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 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.

We hope our detailed responses to the referee's comments below will alleviate many doubts. In this paragraph we provide an alternate perspective on the effects of the uncertainties they have detailed. Our statements about increased cleanliness are definitely speculative but it is the simplest explanation and a common problem in nucleation experiments. The large discrepancies between counters we have argued are two-fold. In one case, the differences have (i) revealed a source of error or artifact in our DEG system that improves the analysis of the present measurements and (ii) this artifact led us to calculate ion-mediated nucleation with our model and these calculations indicate that IMN could play a significant role at low sulfuric acid abundances. The other discrepancy (the UCPC Np being larger than the DEG Np) seems to be completely traceable to a cylinder changeover event where particle counts were elevated for a week or two. We note that another referee asked that comparisons to previous experiments be included in an additional graph which we are glad to do as it highlights how the results from PhoFR have improved. We agree that we should temper our conclusions regarding comparisons with other studies because of the uncertainties in the measurements.

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.

Excellent point: the previous abstract lacked focus. We have removed a few sentences and now highlight the changes in the results (about an order-of-magnitude or larger in some cases) that have occurred since our initial publication.

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.

This comment prompted a good, hard, long look at the text and led to extensive reworking of the discussion of the UCPC corrections and a new set of figures comparing it to the DEG system is presented in the Supplement.

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.

We agree and three paragraphs will be removed. We will modify some portions to highlight the changes in the measurements from those presented in our previous publication.

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.

This is an important point that we had quantitatively skirted in the paper. We have prepared a paragraph summarizing the effects on the model predictions and how the cluster energetics need to be modified to achieve agreement between model and measurements.

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.

We acknowledge these problems (yes, quite numerous in the Supplement) and will pay close attention to the captions in the revised version.

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?

Our rambling text here led to a misunderstanding of the corrections and we have extensively revised it to make clear the following information. The 20 % undercount was due to not applying an activation efficiency: we have chosen now to instead actually apply the activation efficiency. The 5 % loss that is not (and won’t be) applied is due to the sampling through a sharp right angle. Larger losses exist: we did state that the diffusional loss of nanoparticles was calculated using Gormley-Kennedy and in the revision we list typical losses that range up to 60% at 2.7 nm. According to the literature, the two counters have activation efficiencies that are similar down to about 2.5 nm, which is the lower-limit for the comparisons. The composition dependent activation efficiency is an uncertainty and we suppose they are similar whether DEG or butanol fluids; yet we focus on the leading-edge particles with the DEG system whereas that cannot be readily done with the UCPC data.

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?

The DEG system background count rates are measured every day at the start of the measurements and occasionally again at the end. These instruments have not been calibrated but are operated in accord with the literature sources we reference.

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 pulseheight analysis, shouldn't these particles (which are probably very small at detection) be clearly distinguishable from particles formed in a flow tube?

In principle this is true however we think neither are clearly distinguishable from 'normal' nanoparticles. The charger ions are at much lower abundance than the neutral particles furthermore the pulse-heights for clusters and particles of 3 nm or smaller become very spread out and do not form identifiable peaks in the distributions.

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?

We now present a comparison of nanoparticle abundance measurements in the Supplement. The two instruments compare admirably, albeit up to 30% different in one case, over the size range of 3 to 12 nm diameter. Furthermore, we have now traced the anomalously high UCPC measurements to 4 measurement days just after a liquid nitrogen cylinder change. Why this intermittent dust event (or whatever) apparently affected the UCPC instrument more than the DEG system is not known. It may be a clue as to the identity of what caused this (or the other) cylinder-change events.