

Interactive comment on “Photolytically-Generated Sulfuric Acid and Particle Formation: Dependence on Precursor Species” by David R. Hanson et al.

Anonymous Referee #1

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In the manuscript "Photolytically-Generated Sulfuric Acid and Particle Formation: Dependence on Precursor Species", the authors Hanson et al. present a set of well carried out flow tube experiments of sulfuric acid formation and new-particle formation. The experiments, accompanied by model simulations, are explained very well, and the analysis and interpretation of the obtained data is convincing (though I feel could be streamlined a bit). I especially like the good level of detail in section 2 ("Methods"). The paper concludes with a comparison of the experimental results to existing literature and discusses the effects mainly of adding base compounds (ammonia and dimethylamine) to the system – not only in the authors' experiments, but at this kind of new-particle formation experiments in general. In total, I think this is interesting work that deserves publication. I did find several points where the manuscript could be substantially im-

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proved or at least clarified. I think that overall these "main comments" concern details of how the results are presented, but I believe they need to be considered prior to acceptance. Finally, although this is a convincing, interesting and detailed study of flow tube SA nucleation (and including an interesting application of the authors' model, which seems to work out quite well), I have found that scientifically it eventually "only" corroborates our existing understanding, at least mostly. I.e. it has remained unclear to me what aspects of the study ultimately contribute "new knowledge". The authors may in general want to better work out where such added value (to the community) exactly lies.

Main comments:

A central topic of the Title, i.e. the role of precursor species in H₂SO₄ new-particle formation, seems not well represented in the introduction. I suggest better guidance here (in the intro) for the reader as to where the paper will be heading to (hopefully, presuming at this stage, to the role of precursor species). Indeed, it kind of remains unclear, at first, what is actually meant by 'precursor' (e.g. after reading the abstract). And the word 'precursor' actually only appears once in the entire text, referring (I believe) to involved in the reactions leading to the formation of H₂SO₄. But it hasn't been clear to me until quite a bit into reading the manuscript, if this was the (only) kind of 'precursor' the authors had in mind with the title. ... Finally, after reading the manuscript, I actually doubt that the title is appropriate, as I don't actually see the "dependence on precursor species" in both SA and particle production as a main topic of the work as a whole. Maybe that will change in a revised manuscript. But essentially, I am seeing a study of SA formation and subsequent particle formation, with most of the work going into explaining what drives particle formation and growth rates. It is certainly carefully carried out and explained (and almost throughout nice to read), but ends up mostly confirming the community's understanding of the underlying processes. 'Dependence on precursor species' is part of this, but I feel it is not the overall "new thing" here.

Fig. 2 would benefit from a discussion, better (if possible) display of, uncertainty esti-



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mates. E.g., the authors themselves mention large corrections applied in case of small particle sizes (section 3.1, 2nd paragraph).

Page 6, line 5 & Fig. 2: Has the change in particle size distributions (PSD) between 2/23 and 5/15 (Fig. 2b) occurred gradually? With only those two chosen dates shown in Fig. 2b, one wonders how reproducible the PSD were overall, also considering substantial variations in 'baseline' total number concentrations (Fig. 2a).

Fig. 4: The legend of panel (a) needs some explanation. The last sentence of the caption misses a verb or something.

Section 3.2.2 (varying SO₂) First (page 9, line 5 & Fig. 5, I suggest to also show the model case excluding the HO₂+SO₂ reaction be in Fig. 5. That would quickly illustrate how model results improve and also make this paragraph easier to understand.

Then, I am not sure I completely follow the matter of the NH₃. 70 pptv of NH₃ at inlet were assumed in the modeling (also lines in Fig. 5), but do I understand correctly that no NH₃ was added for the experimental data shown, and NH₃ is assumed as contaminant? Especially, as later in this section the potential role of ppq levels of dimethylamine is discussed, I'd be curious to see how the model would play out in the absence of any contaminant (i.e. also without NH₃). That would maybe lead to the question: How much dimethylamine would be needed INSTEAD of NH₃ to ~fit the experimental data? Again, I might have run into a misunderstanding, in which case some clarification would benefit the section...

Fig. 6: The legend of panel (b) needs some explanation. (Cf. comment on Fig. 4 above.) Same issue also in Figs. 9 and 10.

Comparing Figs. 6b and 4a, and as per the related discussions in section 3.2, it looks like the addition of NH₃ makes the leading-edge mode easier to fit, as the <10-nm minimum is more pronounced. This is in agreement with the model simulations (Fig. S1). However, in Fig. 2b (and discussion), the less pronounced minimum had been

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attributed to more contaminants contributing to new-particle formation in the earlier (vs later) times of spring. (Actually, Fig. 2b vs. Fig. S1 is already discussed in section 3.1 also.) So from that, one could conclude at least that "contaminant" \neq NH3. But following the CLOUD works and others, it seems most likely however that NH3 or other base compounds (amines) would be the primary suspects as for the kind of contaminant suspected. So I see a contradiction here. To resolve that, I suggest the authors discuss somewhere, how purported contaminants would make that minimum ($\sim 2.4\text{nm}$) less pronounced, whereas if bases ("contaminants") were added upstream the opposite would be observed. (And, if applicable, if effective contaminants to blame for Fig. 2b could be something other than bases.) Is it merely the different spatial distribution of contaminants vs. added bases in the flow tube? But if so, does the model manage to simulate those observations, and how does that align with my comment on (understanding of) section 3.2.2 above?

Section 3.2.3, last paragraph: Is the DMA simulation (I assume it is simulation results) shown somewhere? What is "experiment base"? Not sure I understand that sentence. And maybe as a consequence, I am also not sure I understand the follow-up sentence (page 10, line 1). In any case, I think the sudden introduction of amides and some not-more-closely defined "strength" is confusing.

Section 3.2.6, DMA additions: It is stated that N_p increases \sim linearly with [DMA]. Could be good to show, similarly to Fig. 8? (In the Supplement possibly.) Same for D_{le}. Actually, there is reference to a N_p-vs-[SA] figure in the Supplement, but again it is very hard to find it.

Not sure how that would work out, but maybe there could be unified plots of N_p vs. [X] (and of D_{le} vs. [X]), i.e. showing all X in one figure. In general, the various effects of changing inputs on N_p and D_{le} are presented somewhat inconsistently. E.g., N_p vs [NH3] is shown (Fig. 7), but N_p vs [DMA] is not, neither is D_{le} vs [NH3] (whereas D_{le} vs [HONO] and D_{le} vs [RH] are shown). Another example is maybe Fig. S9 in the Supplement: It shows model results together with experimental data for some



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cases but not for others. I could imagine that the paper would benefit from a more systematic presentation of the various results.

Page 13, line 27 vs. line 10 & Fig. 11: First (and Fig. 11), it says that the H₂SO₄-power dependence here was close to those by Yu et al. and the findings from CLOUD. Then, a H₂SO₄-power dependence from CLOUD of 2.6 is mentioned to be somewhat lower than the one found here. Why this difference (apparent contradiction)?

Minor comments:

Page 2, paragraph starting at line 12: Instead of only listing the questions approached by the community in recent years, I think it would be more instructive to also shortly summarize the state-of-the-art in our ability to answer the listed questions.

Page 2, paragraph starting at line 18: Not clear, what levels of contaminant base compounds were (a) determined or estimated to have been present in the cited past studies vs. (b) suggested to have played a role in altering the outcome of the respective results.

Page 3, line 4: Though clarified later, I was confused here, if the results presented in the paper were all obtained with that Teflon screen in place, or only some? Anyway though, how was the "jetting" from the inlets manifest, so that it was decided to include the screen? In other words, why was it decided to put the mesh there?

Page 7, line 18: I am unfamiliar with the meaning of "truncated" here.

Fig. 5: Caption mentions orange lines, but plots are B&W.

Page 9, line 31: Please indicate more precisely where in the Supplement the information is. I couldn't actually find the place for certain.

Page 10, line 5: Don't see red squares in Fig. 7.

Page 10, line 8: Again, would prefer a more specific reference to where in the Supplement.

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Page 13 & Fig. 11: As the Sipila et al. (2010) results are discussed, it could be nice to present them also in some way in Fig. 11.

Page 13, line 33 (and before/after): I can't quite follow these sentences, pitching the Glasoe et al. data against various other datasets (including the present one). Please clarify. To accompany the discussion of the effects of NH₃, it may be illustrative to show a figure similar to Fig. 11 (i.e. comparison to literature results) but showing J-vs-[NH₃].

Fig. 9 has two sets of data for DMA = 0 pptv (one denoted as "0", the other as "0.0" in the caption). Is there a difference or where these just repeats?

Fig. 11, including caption: Explanation of the dotted line and the marking "x^3.7" is missing. It would also be good to be more precise with the citations in the legend. (E.g., "Kurten, 292K" doesn't assure me I'll be ending up with the correct work if I decide to check it out.)

Fig. S5 misses a caption.

Fig. S9 as well.

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