Reviewer 1 (Stage 2)

COMMENTS

The new Reviewer's comments (Italic), Author's answers (normal font) to the original comments (bold font), Author's additions (yellow highlight) made at Stage 1 and the reference list are given below.

The manuscript presents a series of MCMC simulations aimed at determining cluster evaporation rates from concentration measurements. The topic of the paper is interesting and important . The paper's well-written and easy to follow. After a thorough validation, the proposed approach could possibly be developed into a useful theoretical tool linking cluster concentrations and evaporation rates. However, I have to recommend major revisions because the number of issues to be addressed before the paper can be further considered for publication is quite large and some of them are serious.. Comments

I. Introduction is a way too self-referential, dedicated almost exclusively to own work and fails to acknowledge important contributions made by others. It also contains some misleading statements that need correction.

There were 15 references in the Introduction, and only two of them were papers where I am a coauthor. I have trouble seeing this as "way too self-referential". The new count after the revisions I have made is 19 references including 4 where I am a co-author, which still seems quite reasonable.

While 18 of 35 studies cited in the manuscript (over 50%) are the ones produced the Helsinki group to which the Author belongs, the Author is still not willing to acknowledge relevant contributions by others (see the Author's response to Comment 1.1 and others). This approach is far from the scholarly one and shall be corrected prior to publication.

1.1 The clusters considered in the paper are relevant directly to the Ion -Mediated Nucleation (IMN), which is an important source of new particles in the Earth's atmosphere (see e.g. Geophys. Res. Lett., 27, 883-886, 2000; J. Geophy. Res., 106, 4797-4814, 2001; Atmos. Chem. Phys., 8, 2537-2554, 2008; Atmos. Chem. Phys., 12, 11451-11463, 2012). A brief discussion on these matters accompanied by the corresponding references should be included in the Introduction to the revised manuscript. A mention of ions and ionic clusters was indeed missing. However, as Yu and Turco (2000) were neither the first to suggest ion-induced cluster formation nor the first to demonstrate it experimentally, I decided to cite the CLOUD experiments instead.

Page 1, lines 15–18: "The experiments of Kirkby et al. (2011); Almeida et al. (2013) have also shown that the first steps of cluster formation can proceed along an ionic pathway, and that this process can dominate over the electrically neutral pathway when there are not enough base molecules or other impurities available to stabilize the small neutral sulfuric acid clusters."

It is important to note that Yu and Turco (2000) were first to demonstrate the relevance of ions to atmospheric nucleation and to show that IMN, which involves not only ions but also neutrals, is an important source of secondary aerosols in the Earth's atmosphere. In fact, they have shown that "the first steps of cluster formation can proceed along an ionic pathway" and that "that this process can dominate over the electrically neutral pathway when there are not enough base molecules or other impurities" over a decade earlier than Kirkby et al. (2011) and Almeida et al. (2013). Their original *work and other papers on IMN suggested by the Reviewer are well-known in the field and relevant directly to the manuscript being reviewed, and, thus, they shall be properly cited and briefly discussed in the revised manuscript.*

1.2. The discussion on quantum-chemical studies on charged sulfuric acid-ammonia and sulfuric acid-ammonia-water clusters is limited to Almeida et al., 2013; Olenius et al., 2013b and fails to acknowledge a number of relevant contributions made by others (e.g. JPC A 116(24) 5886-5899, 2011; J. Phys. Chem., A, 117, 133-152, 2013; Atmos. Chem. Phys., 9, 4031- 4038, 2009; PCCP, 10, 7073 - 7078, 2008). References to the aforementioned and other relevant studies should be included in the revised manuscript.

The discussion about which is the best quantum chemistry method for atmospherical clusters has been going on more than long enough (Nadykto et al., Entropy 2011, 13, 554–569; Kurtén, Entropy 2011, 13, 915–923; Nadykto et al., Nadykto et al., Chem. Phys. Lett. 2014, 609, 42–49; Kupiainen-Määttä et al., Chem. Phys. Lett. 2015, 624, 107–110), and I see no reason to continue it. As the cluster energies cannot be measured directly, there is no way to find out which method gives the best predictions, or whether there even is any method that could be trusted. The whole point of this paper is to find a new way to obtain information on cluster properties, so that we no longer need to rely on quantum chemistry calculations at all. I have now tried to explain this more clearly in the Introduction.

Page 2, lines 11–15: "As evaporation rates depend exponentially on the cluster formation energies, theoretical evaporation rates may easily be wrong by several orders of magnitude. Different quantum chemistry methods can give qualitatively very different predictions for cluster concentrations (Kupiainen-Määttä et al., 2013; Kupiainen-Määttä et al., 2015), and it is not clear whether any of the methods can be trusted. Also the treatment of the collision rates is highly simplified, but errors of more than a factor of two or perhaps ten are unlikely."

The quantum chemistry data is used only to provide a test case for the MCMC data analysis method. I could just as well have used some other quantum chemistry data set or simply random numbers, but it seemed more sensible to use cluster energies that reproduce the measured cluster distributions qualitatively, if not quantitatively. However, the test data is not claimed to mimic perfectly the true cluster concentrations.

"As evaporation rates depend exponentially on the cluster formation energies, theoretical evaporation rates may easily be wrong by several orders of magnitude. Different quantum chemistry methods can give qualitatively very different predictions for cluster concentrations (Kupiainen-Määttä et al., 2013; Kupiainen-Määttä et al., 2015), and it is not clear whether any of the methods can be trusted. Also the treatment of the collision rates is highly simplified, but errors of more than a factor of two or perhaps ten are unlikely."

Several claims made in the response to Comment 1.2: "...cluster energies cannot be measured directly.." , "there is no way to find out which method gives the best predictions... or ... could be trusted", are obviously unjustified. First of all, the cluster energies have been being measured since 1960s and the fully referenced NIST Chemistry WebBook (NIST Standard Reference Database Number 69) http://webbook.nist.gov/chemistry/ contain information on measured energies (enthalpies, entropies and Gibbs free energies) for several thousands of reactions involving ions that can be and are commonly used, alongside with higher-level ab initio studies, in validating DFT methods commonly used to study atmospheric clusters (see, for example, e.g. refs. [1-9] attached below). The relevant literature contains tons of benchmarking studies that are commonly used to justify the use of a specific

DFT method. Thirdly, the Author claims that errors in collision cross sections produced by kinetic models can be in error by a factor "of two or perhaps ten" . Where the "perhaps ten" is coming from?

Fourthly, the Author claims that "Different quantum chemistry methods can give qualitatively very different predictions for cluster concentrations" and cites two own papers (Kupiainen-Määttä et al., 2013; Kupiainen-Määttä et al., 2015 [10]) to support this claim. It is important to note that Kupiainen-Määttä et al., 2015 [10] is actually a Comment to Nadykto et al. 2014 [9], in which it was shown that anomalously large difference between the conventional quantum-chemical ab initio and DFT methods on one side, and the composite B3RICC2 method on the other side , is caused by the deficiency of the B3RICC2 method [11] developed and used by the Helsinki group (see both Nadykto et al. 2014 [9], and Reply of Nadykto et al. (2015) [12] to Kupiainen-Määttä et al., 2015 [10], in which the conclusion about the deficiency of the B3RICC2 method has been fully confirmed).

This indicates that the paragraph

"As evaporation rates depend exponentially on the cluster formation energies, theoretical evaporation rates may easily be wrong by several orders of magnitude. Different quantum chemistry methods can give qualitatively very different predictions for cluster concentrations (Kupiainen-Määttä et al., 2013; Kupiainen-Määttä et al., 2015), and it is not clear whether any of the methods can be trusted. Also the treatment of the collision rates is highly simplified, but errors of more than a factor of two or perhaps ten are unlikely."

shall be either deleted or adequately revised, with acknowledging not only the Comment by Kupiainen-Määttä et al., 2015 [10] but also the original paper Nadykto et al. 2014 [9] and Reply to the Comment Nadykto et al. 2015 [11].

1.3. MC has been widely used in nucleation and cluster formation research since 2000s. In particular, a well-known MC-based DNT (Dynamic Nucleation Theory) has been developed by Kathmann and Garrett with co-workers at the PNNL (e. g. PRL82(17):3484-3487, 1999. JPC B 105(47):11719-11728, 2001, J.Chem. Phys. 120(19):9133-914, 2004; . It would be useful to include a brief discussion on earlier applications of MC to nucleation and cluster formation in the revised manuscript.

In DNT, Monte Carlo has been used for computing an integral. This is different from using Monte Carlo for parameter estimation as is done in the present paper.

In my opinion, the difference in the way how MC is used does not justify not acknowledging the earlier relevant work. I think that Author shall include a brief discussion on the earlier MC studies in nucleation research and references to the aforementioned papers in the revised manuscript.

1.4. The statement that "At the same time, modeling of particle formation has also advanced greatly in the past few years. For the first time theoretical predictions of cluster distributions (Olenius et al., 2013b) and particle formation rates (Almeida et al., 2013) agree qualitatively with experimental findings." is partly misleading because predictions of particle formation rates in Almeida et al., 2013 clearly disagree with the experimental data (Chem. Phys. Lett,, 624, 111-118, 2015). The statement should be corrected.

The results are stated to agree qualitatively. This does not imply that they would match perfectly.

The claim that "particle formation rates (Almeida et al., 2013) agree qualitatively with experimental findings" is strictly wrong because it has been shown (Nadykto et al (2015) [12]) that particle formation rates computed based on erroneous (Nadykto et al (2014) [10], 2015 [12]) B3RICC2 *thermochemistry [11] not only disagree with experimental nucleation rates data but also exhibit totally wrong, nearly zeros, dependency on amine concentrations [12]. Also, the "qualitative agreement" of "theoretical predictions of cluster distributions with experiments pointed out in the study of Olenius et al., 2013b, which is based on the very same erroneous B3RICC2 [11] thermochemistry, is a questionable achievement because the agreement may indicate problems in other parts of the computational methodology used in Olenius et al., 2013b that could led to the "qualitative agreement" due to the cancellation of errors only.*

In the view of these circumstances, the discussion on "agreement" of Olenius et al., 2013b and Almeida et al., 2013 with experimental data shall be either properly revised or, preferably, deleted.

1.5. **The author states that "This approach has been shown to give qualitative agreement with experiments (Almeida et al., 2013; Olenius et al., 2013b), but several very drastic assumptions are involved. First-principles molecular dynamics simulations (Loukonen et al., 2014a, b) have shown that one harmonically oscillating cluster structure is far from a realistic description of the thermal motion of molecules in a cluster, implying that the traditional way of computing cluster formation free energies may be a rough approximation". However, this statement is obviously misleading because conclusions obtained using lower level theory such as ab initio MD Loukonen et al., 2014a, b are not applicable to results obtained using higher level theory such as ab initio or DFT. Unharmonic corrections for DFT level with typical scaling factors of 0.95-0.99 are very low and cannot significantly impact cluster formation rates. Also , the impacts of local minima on resulting thermochemical properties can be easily calculated using the Gibbs-Boltzmann distribution. This statement should be either modified or deleted.**

The simulations of Loukonen et al. used DFT to compute the energies and forces, so it is unclear why the conclusions "are not applicable to results obtained using higher level theory such as [...] DFT". In any case, the problem is not so much the anharmonicity of vibrations within or even between the molecules, but the observation that the molecules rotate inside the cluster breaking bonds and forming new ones. This has been clarified in the revised paper.

Page 2, lines 8–11: "First-principles molecular dynamics simulations (Loukonen et al., 2014a, b) have shown that one harmonically oscillating cluster structure is far from a realistic description of the thermal motion of molecules in a cluster, as molecules may rotate inside the cluster continuously breaking intermolecular bonds and forming new ones. This implies that the traditional way of computing cluster formation free energies may be a rough approximation."

First of all, first-principles molecular dynamics simulations involve far large list of assumptions and approximations than conventional DFT, on which they are partly based. In addition to "first principles"/DFT, ab initio molecular dynamics involves lower-level classical theory ("molecular dynamics simulations, where the atomic nuclei evolve in time according to the classical equations of motion", "GTH pseudo-potentials were used for the core electrons", simulation box was 20 Å X 20 Å X 20 Å , simulation times and many others (see Simulations and Collision Simulations sections in Loukonen et al., 2014a, b [13,14]). Also, the computations were done for a single density functional, with no sensitivity studies of model results to the density fucntionals used, input parameters, basis sets, pseudopotentials, box size, cut-offs etc. carried out. Secondly, the computations in Loukonen et al., 2014a, b [13-14] represent for a limited set for small NEUTRAL CLUSTERS ONLY THAT ARE NOT RELEVANT TO THE IONIC CLUSTERS STUDIED HERE.

This shows clearly that the aforementioned papers of Loukonen et al., 2014a, b [13-14] are inconclusive and irrelevant to the present study. This also indicates that attempted attacks on quantum-chemical methods in the present work are unfounded and, thus, the statement

"First-principles molecular dynamics simulations (Loukonen et al., 2014a, b) have shown that one harmonically oscillating cluster structure is far from a realistic description of the thermal motion of molecules in a cluster, as molecules may rotate inside the cluster continuously breaking intermolecular bonds and forming new ones. This implies that the traditional way of computing cluster formation free energies may be a rough approximation."

shall be deleted.

II. The source of thermochemical data used for computing evaporation rates in Table 1 is unclear. The MC fitting data were compared to Ortega et al. (2014) only. The author states that "Also evaporation rates estimated from quantum chemical Gibbs free energies Ortega et al. (2014) are presented in Table 1 for comparison". However, I wasn't able to find any data on Gibbs free energies in Ortega et al. (2014). Neither delta H nor delta S values were found in there. Delta G values seem to be missing in Ortega et al. (2014), too. Please, clarify the source of the data and include computations of evaporation rates based on quantum data obtained by others in Table 1 of your paper.

The evaporation rates were discussed by Ortega et al., while the cluster energies were published already by Almeida et al. (2013). This has been corrected in the revised manuscript.

Page 15, lines 15–16: "Also evaporation rates estimated from quantum chemical Gibbs free energies (Ortega et al., 2014; Almeida et al., 2013) are presented in Table 1 for comparison." Unfortunately there don't seem to exist any other data sets with quantum chemical Gibbs free energies for all the relevant clusters, which could be included in the Table. Herb et al. (2013) have done calculations on some of the smaller clusters, and these results were used as a comparison already in the submitted version of the manuscript.

Page 18, lines 6–9: "The stability of the dimer and trimer and the instability of the tetramer are consistent with cluster formation energies calculated with different quantum chemical methods (Ortega et al., 2014; Herb et al., 2013) and with semi-empirical estimates combining measurements and quantum chemistry (Lovejoy and Curtius, 2001; Curtius et al., 2001)."

III. Temperature dependency of evaporation rates is very important; however, the analysis of the temperature dependent evaporation rates is missing. I would suggest the author to perform a study of evaporation rates for a few clusters at the room temperature and T=273.15 K and compare MC fitted evaporation rates with those obtained using quantum methods in Ortega et al. (2014) and other related studies.

Studying the temperature dependence of the evaporation rates would certainly be interesting, but it cannot be done using MCMC analysis without experimental input data. Olenius et al. (2013) do present some data also at 292 K and 248 K, but the data sets are unfortunately too small.

IV. It is well-known that uncertainties in measured cluster concentrations may be pretty big due to impurities, charging and other issues. The influence of the experimental uncertainties on MC fitted evaporation rates and fragmentation in the mass spectrometer should be discussed in some detail.

It is unclear how impurities and charging would cause uncertainties in these measurements: the clusters are detected with a high-resolution mass spectrometer, so any impurities in them could not go unnoticed, and the clusters are ionic to begin with, so they do not need to be charged before detection.

Actually, there exist a number of sources of large uncertainties in measured particle number concentrations. Some of them have already been pointed out by the Author in the Experimental Cluster Distribution Section (page 3):

"The clusters were detected using a high resolution APi-TOF (Atmospheric Pressure interface Time-Of-Flight) mass spectrometer. The largest clusters considered in the study contained one HSO4 – ion, four H2SO4 molecules and four ammonia molecules. However, it is likely that most of the clusters initially also contained some water molecules, although none were detected, and water was concluded to evaporate from the clusters inside the APi-TOF. The clusters were also assumed to lose some or all of the ammonia molecules inside the instrument prior to detection."

where uncertainties related to critically important hydration effect and lost of ammonia prior to detection are clearly acknowledged. These uncertainties may have a very large impact on measured particle formation rates, and, thus, some estimates of their impacts shall be included in the revised manuscript. The Author could use factors of 10 and 100 as the model "typical uncertainties" in measured particle number concentrations.

References

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