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Comment on acp-2021-319

Anonymous Referee #2

Referee comment on "High Homogeneous Freezing Onsets of Sulfuric Acid Aerosol at Cirrus Temperatures" by Julia Schneider et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-319-RC2, 2021

General Comment

This manuscript titled "High Homogeneous Freezing Onsets of Sulfuric Acid Aerosol at Cirrus Temperatures" by Schneider et al. reports homogeneous freezing of aqueous sulfuric acid aerosol using the AIDA chamber at conditions relevant for cirrus cloud regime. The highlight of this study is the significant deviation of the onsets of ice formation from the water activity criterion (WAC) (Koop et al., 2000) at temperatures below about 200 K. The manuscript is well-written, clearly discussing the uncertainties in their measurements and the underlying assumptions.

However, the discussion/conclusions rely entirely on a single type of aerosol particle, with the absence of any physical interpretation for deviations from WAC, and in-depth discussion of mixing time of investigated aerosol particle at temperatures below 200 K. Nonetheless, I recommend the manuscript for publication after the authors have addressed the following major questions and revised the manuscript accordingly.

Major Comments

1. Kinetics of sulfuric acid aerosol particles at cirrus temperatures: I understand that not much work has been done related to the activation kinetics and particle phase at such low temperatures. The authors handled this issue with their test for kinetic limitations at 197 K. However, the majority of their ice supersaturation results still comply with the WAC at around that temperature. I am curious why a similar kinetic test was not considered at, e.g. 190 K, where the deviations are suggested to be significantly higher?

2. Thermodynamic equilibrium: Based on previous work (Williams and Long, 1995), it won't be surprising that these sulfuric acid aerosol particles are extremely viscous at such low temperatures, likely approaching glassy state (if not already). This could really slow down the mixing. This casts some doubts on whether the particles attained

thermodynamic equilibrium condition. I strongly recommend adding a discussion related to this issue and the implications it can have on the presented results and its interpretation.

3. Physical interpretation of the deviations from WAC: There is no attempt made at understanding the microphysical picture underlying the reported deviations from WAC. It is unclear why sulfuric acid system would behave in such a fashion. I recommend that the authors state this lack of understanding clearly in the manuscript.

4. Atmospheric models: Sulfuric acid aerosol particles certainly dominate in the stratosphere, however, there are several studies showing the presence of various other components such as organics and inclusions of aluminum and silicon (Murphy et al., 2014), with even more variety of components present in the upper troposphere. While the presented study focuses only on sulfuric acid aerosol particles. Keeping this in mind as well as the comments stated in 1-3 above, I find the authors' suggestion to use their parameterization in atmospheric models over WAC a bit far fetched. I do not agree with this suggestion and recommend removing this part. Inaddition, the authors should state this caveat in their abstract, discussion and conclusions.

There needs to be more work done on other atmospherically relevant aerosol particles at such low temperatures and high ice supersaturation conditions, to establish whether the deviations from WAC reported here are universal or not.

Minor comments:

Figure 4: Could the uncertainties in predictions from Koop et al. (2000) be added in this figure for clarity.

L6: WAC not a function of size of the aqueous aerosol particles. Please correct.

L255: Please mention/reference the specific E-AIM models used here and for evaluating the data from other studies shown in Fig. 1

Technical comments:

L8: "...laboratory-based homogeneous..."

L11: "Aqueous sulfuric acid aerosol particles of high purity were generated by..."

L47: "...to be equal to relative humilities."

L80: "...and the potential deviation from..."

L107: "...pump starts..."

L122: a period missing at the end of the sentence

Fig3. Caption: "...AIDA chamber as a function of time since pump start ..."

Fig6. Caption: "The fit shown in panel (a) is constrained..."

L353-54: "...freezing onset may explain the high ice saturation ratios..."

References

Koop, T., Luo, B., Tsias, A., and Peter, T.: Water activity as the determinant for homogeneous ice nucleation in aqueous solutions, Nature, 406, 611-614, 2000.

Murphy, D. M., Froyd, K. D., Schwarz, J. P., and Wilson, J. C.: Observations of the chemical composition of stratospheric aerosol particles, Q. J. R. Meteorolog. Soc., 140, 1269-1278, https://doi.org/10.1002/qj.2213, 2014.

Williams, L. R., and Long, F. S.: Viscosity of Supercooled Sulfuric Acid Solutions, J. Phys. Chem., 99, 3748-3751, 10.1021/j100011a050, 1995.