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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ion-mediated nucleation as an important global source oftropospheric aerosols" *by* F. Yu et al.

F. Yu et al.

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Reply to Referee #4's comments

The authors thank the referee for the constructive comments. Our point-to-point replies to the comments are given below (The Referee's comments are in Italic).

1. *As also the authors note, the role of ion induced nucleation and even the possible ion-induced nucleation mechanisms are somewhat unresolved. Taking this into account, the authors treat the subject from a slightly too narrow and purpose-oriented point of view. Because of these clear discrepancies between different studies, the authors should very carefully demonstrate e.g. their model calculations and the uncertainties in their approach. The authors for instance imply that e.g. Laakso et al. (2007) have interpreted their data on atmospheric charged fraction in an incorrect way.*

When making this kind of statements, the authors should explicitely give the concrete physical aspects of their approach that differ from the data interpretation of Laakso et al. (2007). Now the differences between the two approaches are not clear.

In our reply to Ari Laaksonen's comments (ACPD, 7, S6603-S6605), we have shown that both Laakso et al. (2007)'s analysis (based on a simplified analytical formula) and our own investigation (using both a different analytical approach and a detailed numerical model; Yu and Turco, 2007) indicate the dominance of IMN in a large fraction of nucleation event days reported by Laakso et al. (2007). That is, when the Laakso results are objectively interpreted (as opposed to statements made in conclusions), differences between our approach and theirs are not very large. This comparison will be available in the revised paper.

2. *Besides the afore-mentioned work by Laakso et al. (2007) also recent studies by e.g. Iida et al. (2006) and Kulmala et al. (2007) based on atmospheric measurement data from the boundary layer indicate that the observed ion concentrations and charged fractions are not enough to explain the observed total particle formation rates in the considered sites (Boulder, Colorado, US and Hyytiälä, Finland). What do the authors think about these studies? These studies should be also commented more thoroughly in the paper to reflect the different scientific conceptions of the role of ion-mediated nucleation.*

To address the referee's comment, we are adding a subsection in the revised paper to consider more thoroughly the recent publications by Iida et al. (2006), Laakso et al. (2007), and Kulmala et al. (2007).

I. **Comments on the paper of Laakso et al. (2007)**

As we pointed out previously, the results presented in Laakso et al. (2007) may actually

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support the significance of IMN, which contradicts their stated conclusion but not their data.

II. **Comments on the paper of Iida et al. (2007)**

Based on the measurements carried out at NCAR's Marshall Field Site (Boulder, Colorado) during 03/2004-09/2004 and 05/2005-10/2005, Iida et al. (2006) found that charge fractions (CFs) of freshly nucleated particles below 5 nm were significantly below stationary-state values for much of the data. Iida et al. (2006) concluded that, while ions were obviously involved in nucleation events on some days, overall ions contributed <1% of new particles. The CFs measured in Boulder, Colorado (Iida et al., 2006) are clearly different from those measured in Hyytiälä, Finland (Vana et al., 2006; Laakso et al., 2007), which show significant overcharge of freshly nucleated particles (< 5nm) for a large fraction of nucleation event days. We also note that the measurements of Vana et al. (2006) and Laakso et al. (2007) show CFs close to equilibrium values for particles > 5 nm. However, the data of Iida et al. (2006) show significant undercharging for particles in the 5-10 nm size range. While overcharging is an indication of the importance of ion-mediated nucleation, significant undercharging is likely due to the dominance of neutral nucleation. Thus, the significant undercharging reported in Iida et al. (2006) could indeed indicate the dominance of neutral nucleation. Based on the limited information provided in Iida et al. (2006), our IMN model likewise predicts negligible IMN nucleation rates under the atmospheric conditions prevailing at NCAR's Marshall Field Site – namely the higher ambient temperatures (T>~290K) at the time of the experiments. However, IMN would become significant, according to our estimates, during periods of relatively low temperature (<~285 K). After saying this, and acknowledging recent advances in the measurement techniques for detecting small clusters and CFs, we also want to emphasize the possible remaining uncertainties in current observations and analyses of charged fractions that need to be addressed:

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(1) As pointed out in Iida et al. (2006), accurate measurements of CFs require accurate information on size-dependent sampling and detection efficiencies. The penetration and detection efficiencies are generally low for freshly nucleated particles (< 5 nm) and are subject to greater uncertainty accordingly. Most importantly, charged and neutral small nanoparticles may have quite different penetration efficiencies. Due to the enhanced wall loss associated with electrostatic image effects, charged nanoparticles may have lower penetration efficiencies and thus possibly a systematic bias toward undercharging in the observational results. This effect of enhanced wall loss of charged nanoparticles was not addressed in recent papers reporting CF measurements (Vana et al., 2006; Iida et al., 2006; Laakso et al., 2007). It is interesting to note that both Iida et al. and Laakso et al.'s measurements show consistent undercharging of 3-5 nm during periods without new particle formation. It is unclear if this substantial undercharging is a result of the enhanced wall loss of small charged particles, or due to some other causes.

(2) The levels of overcharging (and undercharging) depend on the calculated equilibrium (or stationary state) charged fractions for the specific local conditions; hence, the reference charged state may have a significant uncertainty that propagates into the overcharging (undercharging) results and interpretation.

(3) To assess the relative importance of neutral versus ion nucleation using observed charging states of freshly nucleated particles, analytical methods based on a variety of assumptions are used to derive the charged particle fractions at ~1 nm by extrapolating from observed charged fractions of 3-5 nm particles. The analytical methods employed in Iida et al. (2006) are approximate. For example, during a nucleation event on June 1, 2004, the 3-5.5 nm particles were clearly overcharged, with overcharging ratios above 2 (Fig. 5 of Iida et al., 2006). Based on our detailed kinetic modeling, an overcharging ratio above 2 for 3-5 nm particles would clearly indicate a significance contribution of IMN, whereas Iida et al. (2006) inferred that IMN only contributed ~0.4% of the observed particle formation. Further research is clearly needed to resolve the source

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of this discrepancy.

III. **Comments on the paper of Kulmala et al. (2007)**

Kulmala et al. (2007) present their recent multiple-instrument measurements of the concentrations of neutral and charged nanometer-sized clusters, taken in Hyytiälä, Finland in Spring 2006. There are three main conclusions: (i) A pool of neutral clusters in the sub-3nm range is continuously present (total 1.8-3 nm clusters around 1000-2000 cm^{-3}); (ii) Particle formation starts from diameters of ~1.5 nm; and (iii) neutral nucleation dominates over ion-induced nucleation. The measurements presented in Kulmala et al. (2007) are clearly unique and useful in delineating the predominant nucleation mechanisms. Nevertheless, a number of questions can be raised about the specific conclusions drawn by Kulmala et al..

(i) It is not surprising to observe the presence of neutral sub-3 nm clusters during nucleation periods. Yu (2006a) showed the existence of a mode of sub-3 nm neutral clusters resulting from IMN during nucleation events. These are the result of ion growth and neutralization via recombination, which occurs continuously in the ambient atmosphere. Accordingly, these neutral clusters are very likely the result of ion-mediated processes that generate new thermodynamically stable particles upon which other vapors can later condense (this is an activation process, or heterogeneous nucleation, not homogeneous nucleation). There is further discussion of this point later, as Kulmala et al. discount recombination as a source of the proposed neutral clusters.

What is more mysterious in the Kulmala et al. data is the lack of obvious diurnal variations in the neutral cluster concentrations (as shown in Fig. 2 of Kulmala et al., 2007). For example, if H_2SO_4 is the key specie involved in the formation of these neutral clusters, as suspected, a clear diurnal variation would be expected (Yu, 2006a). Kulmala et al.'s conclusion that there is a constant presence of sub-3 nm neutral clusters appears to be based on their NAIS-negative measurements (e.g., Fig. 2 of Kulmala et al.,

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2007). However, based on the limited NAIS-positive and UF0-02proto CPC pair data also presented in the paper, one can infer that there exists an obvious diurnal variation in the small neutral clusters (which is opposite to the results emphasized in the paper), as we show below.

Firstly, Figure S2 in Kulmala et al. (2007) clearly shows that neutral cluster concentrations at night measured by the NAIS-positive detector are much lower than those seen by the NAIS-negative detector. For example, the number concentrations of 2.4-3 nm and 1.8-2.4 nm particles during nighttime based on NAIS-negative data are constant at around 300 cm^{-3} and 1100 cm^{-3}, respectively. However the corresponding concentrations based on NAIS-positive data are closer to 0 and ~500 cm^{-3}, respectively. Furthermore, NAIS-negative and NAIS-positive data give completely different concentrations of sub-1.8 nm particles (see Fig. S9). In principle, the NAIS-negative and NAIS-positive detectors should give same results if properly calibrated (which appears to be the case during nucleation periods). The large difference in the measured concentrations at least suggests a substantial uncertainty in the NAIS data.

Secondly, the cluster number concentrations between 1.8 and 3 nm observed by the UF0-02proto CPC pair instrument (Fig. 3 of Kulmala et al., 2007), while close to the NAIS values during nucleation events, are much lower – even approaching zero – during the non-nucleation periods (before 9:30 and after 15:00 for the two days presented). The UF0-02proto CPC pair data are not given before 9:00 and after 18:00. During the 9:00-9:30 interval, before the nucleation events have started, the concentrations of 1.8-3 nm particles detected by the UF0-02proto CPC are close to zero, while the values based on NAIS are above 1000 cm^{-3}. During the post-nucleation period (after 15:00), the concentrations of 1.8-3 nm particles detected by the NAIS are a factor of more than 5 higher than those measured by the CPC.

In summary, there exist large differences among the number concentrations of 1.8-3 nm particles ($N_{1.8-3nm}$) measured by the various instruments (NAIS-positive, NAIS-negative, and UF0-02proto CPC pair) fielded by Kulmala et al.. Based on the limited

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NAIS-positive and CPC data presented in the paper, $N_{1.8-3nm}$ shows obvious diurnal variations. Further, the concentrations of charged 1.8-3 nm clusters measured by AIS and BSMA (Fig. 3C and Fig. 3D) show clear diurnal variations, which are consistent with IMN predictions.

Resolving uncertainties in the observed diurnal variations of the 1.8-3 nm particles has important implications regarding the nucleation mechanism. If the NAIS-negative measurements are correct, there must be a continuous and constant nucleation source all day and night to maintain the continuous (and almost constant) presence of a few thousand 1.8-3 nm particles per cc. The authors do not offer a nucleation mechanism to explain this, but suggest ammonia bisulfate as a candidate for the observed 1.8-3 nm clusters. Even disregarding all of the recent studies showing that ternary nucleation does not occur under conditions normally found in the lower troposphere (Yu, 2006b; Merikanto et al., 2007), kinetically the concentrations of H_2SO_4 at night (~5x$10^5 cm^{-3}$ or less) are far too low to produce the observed 1.8-3 nm clusters. Therefore, if the NAIS-negative measurements are correct, species other than H_2SO_4, H_2O, and NH_3 must dominate the formation of the observed 1.8-3 nm particles, implying a completely new nucleation mechanism that works fairly uniformly 24 hours a day. On the other hand, if the CPC measurements are correct, the obvious diurnal variations in the 1.8-3 nm particles can be accounted for by nucleation involving H_2SO_4 (and associated water), while conclusions based on NAIS data must be re-evaluated. For example, the charged fractions of 1.8-3 nm on April 23, 2007 (Fig. 5) may actually be much higher, as the total 1.8-3 nm particle concentration measured by NAIS is a factor of around 2 higher those based on the CPC (Fig. 3).

(ii) The conclusion that particle formation starts at diameters of ~1.5 nm is consistent with the critical sizes of ~1.3-1.7 nm predicted by the IMN model (Yu, 2006a) under typical conditions during nucleation events observed in springtime in Hyytiälä, Finland. The observed critical size of around 1.5 nm (containing about 10 H_2SO_4 molecules and associated water molecules) effectively excludes the possibility of a simple binary

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kinetic nucleation mechanism (J= K $[H_2SO_4]^2$) as proposed in a number of previous studies that assume critical clusters contain only two H_2SO_4 molecules. This important point is not emphasized by Kulmala et al., even though many aerosol modelers are now using the easy-to-apply empirical binary mechanism.

(iii) The conclusion concerning the dominance of neutral nucleation at least under boreal forest conditions is clearly debatable, for the following reasons.

(1) It now appears that both Laakso et al.'s (2007) analysis (based on an analytical formula) and our own investigation (as described above; Yu and Turco, 2007) indicate the dominance of IMN in a large fraction of the nucleation event days reported by Laakso et al. (2007) (also see Yu et al., ACPD, 7, S6603-S6605). This revised interpretation has not been challenged by new quantitative assessments, although uncertainties remain as outlined earlier.

(2) Freshly nucleated particles are overcharged for about 90% of the nucleation event days reported by Laakso et al. (2007). Kulmala et al. (2007) state that significant overcharging was observed in two (April 24, May 10) out of four exemplary nucleation event days (April 23, 24, 30, May 10) discussed in their paper (Table S2). For example, the charged fractions for 1.8-3 nm particles on April 24, 2006 reached 8% (Fig. 5) which is much higher than the equilibrium (or steady-state) values of ~1%. Such an overcharge must be explained by the dominance of IMN (see our discussion in ACPD, 7, S6603-S6605). Kulmala et al. (2007) also state that on the other two days –April 23 and 30 – the aerosol was undercharged or close to the steady state charge distribution. However, the data presented in Fig. 5 shows that on April 23 the1.8-3 nm particles are clearly overcharged as well during the nucleation period (9:00 -12:00). The overcharging ratios are as large as ~6, and this may be doubled if the total 1.8-3 nm particle concentrations measured by the CPC are used to calculate the charge fractions.

(3) The authors argue that the contributions of ion-ion recombination to neutral cluster formation is negligible (page 90, first paragraph in the middle column) based on

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the estimated total cluster concentrations (Nn) and those due to ion-ion recombination (Nn,rec). However, the Nn and Nn,rec values given in Table S3 are questionable. Nn was calculated assuming Nn = J2/I where I is defined as the heterogeneous nucleation rate per cluster (see Eq. S4). Nucleation is a dynamical process involving cluster growth, evaporation, and coagulation. The physics behind the selection of I is unclear, and the authors do not discuss how the values of I given in Table S3 were calculated. An Nn value of 18500 on April 23 at least is inconsistent with the NAIS-positive measurements shown in Fig. S10. There is no size distribution available for April 30, but an Nn value larger than 50000 is given. The authors do not provide the values of CoagS (in Eq. S10), but their estimated values of Nn,rec are much smaller than what we predict based on our detailed kinetic model for the typical nucleation conditions in Hyytiälä (where Nn,rec ranges from several thousands to over 10000 cm^{-3}, depending on the condensation sink and meteorological conditions).

In summary, the data presented by Kulmala et al. (2007), like those of Laakso et al. (2007), may actually support the IMN mechanism. Of course, we cannot claim that IMN is the only nucleation mechanism occurring in the atmosphere. Those cases showing clear undercharge of freshly nucleated particles suggest a neutral nucleation mechanism, which unfortunately has not been quantified and whose physical-chemical basis is unclear. Even so, such cases appear to be very limited based on the measurements of Laakso et al. (2007).

3. *In my opinion it is not enough to include only results on the ion-induced/ion-mediated nucleation in this kind of paper. Similar calculations should be presented also for other nucleation mechanisms (e.g. binary and ternary nucleation, or the semi-empirical cluster activation theory as done by e.g. Spracklen et al., 2006), at least for some sites. Without this kind of comparison it is impossible to assess the relative role of ion-induced nucleation. Therefore I think that the MS is not stand-alone enough to be published as an independent paper. Particularly statements like "The general agreement between*

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simulations and observations demonstrated above strongly supports the important role of IMN in generating new particles in global troposphere" (p. 13609) should not be made without demonstrating how the other approaches succeed in producing qualitatively correct results.

It is well known that binary nucleation cannot explain nucleation events observed in the lower troposphere. The earlier parameterized versions of the ternary nucleation mechanisms predicted unrealistically high nucleation rates over the entire globe (Lucas and Akimoto, 2006), and are no longer accepted. Further, a ternary nucleation model constrained by laboratory measurements (Yu, 2006b), and the more recent parameterizations of the revised ternary nucleation theory (Merikanto et al., 2007), show that ternary nucleation is negligible in the lower troposphere. The semi-empirical cluster activation theory (J=A[H_2SO_4]) is parameterized based on observed particle formation rates and instantaneous [H_2SO_4]. As we pointed in our reply to Ari Laaksonen's comments, such nucleation rates, which are based only on the instantaneous concentration of H_2SO_4, neglect all of the complex nonlinear physics of cluster formation and growth. The single prefactor term that is given as a "constant" is derived from a simple regression for a particular set of data and the physics behind the prefactor is unclear. Since the "constant" A appears to vary significantly with other conditions at the measurement sites in ways that are not parameterized, it is unclear how appropriate to use this formula (with a single constant value of the prefactor) in simulating nucleation in global atmosphere for widely different conditions.

The focus of our current paper is to study the possible absolute contribution of IMN relative to field observations, not the contributions relative to other mechanisms that might occur but that cannot presently be quantified in any case. What we point out in our paper is that the IMN mechanism, which now also appears to be supported for specific conditions by overcharge measurements, produces distributions and rates of particle formation that closely correspond to those seen in the global troposphere. We think that the results presented in this paper represent a significant contribution

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to the discussions about particle nucleation mechanisms and their global roles. The information in our paper is original, is based on rigorous simulations and data comparisons, and has been extensively vetted. Nevertheless, as we stated in an earlier reply to another referee, we are modifying the text to take a more modest, and fair, position that "The general agreement between simulations and observations demonstrated here suggests that IMN may play an important role in generating new particles in global troposphere."

4. *I agree with Ari Laaksonen's interactive comment that the authors should present a detailed exemplary analysis for at least one site where they demonstrate the model calculations. For instance an exemplary day with measured values of SO2 and sulphuric acid concentrations, ion production rates, particle and ion size distributions, radiation, temperature and atmospheric particle growth and formation rates are used should be presented.*

While many nucleation events have been reported in the literature, unfortunately complete sets of measured values of sulfuric acid concentrations, ion production rates, particle and ion size distributions, radiation, temperature and atmospheric particle growth and formation rates have not been forthcoming to carry out a well-controlled case study. This is true, in fact, regarding all putative nucleation processes, and points to the complexity of nucleation and the need for more constraints, such as the electrical charge data. To compensate for the lack of precise data, we have taken the approach of using reconstructed data based on various available measurements, general knowledge of atmospheric processes, and other modeling studies. One attribute of this approach is that it allows sensitivity studies to be carried out to assess the main sources of uncertainty in predictions. See also our reply to Ari Laaksonen's comments on this matter.

5. *Related to the previous comment, the authors should comment on how the dynamics*

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of the aerosol size distributions and the gas concentrations are treated in the model. It has been observed in several studies that e.g. the boundary layer dynamics as well as the daily evolution of the aerosol size distribution (the evolution of e.g. the CS and the nucleation mode) affect strongly the occurrence of nucleation and behaviour of the freshly formed nucleation mode. Does the nucleated mode contribute to the values of the CS?

Full size-resolved aerosol microphysics, as treated in the IMN model, is not explicitly considered in the present GEOS-Chem model we used, although particles of different types are dealt with separately. However, the predicted nucleation rates are based on a multi-variable look-up table that is derived from extensive IMN simulations. The calculation of sulfuric acid vapor concentrations is discussed in page 13604 of this paper. As we note on line 8, page 13612, the contribution of nucleation mode particles to CS is not estimated in this paper, as that would entail far more extensive global computations and analysis. The present work is focused on the contributions to the initial particle production. Uncertainties associated with CS calculations are emphasized on page 13612.

6. *The model input values for the different sites could be presented in similar look-up tables that has been done for the experimental data.*

The simulated results shown in this paper represent annual mean values for rates calculated with a model time step of 30 minutes for each 2x2.5 degree grid box. We are not sure what the referee means here.

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Interactive comment on Atmos. Chem. Phys. Discuss., 7, 13597, 2007.