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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measurement Report: Sulfuric Acid Nucleation and Experimental Conditions in a Photolytic Flow Reactor" *by* David Roy Hanson et al.

Anonymous Referee #2

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The article presents upgrades to a photolytic flow reactor system to study nucleation of sulfuric acid and presents some new results using the system. Although sulfuric acid-water (+base) nucleation has been studied extensively by different teams, there are discrepancies in the results obtained using different measurement equipment, so there is a need for validating earlier studies and improving the measurements. Therefore I think the article is in principle worth publication as measurement report. However, the article needs revision for clarity and more discussion on the uncertainties. The authors believe that the differences in their new results compared to their earlier study (Hanson et al. 2019) is due to improved cleanliness of the system, but since there are no actual measurements of the contaminants this remains speculative. Also, the

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authors found large discrepancies in the results obtained using two different particle counters. Given the uncertainties, I have doubts how well the results can be compared to other nucleation studies.

General comments:

At first read it was hard to understand the main aim of this measurement report and its connection to the previous study by the same team (Hanson et al. 2019). I think it would be beneficial to state the objectives more clearly in the introduction paragraph.

Chapter 3.4.: I would separate the discussion of why DEG-CPC shows considerably higher counts than UCPC (this should be actually discussed a bit more, see my questions below) from the discussion of which nucleation processes affect the UCPC data (r232-276). To me these seem to be two separate issues each deserving their own chapter.

The summary and conclusions chapter would benefit from shortening and streamlining it. I would concentrate on summarizing what is improved from the 2019 study and what new knowledge that brings, and remove most of the speculation (e.g. related to CLOUD data) that was already discussed in the Results&Discussion part.

As you mention, some recent studies suggest an enhanced collision rate of sulfuric acid molecules (Stolzenburg et al. 2020 but also Halonen et al. 2019) leading to faster growth rates. How much would it affect your results if you include such collision enhancement in your calculations? Can you provide an uncertainty estimation for Fig 7? You note this qualitatively in the conclusions, but maybe this discussion could be moved to results and discussion section and addressed more quantitatively.

Figures: The figure captions and variable names in legends should be revised throughout the article and supplement so that they are self-explanatory. Currently the figures cannot be understood without reading the whole text. E.g. the difference between NH3_52 and NH3_D52 and meaning of M1 (red squares) in Fig S1 are not clear. It

would be helpful if it was made clearer which results are from this study and which are obtained earlier with the same system.

Detailed comments:

I have several specific questions regarding the particle counting, which need to be clarified as it is one of your main new findings, that the DEG system and UCPC show large discrepancies at low H2SO4 (lower particle concentration).

On p3 r82-85 you write: “While there may be a ∼20% undercount in the UCPC results as detailed in the previous paragraph, this may be counteracted somewhat as the UCPC detects more particles than are in the leading edge of the particle size distributions of the DEG system. It is difficult to quantify this amount because the pulse-height response of the instrument depends on the composition of the particles [O,Dowd et al. 2004; Hanson et al. 2002].” The assumed 5% losses for UCPC seem quite low, is there any measurements to characterize the size-dependent losses in the setup used? Does the undercounting depend on the size distribution of the particles you produce, as the two instruments certainly have different detection efficiency curves? Why and how does the composition dependency of pulse-height analysis play a role here, if I understood correctly you use it only to calculate the total concentration?

How often did you measure the background (zero) of your counters, especially the DEG-counter? I’m asking because if you have even very few background counts from homogenous nucleation of DEG, it would be interpreted as large signal in the MPS system. How and how often are these instruments calibrated?

On p9 you speculate about different processes that may affect the concentration measured with UCPC. One possibility brought up is particles formed in a charger (r230) and second the direct detection of sulfuric acid clusters (r254). If your CPC uses pulse-height analysis, shouldn’t these particles (which are probably very small at detection) be clearly distinguishable from particles formed in a flow tube?

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r277-285 you note that sometimes the relation between UCPC and DEG measured concentration changes (by several factors). To me it sounds the reason has to be technical, as you also speculate. Isn't there any diagnostics you can use to evaluate when one of the counters are measuring incorrectly to eliminate this data? Maybe provide a comparison of the UCPC and DEG measurements in the supplement?

References: Halonen, R., Zapadinsky, E., Kurtén, T., Vehkamäki, H., and Reischl, B.: Rate enhancement in collisions of sulfuric acid molecules due to long-range intermolecular forces, Atmos. Chem. Phys., 19, 13355–13366, https://doi.org/10.5194/acp-19-13355-2019, 2019.

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