

Interactive comment on “Atmospheric homogeneous nucleation of H₂SO₄ and H₂O” by D. R. Benson et al.

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Response to Anonymous Referee #3

The paper reports laboratory results on homogeneous nucleation of H₂SO₄ and H₂O under atmospherically relevant concentrations. The paper is revising previous findings by the group (Benson 2008, Young 2008), observing nucleation at lower H₂SO₄ threshold concentrations, due to modifications at the experimental setup (e.g. better RH control, longer residence times, nozzle to introduce the vapor in the center of the flow tube). H₂SO₄ and NH₃-background concentrations are measured directly by CIMS, which is certainly the strength of the paper. However, a CPC (TSI3786) – cut off between 2.5 and 3nm – is used for particle detection. As outlined in Sipilä et al. (2010) and Berndt et al. (2010) the results might therefore be biased by the insufficient

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detection efficiency of the CPC and the limited residence time in flow tubes (nucleated particles do not have the time to grow to 3nm, thus are not detected). This would affect the slopes in the log(J) vs. log(H₂SO₄) plots and therefore the main result of the paper (critical cluster consists of 4-5 H₂SO₄ molecules). This is an important and crucial point and needs further verification before the paper is published in ACP.

RE: Dr. Dave Benson is not immediately available because of personal circumstances and as co-corresponding author, I am responding to the reviews on his behalf. We thank the review for helpful comments and we provide here point to point response for each comment.

We agree with the reviewers that as shown by these two mentioned papers, using this new PSM or PH-CPC, as compared to CPCs, it can increase the particle concentrations at lower H₂SO₄ concentrations and will affect the slope of J vs. [H₂SO₄] in general. This is an important comment and we previously did mention this in the manuscript (e.g., P29053 lines 2-3; P29060 lines 20-22). We have made additional clarification in the revision that our main conclusion on log(J) vs. log(H₂SO₄) may also have been affected by low counting efficiencies at small sizes in CPC, in the revision as the following:

(Page 16 line 365 – page 17 line 369): “Our laboratory observations also show that the slope of Log J vs. Log [H₂SO₄] ranges between 4 – 6. [Berndt et al., 2010; Sipilä et al., 2010] have showed that using this new PSM or PH-CPC, as compared to CPCs, it can increase the particle concentrations at lower H₂SO₄ concentrations and will affect the slope of J vs. [H₂SO₄] in general. So there is the possibility that our measured Log J vs. Log [H₂SO₄] may also have been affected by low counting efficiencies at small sizes in CPC. However, whereas the slopes for J vs. [H₂SO₄] in our study with CPC was higher (3-5) than in [Berndt et al., 2010; Sipilä et al., 2010] with PH-CPC/PSM (1-2), the slope of J vs. [NH₃] was the same (1) with CPC [Benson et al., 2009a; Benson et al., 2010b] and new particle counters [Berndt et al., 2010]. It is unclear why these different particle counters would only affect one slope and not the other(s). Cluster

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CIMS measurements also showed that the critical cluster for THN contains likely only one NH₃ molecule [Hanson and Eisele, 2002]. Similarly to NH₃, the slope of Log J vs. Log [trimethylamine] (measured by CPC) was also 1 [Erupe et al., 2010]; considering the similar chemical properties and very similar effects on nucleation by trimethylamine and NH₃, we believe this trimethylamine slope is also meaningful."

While these studies have shown that with these two new particle counters the slopes became 1-2 for J vs. [H₂SO₄], from the thermodynamics view point, it is also difficult to explain how a gas phase H₂SO₄ molecule (monomer) or a dimer (which easily to evaporate) can act at the critical cluster, without any involvement of ternary species. We also believe that the direct comparisons made between the laboratory-obtained slopes (in BHN or THN studies) and those atmospherically observed values will not bring any new insights, with the current knowledge of the field, because these comparisons are not comparing "apple and apple". (P29061 last paragraph).

Major comments: 1. To overcome these problems mentioned above (Sipilä et al. 2010) the authors argue that the real particle growth rate (GR) in their system is substantially higher (28nm/h) than expected from condensation of H₂SO₄ (1nm/h). Ammonia background concentrations might be responsible for the "observed" high growth rates (meaning: 1nm/h explained by H₂SO₄, 27 nm/h explained by NH₃). It seems very unlikely that NH₃ (20-100ppt) can explain such high GR. First of all, in a study by Zhang et al (2009) it was shown that NH₃ (3×10^{14} molecule cm⁻³) contributed negligibly to growth of freshly nucleated particles. And second, atmospheric observations typically report particle growth rates of 2-5nm/h in the presence of much higher NH₃ concentrations (e.g. 1-10ppb of ammonia; Pryor et al., 2010). This leads to the following questions/conclusions: a. Is the system contaminated with other low volatile species that grow the particles to 3nm? What are those species? Do those species affect nucleation or only contribute to growth? Is it still homogeneous nucleation of sulfuric acid? b. Or are the results indeed biased by the issues reported in Sipilä et al. (2010) and therefore the slopes and critical cluster sizes are wrong?

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RE: These are very insightful comments. We do agree with the reviewer that the tens or hundreds pptv level of NH₃ actually cannot explain the elevated GR; this was seen by (Zhang et al., 2009; Pryor et al., 2001) as the reviewer pointed out. We have seen also from our NH₃-study [Benson et al., 2010c] that sub-ppbv ammonia does not change GR substantially. In fact, the slope of Log J vs. Log [NH₃] is only one [Benson et al., 2009b; Benson et al., 2010c]; indicating NH₃ involvement is different from H₂SO₄, for which the slope of J vs. [H₂SO₄] ranges from 3-5 (with the same CPC). So it is possible that these two precursors are contributing differently to condensation growth (and possibly to nucleation also). We have seen also a similar trend with trimethylamine which has only moderate effects on nucleation and GR [Erupe et al., 2010], like NH₃. We don't know if other amines can affect more – seems tert-butylamine shows more enhancement [Berndt et al., 2010], but the concentrations used in this cited study were quite high (at tens of ppbv range).

The above discussion is also related to b) the results indeed biased by the issues reported in Sipilä et al. (2010) and therefore the slopes and critical cluster sizes are wrong? One thing is, as mentioned above, H₂SO₄ and ammonia/amines certainly contribute to condensation growth differently. At least from our studies, it seems definitely not like: 28 nm hour⁻¹ = 1 nm hour⁻¹ (from H₂SO₄) + 27 nm hour⁻¹ (from NH₃ impurities). This linearity cannot explain the net difference in GR seen in the NH₃ ternary [Benson et al., 2009b] and amine studies [Erupe et al., 2010] as compared to BHN. Also, GR is not related to the absolute [NH₃] rather than the difference of [NH₃] compared to its saturation vapor pressure; for H₂SO₄, the saturation vapor pressure is by chance very low so GR can be considered to be directly proportional to the measured [H₂SO₄]. But this is not the case for NH₃ (<http://www.aim.env.uea.ac.uk/aim/aim.php>); and the NH₃ saturation pressure also sensitively dependent on RH and particle acidity, in addition to temperature. Furthermore, we have to consider Kelvin effects; which can be also different between NH₃ and H₂SO₄, which is unknown though. Additionally, the current condensation theory does not incorporate the ternary species and does not incorporate the chemical interaction between acid and base and the possible cat-

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alytical effects of NH_3 on H_2SO_4 cluster formation [Benson et al., 2010c]. With this current status of knowledge, we cannot quantitatively examine GR. But we know that a monomer or a dimer of pure H_2SO_4 cannot be the critical cluster, which is against H_2SO_4 thermodynamics [Zhang, 2010].

With regard to (a) how the system is contaminated, we have discussed in detail in Experiments section: these contamination issues were also raised by other studies – and have become a sensitive priority topic especially since the CLOUD studies recently showed nitrogen containing clusters even only with H_2SO_4 gases being introduced in the system (e.g., Jasper Kirkby, private communication; D. Worsnop AAAR 2010 presentation, and many other presentations). Based on [Berndt et al., 2005; Berndt et al., 2010; Brus et al., 2010; Duplissy et al., 2010; Sipilä et al., 2010], seems that these reactors (FMI, IFT, and CLOUD) are made of stainless steels, and from what we know from those comprehensive studies which have examined ammonia contaminations [Benson et al., 2010a; Neuman et al., 2003; Nowak et al., 2002; Nowak et al., 2006; Nowak et al., 2007; Yokelson et al., 2003a], it is highly possible that these setups are more susceptible to ammonia contamination (although ammonia or amines were not quantified in these cited studies and only possible ammonia impurity ranges were given, e.g., < 500 pptv in the FMI chamber; but this can be an even more critical issue for temperature dependence studies, since the adsorbed ammonia at lower temperatures can be released at higher temperatures to interfere as ternary species). In our setup, we instead used some certain types of Teflon (there are also several other technical efforts related to reducing ammonia contamination; indeed our NH_3 contaminants measured with CIMS were about 20-100 pptv at different RH). We don't know if these 20-100 pptv of NH_3 can be negligible in terms of BHN – but, from our own studies, we also clearly know that these hundreds of pptv levels of NH_3 do not affect nucleation significantly [Benson et al., 2010c], even when considering background impurities, only until at tens ppbv NH_3 , we had significant enhancements [Benson et al., 2009b]. There was a distinctive difference in enhancement, depending on NH_3 concentrations. That may be the reason that IFT group has used high concentrations of NH_3 (tens or hun-

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dreds of ppbv) and tert-butylamine (tens of ppbv) to significant enhancement by them even with newer particle counters [Berndt et al., 2010].

As with regard to other organic contaminations such as amines, very little is known. We are currently developing CIMS technique to measure amines [Erupe et al., 2010] and other organic compounds, and in future studies, we plan to measure these species with high sensitivity to find out these trace species that may also participate in nucleation and growth.

Finally with regard to another question in (b): Is it still homogeneous nucleation of sulfuric acid? As we have mentioned above, we don't know if these 20-100 pptv of NH_3 is negligible in terms of BHN – but, we also clearly know that these hundreds pptv of NH_3 do not affect nucleation significantly [Benson et al., 2010c], even when considering background impurities, only until at tens ppbv NH_3 , there is significant enhancement [Benson et al., 2009b; Berndt et al., 2010]. Also importantly, numerical simulations have shown that not just the presence of chemical species other than H_2SO_4 automatically makes the system as ternary or multicomponent [McGraw and Zhang, 2008]. Rather, even when the system contains several chemical species together (e.g., H_2SO_4 and organics), it can be only the BHN scheme or the THN or multicomponent scheme depending on the actual conditions, including concentrations of these precursor species. This is an important point we need to take into account in nucleation studies.

We have included these discussions in the revision:

(Pages 14-16 in Discussion section): “We have used CIMS to quantify the possible impurity concentrations of NH_3 (20-100 pptv at RH from 6-40%) and trimethylamine (approximately 15-85 pptv at RH 6%) in our nucleation system and examined how these base molecules would affect our BHN system, especially in terms of GR and the slope of $\text{Log } J$ vs. $\text{Log } [\text{H}_2\text{SO}_4]$. NH_3 and amine contaminations in homogeneous nucleation studies have become an important topic in the nucleation community, especially

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since the recent Cosmics Leaving OUtdoor Droplets (CLOUD) [Duplissy et al., 2010] experiments showed nitrogen containing clusters even only with H₂SO₄ gases were introduced in the system (Jasper Kirkby, private communication). Based on [Berndt et al., 2005; Berndt et al., 2010; Brus et al., 2010; Duplissy et al., 2010; Sipila et al., 2010], nucleation reactors at Finnish Meteorological Institute (FMI) and Leibniz Institute for Tropospheric Research (IfT) and the CLOUD chamber are made of stainless steels, and from previous comprehensive studies which have examined NH₃ contaminations [Benson et al., 2010a; Neuman et al., 2003; Nowak et al., 2002; Nowak et al., 2006; Nowak et al., 2007; Yokelson et al., 2003b], it is possible that these setups are more susceptible to NH₃ contamination, although NH₃ or amines have not been quantified in these cited studies and only possible NH₃ impurity ranges were given, for example, < 500 pptv in the FMI flow reactor. This can become even more critical for temperature dependence studies, since the adsorbed NH₃ at lower temperatures can be released into the gas phase at higher temperatures to interfere BHN as ternary species. In our setup, we have instead used specific types of Teflon along with several other technical efforts to reduce NH₃ interferences.

From [Pryor et al., 2010; Zhang et al., 2009] studies, it seems that tens or hundreds pptv level of NH₃ actually cannot explain the elevated GR. We have seen also from our NH₃-THN study [Benson et al., 2010b] that sub-ppbv NH₃ does not affect H₂SO₄ nucleation substantially. In fact, the slope of Log J vs. Log [NH₃] was only 1 [Benson et al., 2009a; Benson et al., 2010b]; indicating NH₃ involvement could be different from H₂SO₄, for which the slope of J vs. [H₂SO₄] ranged from 3-5. Therefore, it is possible that these acid and base precursors are contributing differently to condensation growth and nucleation. We have seen also a similar trend with trimethylamine which had only moderate effects on nucleation and GR [Erupe et al., 2010], like NH₃. We don't know if other amines can affect more efficiently; tert-butylamine showed more enhancement [Berndt et al., 2010], but the concentrations used in this cited study were at tens ppbv range. It is unlikely that the measured 28 nm hr⁻¹ GR can be simply explained by 1 nm hr⁻¹ from H₂SO₄ condensation and an additional 27 nm hr⁻¹ from NH₃ and amine

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impurities, because such linearity cannot explain the net difference in GR seen in the NH₃ [Benson et al., 2009a] and amine studies [Erupe et al., 2010], as compared to BHN. Also, GR is not related to the absolute [NH₃] rather than the difference of [NH₃] compared to its saturation vapor pressure; for H₂SO₄, the saturation vapor pressure is very low so GR can be considered to be directly proportional to the measured [H₂SO₄]. But this is not the case for NH₃ (<http://www.aim.env.uea.ac.uk/aim/aim.php>); additionally, the NH₃ saturation pressure depends on both RH and particle acidity (PH), in addition to temperature. One also should consider Kelvin effects; which can be also different between NH₃ and H₂SO₄, which is unknown though. Additionally, the current condensation theory does not incorporate the ternary species, the chemical interaction between acid and base and the possible catalytical effects of NH₃ on H₂SO₄ cluster formation [Benson et al., 2010b]. With this current status of knowledge, we cannot quantitatively examine GR, especially without knowing the mode size (which is smaller than 2.5-3 nm cutting size in TSI 3085 nano-DMA).

Whether these impurities can affect BHN or not is unclear. But as discussed above, from our THN studies with MH₃ and trimethylamine, sub-ppbv level of base species had very moderate effects on nucleation [Benson et al., 2010b; Erupe et al., 2010]. We have seen only significant effects with high [NH₃] at the tens ppbv level [Benson et al., 2009a]. There is also another important theoretical aspect we should take into account in homogeneous nucleation studies. Even if the system has multiple chemical species, we cannot simply assume that nucleation would take place through THN or multicomponent processes; rather this depends on several conditions including how much we have these ternary species in the system, for example, and sometimes, nucleation can take place solely via BHN even in the presence of ternary species [McGraw and Zhang, 2008], which certainly does not exclude the case of these NH₃ or amine impurities."

2. Related to the same issue: In the response to the comments of reviewer 1 you state, "If values closer to the collision frequency are used, growth rates would be at least 40 nm hr⁻¹". Could you please provide the detailed calculations and references to support

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the statement? This would be a major step forward.

RE: Dave Benson has indirectly derived this 40 nm hour⁻¹ based on [Kuang et al., 2008a]. Since Kuang et al.'s prefactor constants (in Kinetic nucleation parameterization) are 40 to 1000 times lower than those calculated from the collision limited process, if we assume this prefactor is related to GR – which is also another highly hypothetical assumption, then we can expect 40 higher GR than those derived from time difference (between H₂SO₄ and particle concentration peaks). The 28 nm hour⁻¹ (which is the upper limit) reported in our paper was estimated by assuming that CPC measured sizes are 3 nm at least, but when we measured sizes with nano-DMA (TSI 3085), the sizes were clearly smaller than the cutting size (indicated by the particle concentrations decreasing from the lowest size we can measure, 2.5-3 nm, to large sizes). Also, as mentioned above, we don't understand the role of base molecules in nucleation and condensational growth. From these reasons, quantitatively discussing GR is not useful at present – but we will look into this issue in the future with proper size distribution data. We have included the following discussions:

(Page 11 lines 238-243) “The time difference between [H₂SO₄] and particles was nearly the same as the residence time (Figure 3). From this time difference, we derived a GR of ~ 28 nm hour⁻¹. But this GR should be regarded as the upper limit, since it was estimated by assuming that particles are larger than 3 nm. When we measured sizes with a nano-DMA (TSI 3085), however, the mode sizes were smaller than the cutting size (2.5-3 nm in CPC), indicated by the particle number concentrations decreasing from this cutting towards larger sizes.” (Page 16, lines 340-344) “Additionally, the current condensation theory does not incorporate the ternary species, the chemical interaction between acid and base and the possible catalytical effects of NH₃ on H₂SO₄ cluster formation [Benson et al., 2010b]. With this current status of knowledge, we cannot quantitatively examine GR, especially without knowing the mode size (which is smaller than 2.5-3 nm cutting size in TSI 3085 nano-DMA).”

3. The technical improvements seem to be the key to the new results. More detailed

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information –similar to Young et al. (2008) - would be very valuable to assess the individual modifications e.g. The H₂SO₄ concentration profile in the flow tube? What is the effect of the “nozzle” on the H₂SO₄ profile or the nucleation region? Inhomogeneous air mixing as stated on page 29059?

RE: With regard to inhomogeneous mixing, please see our response to the comment on P29059 below more specifically. The majority of the experimental setup was the same as in [Young et al., 2008] which had a comprehensive description along with detailed assessment (including H₂SO₄ profile; the current system has very similar profiles to those shown in the cited paper), and in the present study, we have only explained the modifications – which are actually extremely simple technical modifications to provide improvements. There are three modifications as the reviewer summarized in the beginning: (e.g. better RH control, longer residence times, nozzle to introduce the vapor in the center of the flow tube). (1) The better RH control was done by adding an additional RH port after UV, for independent RH and OH (and thus H₂SO₄) control. (2) Longer residence times were done by a larger I.D tube at higher flow rates. (3) Nozzle (actually a corn shape tube with I.D of 1 cm at the end – as shown in Figure 1) to introduce the vapor was shown in Figure 1 in detail and explained in detail. This corn shaped inlet is in fact a technique used for radical kinetics studies and have been proven for effective wall loss reduction by numerical calculations and experiments ([Donahue et al., 1996] and references therein). We have included some additional clarifications on them, especially with regard to whether this nozzle can make CIMS underestimate H₂SO₄ or not, as the following:

(Page 9 lines 187-191) “We have examined if this “corn-shaped” tube (i.d. 1 cm at the end of the corn) would affect the CIMS measurements near the entrance of the nucleation reactor. When we added NH₃ before the nozzle, the measured concentration was the same as if we added it right before the CIMS inlet. From these results, we believe that the effects of the corn shaped tube on CIMS measurements can be minimal.” Please also see additional information in revised Figure 1. Minor comments:

C12810

29054: Sipilä et al. (2010): If I remember correctly, two type of new particle detectors have been used (PSM + pulse height CPC)!

RE: Correct - we have included pulse height CPC also in the revision (Page 4 line 74).

29054 line 22/23: "While the BHN study by (Sipilä et al., 2010) successfully reproduced the slope of Log J vs. Log [H₂SO₄] derived from γ -Zeld studies (1 – 2) (Kulmala et al., 2004)." Kulmala et al (2004) is probably the wrong reference!

RE: Agree – we have replaced it with [Kuang et al., 2008b; Riipinen et al., 2007; Sihto et al., 2006].

P29055, Line 17-19: "this allows for an ozone-free system and so provides an advantage compared to other studies where OH was produced from ozone photolysis (Berndt et al., 2005, 2006; Sipilä et al., 2010)." Please explain what the advantage of Ozone free experiments should be?

RE: Ozone is one of the three major oxidants (OH/NO₃/Ozone) in the atmosphere. Any organic compounds can react with ozone to produce low volatility compounds that can contribute to nucleation and/or condensation growth. Actually this is likely what's happening in forests – monoterpenes and sesquiterpenes react with ozone to produce low volatility compounds (such as cis-pinic or cis-pinonic acids or peroxides) and they can participate in gas-to-particle conversion processes to produce new particle [O'Dowd et al., 2002; Zhang et al., 2009] or secondary organic aerosols [Kanakidou et al., 2005]. We want to reduce all possible oxidation production with every possible means. In addition, as shown by [Paulson et al., 1997], for example, organic compounds can react with ozone to produce OH (dark OH sources), which we also like to avoid, especially in SO₂ + OH reaction. It is also possible that ozone can participate in heterogeneous oxidation reactions on the wall and on the particles, via aqueous reactions as in clouds and fogs – this may act as another dark H₂SO₄ source [Lee et al., 2008; Young et al., 2008]. We added a brief clarification on this comment:

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(Page 5, lines 106-107) "This ozone-free system would prevent formation of any low volatility oxidation products in the absence of OH."

P29056: "20-100pptv" NH₃: In Benson et al. (2010b) a 1 min-detection limit of 60ppt is reported for the Ammonia-CIMS - mainly limited by chemical noise. How did you derive the 20 ppt background concentration? (longer integration times?)

RE: As we have discussed in the instrumentation paper, the CIMS showed that detection limits depend on many experimental and ambient conditions (mainly temperature and ambient aerosol loadings). We have reported in that paper the overall detection limit (and also conservative value), estimated from ambient studies crossing three different seasons. However, when we have flow tube experiments, situations are quite different, mainly due to the absence of sampling inlet. The main difference is, temperatures are nearly constant in the room air, while in ambient measurements we suffer from the temperature differences between ambient and room air, which can cause tremendous fluctuations in CIMS signals in the sampling inlet (e.g. due to adsorption and desorption of ammonium aerosols on the wall surfaces inside the sampling inlet which can be detected as ammonia after vaporization). These effects are more significant when we have large temperature differences between ambient and room air and so this depends on season and aerosol concentrations and acidity. In lab studies, we have less complication and thus we have more "ideal" conditions for ammonia measurements and we can expect better detection limits – which are ultimately determined by the instrument background (which is different from NH₃ background in the flow tube) and the signal fluctuations. In short, NH₃ detection is much more complicated and difficult than H₂SO₄ from many technical perspectives – as we discussed in Benson et al. (2010b).

We have added some clarifications on this as the following:

(Page 10 line 212 – page 11 line 228) "We have also used CIMS to quantify the background impurity concentrations of NH₃ (20-100 pptv at RH 6-40%) and trimethylamine

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(approximately 15-85 pptv at 6% RH), both of which were likely produced from deionized water. Typically, the detection limit of NH₃-CIMS was about 60 pptv and the overall uncertainty associated with the instrument background and the sensitivity was 30 pptv \pm 30% [Benson et al., 2010a]. But these rather “conservative” values were estimated from ambient measurements crossing three different seasons and therefore, we can assume similar performances for flow tube studies or somewhat better, because of less complication and interference due to the sampling inlet. Ammonium aerosols are easily adsorbed on the wall surface in the sampling inlet and desorbed as NH₃ and this will interfere the CIMS performances for ambient measurements; this effect can be more pronounced with temperature fluctuations. But such interference was likely reduced for flow tube studies due to constant temperatures. Trimethylamine was also measured with CIMS based on the similar ion chemistry as NH₃ [Erupe et al., 2010], but we provide only the preliminary result in the present study and we are in the process of improving the instrument performances. One of the major technical challenges of measuring these sticky base molecules is to efficiently reduce the “CIMS background” signals, which are different by definition from impurity background concentrations in the nucleation reactor, as discussed in [Benson et al., 2010a].”

P29058: “Here, we make a correction that these initial [H₂SO₄] should be a factor of 4.6 lower (due to the 2.3 times lower k₃ and the 2 times lower ion molecule reaction time) than the reported values, but this error does not act the main conclusions of these papers, because of the high WLFs (up to 30).” Could you please explain why k₃ (SO₃+H₂O=H₂SO₄) is a factor of 4.6 lower and please explain the “2 times lower ion molecule reaction time”.

RE: 2 times different molecular reaction time was due to 2 times different flow rates used – but with the same ionization region (that is, 2.5 plum vs. 5 plum in the inlet) – we have clarified in revision (Page 8 line 177).

P29059: “It is also possible that inhomogeneous air mixing was present in the nucleation reactor which could act our WLF measurements. In the future, we plan

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to investigate inch’ own dynamics in the air mixing region and the nucleation reactor, in order to understand how Dina’ errant inch’ own conditions act nucleation experimental conditions.” As stated above the technical details should be assessed more rigorously. E.g. Is there inhomogeneous air mixing. If yes, how does this affect the derived H₂SO₄ concentrations, nucleation rates, etc.

RE: As stated in our ms, we do plan to address how air mixes in the flow tube for our future. Actually we have tried some preliminary simulations a while ago for this flow dynamics in collaboration with Professor Barbara Wyslouzil at Ohio State University – but we also found that since we also have chemical reactions rapidly taking place in the tube (that is, there is interactions between gases) in addition to nucleation, we realized that we need to do more in depth investigations by including these chemical effects into dynamics. This is all we can say this moment with regard to air mixing. We know that flow is laminar flow in each major sections, however.

P29059, Line 20: “measured [H₂SO₄]”. Measured, at the entrance or the end section of the flow tube?

RE: Measured at the entrance of the nucleation reactor (Figure 1); clarified in the Figure caption: “All H₂SO₄ and other gas phase concentrations of NH₃ and trimethylamine reported in this paper were measured at the entrance of the nucleation reactor. Trimethylamine was measured with CMS using a similar ion chemistry as that used in NH₃ measurements [Erupe et al., 2010]. For wall loss studies, we used two CIMSs at the entrance and the end of the nucleation reactor, to simultaneously measure H₂SO₄ (Figure 2b)”.

P29060: The NH₃ background concentration is a strong function of RH. Ammonia has an effect on nucleation. Moreover, if it is the dominating species for the particle growth please explain how you can measure any meaningful nucleation rates at different RH and any meaningful dependence of J on RH.

RE: This is a great point. We have added this following paragraph in response to this

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comment:

(Page 13 lines 275-281) "Since the NH₃ contaminations are dependent on RH, indicating the source of the contaminations, it is possible that we have the "convoluted" effects of RH and NH₃ simultaneously. For instance, Log J vs. Log [NH₃] was 1 [Benson et al., 2009a; Benson et al., 2010a] and Log J vs. Log RH was higher than 1 (Figure 4b), and these results can be interpreted in part by such effects. On the other hand, there was also a distinction in nucleation enhancement factor (EF) vs. [NH₃] and EF vs. RH, with EF linearly increasing with [NH₃] but decreasing with RH [Benson et al., 2010a]."

Minor comments and technical comments:

Please update the format of in-text-citations: e.g. 29053, line 25: (Berndt et al. 2005) should read Berndt et al. (2005), and so on throughout the whole manuscript! Also e.g. p29053, Line 25: "(Berndt et al., 2010;Kurten et al., 2008; Smith et al., 2009) and (Erupe et al., 2010b)" should read (Berndt et al., 2010;Kurten et al., 2008; Smith et al., 2009;Erupe et al., 2010b).

RE: Corrected.

References:

Benson, D. R., L. H. Young, et al. (2008). "Laboratory-measured nucleation rates of sulfuric acid and water binary homogeneous nucleation from the SO₂+OH reaction." *Geophysical Research Letters* 35(11). Berndt, T., Stratmann, F., Sipilä, M., Vanhanen, J., Petäjä, T., Mikkilä, J., Gruner, A., Spindler, G., Lee Mauldin III, R., Curtius, J., Kulmala, M., and Heintzenberg, J.: Laboratory study on new particle formation from the reaction OH + SO₂: influence of experimental conditions, H₂O vapour, NH₃ and the amine tert-butylamine on the overall process, *Atmos. Chem. Phys.*, 10, 7101-7116, doi:10.5194/acp-10-7101-2010, Pryor, S. C., Barthelmie, R. J., Sørensen, L. L., McGrath, J. G., Hopke, P., and Petäjä, T.: Spatial and vertical extent of nucleation events in the Midwestern USA: insights from the Nucleation In Forests (NIFTy) experiment,

C12815

Atmos. Chem. Phys. Discuss., 10, 23287-23344, doi:10.5194/acpd-10-23287-2010, 2010. Sipilä, M., T. Berndt, et al. (2010). "The Role of Sulfuric Acid in Atmospheric Nucleation." *Science* 327(5970): 1243-1246. Young, L. H., D. R. Benson, et al. (2008). "Laboratory studies of H₂SO₄/H₂O binary homogeneous nucleation from the SO₂+OH reaction: evaluation of the experimental setup and preliminary results." *Atmospheric Chemistry and Physics* 8(16): 4997-5016. Zhang, R., L. Wang, et al. (2009). "Formation of nanoparticles of blue haze enhanced by anthropogenic pollution." *Proceedings of the National Academy of Sciences* 106(42): 17650-17654.

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