A$_a$S$_s$W$_w$ in the case, when both NH$_3$ and H$_2$SO$_4$ are present in the nucleating vapors."
What are the rate constants for the conversions of NO$_3^-$ and H$^+$W$_w$? What does H$^+$A$_{1-2}$W$_w$ (or H$^+$S$_s$W$_w$ and H$^+$A$_a$S$_s$W$_w$) mean, i.e. how many ammonia and water molecules does it contain?
In the equations (page 7, lines 192-193), "$N_0^{+,-}$ and Q are the concentration of initial ions not containing H$_2$SO$_4$ and the ionization rate, respectively"
What do the "initial ions" refer to, e.g. H$^+$W$_w$ or H$^+$A$_{1-2}$W$_w$? NO$_3^-$ or HSO$_4^-$?

(29) Eq. (3): Why does the evaporation term for creating H$_2$SO$_4$ monomers from a dimer includes a factor of two ($\delta_{j,2}$), but the corresponding collision term, removing monomers in the collision creating a dimer, does not?

(30) Page 8, lines 212-213: "The methods for calculating β, γ, η, and α for binary H_2SO_4-H_2O clusters have been described in detail in Yu (2006b)."
I was not able to find the descriptions for β, η, and α in the given reference; the paper only seems to re-direct the reader to discussion in 3 other papers. Please briefly summarize how these parameters are obtained.

(31) Page 8, lines 221-222: "N^o is the number concentration of H_2SO_4 at a given T under the reference vapor pressure P of 1 atm."
Isn't N^o simply the number concentration corresponding to the reference pressure P of the QC calculations? What does it have to do with any [H_2SO_4]? In general, the evaporation rate should not be related to the concentration of any compound, as it does not depend on the composition of surrounding vapor (only on the temperature, i.e. the inert gas).

(32) Page 8, lines 223-225: "The temperature dependence of ΔH^o and ΔS^o, which is generally small and typically negligible over the temperature range of interest, was not considered."
Can you give a reference for the negligible temperature dependence?

(33) Page 19, lines 572-573: "mean evaporation rate ($\bar{\gamma}$) of an H_2SO_4 molecule"
Is it assumed that only a single H_2SO_4 molecule evaporates, i.e. no water ligands, for instance, are attached to it? If so, please discuss the validity of this assumption, or even better, average the evaporation rates over all evaporation pathways with different numbers of other compounds attached to the acid molecule.

(34) Page 19, lines 573-574: "The shapes of $\bar{\gamma}$ curves are similar to those of $\Delta \bar{G}_{s-1,s}$ (Fig. 4a) as $\bar{\gamma}$ values are largely controlled by $\Delta \bar{G}_{s-1,s}$."

How is $\bar{\gamma}$ related to the averaged values $\bar{\Delta G}_{s-1,s}$? Isn't $\bar{\gamma}$ calculated based on individual values $\Delta G_{s-1,s}$ (Eq. (10)), i.e. not exactly equivalent to $\bar{\Delta G}_{s-1,s}$?

(35) The discussion on page 19, lines 575-584, feels somewhat confusing: First it's said that the effect of ammonia is significant for larger clusters and of less importance for small clusters (e.g. "the binding of NH_3 to small neutral and charged clusters are weaker compared to that for larger clusters"), but after this it's concluded that "The nucleation rates, limited by formation of small clusters ($s <\sim 5$), depend strongly on the stability or evaporation rate of these small clusters and, thus, on [NH_3]."
So is or is not NH_3 important for the small clusters and nucleation? Please clarify.

(36) Page 19, line 588: "the concentrations of clusters of all sizes are explicitly predicted"
A quasi-unary model cannot be called "explicit"; please re-formulate.

(37) Eq. (13): Is it so that only growth through H_2SO_4 vapor is taken into account in the calculation of the particle formation rate? What about the effects of coagulation and recombination?
The quantity J that can be deduced from measurements -and that also is the relevant quantity for atmospheric modeling- includes all processes through which particles form, not only monomer condensation and evaporation. Therefore, these should be included also in the model-based formation rate.

(38) Figure 1: The figure is confusing, and using patterns to fill the lines or spheres makes it somewhat difficult to read. For instance, it looks like "Condensation" means that electrically neutral clusters are ionized into charged particles (the arrows lead only to the charged blocks), and that "Coagulation / Scavenging" means that positively

charged particles attached to each other or neutral particles. What is the difference between "Coagulation / Scavenging" and "Coagulation"?

Results and discussion

(39) As a general comment, the description of the model should be a bit less ambitious. As one-compound discrete-sectional kinetic models have existed at least since the 1970s, the model cannot be considered "first", nor is it exactly "comprehensive" or "accurate" due to the quasi-unary assumption.
The addition of NH_3 to the previous BIMN model does not make the model very new, either, as it means simply using different thermodynamic data in an existing model - and the main author has also previously published a modeling study entitled "Effect of ammonia on new particle formation: A kinetic H_2SO_4-H_2O-NH_3 nucleation model constrained by laboratory measurements" (Yu, 2006a). Besides, as the authors themselves also bring up, the kinetics of H_2SO_4-H_2O-NH_3 molecular clusters including the different charging states have been previously modeled e.g. by the ACDC program (which the authors quite extensively criticize).

(40) As previously (e.g. Nadykto et al., 2011; Nadykto et al., 2014), the main criticism is targeted at the modeling work by University of Helsinki (and this time also at the particle formation rate parameterization CLOUDpara based on the experimental data from the CLOUD chamber). In general, the authors criticize the ACDC model; however, the output of a clustering model is determined by the input parameters, namely the thermodynamic data. The ACDC program does not use any specific QC data, but the data is instead given by the user.
The ACDC data presented by Kürten et al. (2016) results from QC thermochemistry calculated with the RI-CC2/aug-cc-pV(T+d)Z//B3LYP/CBSB7 method. Therefore, the authors should call this rather e.g. "RI-CC2//B3LYP" data than "ACDC" data. The

Printer-friendly version

Discussion paper

RI-CC2//B3LYP method is known to have a tendency to over-predict cluster stability, as has been discussed for example by the Helsinki group (e.g. Kupiainen-Määttä et al., 2015; Myllys et al., 2016), and thus it is not much used anymore in QC calculations.

(41) Page 4, lines 122-123: "ACDC is also an acid–base reaction model, with the largest clusters containing 4-5 acid and 4-5 base molecules (no water molecules)":
This is not the case, as ACDC is simply a program that solves the kinetic equations (similar to Eqs. (1-6)) for a given set of molecular clusters using given thermodynamic input data, which does not need to involve acids or bases. It is not limited to some fixed specific largest cluster sizes; in the cited studies, the largest sizes were determined by the availability of QC data for the systems of interest.

(42) Page 4, lines 127-130: "In ACDC, the nucleation rate is calculated as the rate of clusters growing larger than the upper bounds of the simulated system (i.e., clusters containing 4 or 5 H_2SO_4 molecules) (Kurten et al., 2016) and thus may over-predict nucleation rates when critical clusters contain more than 5 H_2SO_4 molecules."
It is of course not reasonable to model a system where the critical size region is outside the system boundaries. Thus, this region should be examined before simulating given conditions, as also discussed in the study by Olenius et al. (2013).

(43) Page 4, lines 130-132: "All clusters simulated by the ACDC model do not contain H_2O molecules and the effect of relative humidity (RH) on nucleation thermochemistry is neglected." Page 21, lines 645-646: "an important influence of RH on nucleation rates (which is neglected in both the CLOUDpara and ACDC models)"
The authors of the present manuscript are well aware of the fact that water can be included in the ACDC model: in fact, the effect of cluster hydration was recently the topic of a rather heated discussion between these authors and the researchers at University of Helsinki (Nadykto et al., 2014; Kupiainen-Määttä et al., 2015; Nadykto

et al., 2015; in this case, the question was about H_2SO_4-dimethylamine clusters), including i.a. ACDC simulations conducted as a function of RH.

Hydration can naturally be included in a kinetic model, such as ACDC, given that there is thermodynamic input data for clusters containing water. Please correct your claims about this. The effect of water in the H_2SO_4-H_2O-NH_3 system has been studied by ACDC e.g. by Henschel et al. (2016).

(44) Also the particle formation rate parameterization by Dunne et al. (2016) is criticized. It would be fair to note that the deviations of the parameterization from the CLOUD data are not a new finding, as the uncertainties and weaknesses of the parameterization are discussed rather extensively in the work by Dunne et al. (e.g. supplementary Figures S3-S6).

(45) Page 11, line 333-334: "most of these studies, except for Nadykto and Yu (2007), did not consider the impact of H_2O on cluster thermodynamics"
The effect of H_2O on H_2SO_4-NH_3 clusters containing up to three H_2SO_4 and three NH_3 molecules has been considered by Henschel et al. (2014; 2016).

(46) Page 13, lines 396-397: The sentence "The binding of the second NH_3 to S^-S_3A to form $S^-S_3A_2$ is much weaker than that of the first NH_3 molecule. This indicates that most of S^-A_a can only contain one NH_3 molecule" isn't clear: How does the binding of NH_3 to a cluster containing 3 H_2SO_4 molecules indicate something about the attachment of NH_3 to a bisulfate ion S^-?

(47) Comparisons to CLOUD data (Figures 6 and 7): Many of the comparisons look quite nice indeed. However, **more experimental data over a wider range of conditions should be shown to support the claim that the model is "in excellent**

agreement with CLOUD measurements".

For instance, in the work by Kürten et al. (2016) on CLOUD-based $J_{1.7}$, the model used in the study (ACDC with input thermodynamics computed with the RICC2//B3LYP method) is at some conditions in excellent agreement with CLOUD data, and at some conditions there are significant differences.

Therefore, comparisons with CLOUD data should be shown for **a large set of data**, for example the figures of the study by Kürten et al. (2016), including also electrically neutral cases and a wider range of ammonia concentrations.

(48) Figure 6: The original CLOUD data includes also $J_{1.7}$ for experiments with no ions. Please add these electrically neutral experimental and model data to the figure. It looks like the slope of the modeled $J_{1.7}$ is quite steep when neutral nucleation takes over; it is interesting to see how this compares with the measurements.

(49) Figure 7, top panel: For most lines, there are only 3 experimental data points, which doesn't make the comparison of these data to the model lines very strong. As there is so much CLOUD data available, please pick more representative data from e.g. the work by Kürten et al. (2016).

Especially low but still non-negligible ammonia mixing ratios are not shown in the current comparisons. If the model is said to cover "a wide range of atmospheric conditions", these should be included.

Technical comments:

(50) Change all occurrences of "physio-chemical" to "physico-chemical"; presumably "physio" refers to physiology, not physics.

(51) Page 2, line 35: Change "specie" to "species".

(52) Page 9, lines 240-245: The sentence "In earlier studies, this method has been applied to a large variety of atmospherically-relevant clusters and has been shown to be well suited to study the ones, (...)" is clumsy (i.e. what does "the ones" refer to?); please re-formulate.

(53) Page 9, line 253: Change "basin hoping" to "basin hopping".

(54) Page 11, line 332: It is misleading to list Kürten et al. (2015) as a computational study, as it doesn't present any computationally obtained thermodynamics.

(55) Page 16, line 505: Change "cluster" to "clusters".

(56) Table 1: Please give units for the energy quantities. Please also clarify that "H" and "S" may refer to either the energetics, or the cluster composition (the first column), or use different symbols for some of the abbreviations / quantities. Also change "based" in the footnote to "based on".

(57) The resolution and/or clarity of some figures, mainly 1 and 3, is rather poor. Please fix this.

References (only those not included in the reference list of the manuscript):

Chen et al., Aerosol Science and Technology, doi:10.1080/02786826.2018.1490005 (2018)

Elm and Kristensen, Physical Chemistry Chemical Physics 19, 1122-1133, doi:10.1039/c6cp06851k (2017)

Henschel et al., Journal of Physical Chemistry A 118, 2599-2611, dx.doi.org/10.1021/jp500712y (2014)

Henschel et al., Journal of Physical Chemistry A 120, 1886-1896, doi:10.1021/acs.jpca.5b11366 (2016)

Kupiainen-Määttä et al., Chemical Physics Letters 624, 107-110, https://doi.org/10.1016/j.cplett.2015.01.029 (2015)

Nadykto et al., Entropy 13, 554-569, doi:10.3390/e13020554 (2011)

Nadykto et al., Chemical Physics Letters 609, 42-49, https://doi.org/10.1016/j.cplett.2014.03.036 (2014)

Nadykto et al., Chemical Physics Letters 624, 111-118, https://doi.org/10.1016/j.cplett.2015.01.028 (2015)

Myllys et al., Journal of Physical Chemistry A 120, 621-630, doi:10.1021/acs.jpca.5b09762 (2016)

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-396,

2018.