

## ***Interactive comment on “Temperature-dependent diffusion coefficient of H<sub>2</sub>SO<sub>4</sub> in air: laboratory measurements using laminar flow technique” by David Brus et al.***

**Anonymous Referee #2**

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This paper presents measurements of the wall loss of H<sub>2</sub>SO<sub>4</sub> and its clusters with H<sub>2</sub>O and perhaps DMA or TMA. There are problems with the interpretation of the data and perhaps in the experimental method as well.

Issues:

- 1) - Figures are not good enough. Ascertaining data quality is difficult.
- The abstract lists items that are not fully addressed in the paper, such as independence of results upon flow rate (not clearly shown) and H<sub>2</sub>SO<sub>4</sub> level (there seems to be a dependence in Fig. 4 C), or are not factual, such as the claim that clustering with amines explains the temperature dependence (cluster model gives 3 vs. experimental

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of 5.4.)

Major issues:

2) How the CIMS is connected to the flow reactor needs to be fully explained. Is the CIMS raised and lowered as it is connected to the different ports? Or are there two elbows in the connecting tube and the CIMS is moved horizontally? Also, and forgive my inattentiveness, is the reported concentration the measured value or that in the flow reactor? Also, it was stated that switching the two flow reactors gave data that validated the technique. Please show this data, and if the temperature data is to remain, at all temperatures. The detection of significant concentrations of H<sub>2</sub>SO<sub>4</sub> dimers is important and suggests that there is enough H<sub>2</sub>SO<sub>4</sub> contained in clusters to affect the measurements if these clusters can evaporate. This needs to be more fully explored, i.e., perhaps the general trend that diffusion seems to be 'slow' in this experiment is because dimers or other clusters diffuse more slowly than H<sub>2</sub>SO<sub>4</sub> but then partly evaporate as they travel down the flow reactor. This is possible if indeed there are some amines present that are also lost to the wall, which would tend to lead to decreasing stability of clusters with axial distance.

3) (a) It is not worth much scientifically to use the parabolic velocity - laminar flow equation with the wall loss rate coefficient to get a diffusion coefficient and compare this to a CFD study that assumes a parabolic velocity profile with that diffusion coefficient: it is not too strong a statement to say that NOTHING is validated about the experimental method through that comparison. (b) More importantly, the CFD studies are probably not adequate to the needs of the present study. (i) The gas exiting the mixing region is very likely far from fully developed laminar flow, and (ii) when the flow reactor walls are at temperatures of 10 or 20 C lower than the mixing region walls, there will be buoyancy driven flows, and (iii) the drawing of 7 L/min flow through a small tube is likely to affect the flow patterns and it needs to be shown that this effect on measured H<sub>2</sub>SO<sub>4</sub> does not depend upon which port is being used. It is likely that the details of the mixing region needs to be simulated with a 3D model which would also be required for the

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sampling ports.

4) The authors have a lot of work to do to place this data in context, both to motivate readers and to advance the science and their technique. The scatter in the data is large compared to previous measurements, suggesting that the present data can not improve upon previous measurements of the diffusion coefficient. Furthermore, they suggest that amines had influenced their measurements, but this was speculation and really should be somehow verified experimentally (the 'large' dimer concentrations is supporting evidence). The temperature dependency would be something new, but since there are issues with the 298 K data quality and analysis, what can be said about the 288 and 278 K data? Going back to the 298 K data: the relative change with humidity dependence seems to be about the same as that displayed in the earlier data and their should be a curve plotted with their 298 K data using (the previously determined?) equilibrium constants etc. Yet complications linger with uncertainties in whether amines or dimers are significantly affecting the measurements. Are these diffusion measurements of hydrated H<sub>2</sub>SO<sub>4</sub>, aminated H<sub>2</sub>SO<sub>4</sub>, or a mixture?

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