Response to Referee #2

General Comments

The manuscript by Zhang et al. discusses the organic contribution to nanoparticle growth based on laboratory measurements. Since direct composition measurements in this size range are difficult, there is still limited understanding of the relative roles of sulfuric acid and organics as a function of size. This study contributes to this understanding and is therefore suitable for publication in ACP after some revisions. The analysis and figures are presented very clearly, but the language should still be checked carefully.

We thank the reviewer for the constructive suggestions and comments concerning our manuscript entitled “Unveiling the organic contribution to the initial particle growth in 3-10 nm size range” [egusphere-2025-4421]. We sincerely appreciate these insightful comments, which have significantly improved both the quality of our manuscript and the methodological rigor of our ongoing research.

We have prepared point-by-point responses to the reviewer’s comments below. The original reviewer comments appear in italics. Our responses are presented in blue plain font, while the corresponding revisions in the manuscript appear in blue underlined font.

Major comments

1. Comments and suggestions:

I am puzzled by the large systematic difference between the SA K-values in this study and earlier studies (Table 1). In the text and conclusions (r272), those are attributed to “the nano size effect and different measurement techniques”. However, e.g. Kim et al. 2016 also looked at 10 nm particles, so the “nano size effect” cannot be the explanation there. The authors should thoroughly analyze and discuss the potential reasons for the differences.

Responses and Revisions:

We thank the reviewer for this insightful comment. We agree that the large discrepancy, especially with the 10 nm data from Kim et al. (2016), warrants a more thorough discussion. In response to the reviewer’s point, we acknowledge that the nano size effect alone cannot explain the difference at the specific 10 nm point. Our revised discussion now attributes the observed systematic differences to a combination of several factors:

(1) Fundamental difference in measurement techniques: We emphasize that the κ values measured by our method (SFCPC based on supersaturated condition) and by the

method used in Kim et al. (2016) (nano-HTDMA based on subsaturated condition) are expected inherent different, where SA particles are expected to exhibit comparably higher hygroscopic growth at subsaturated conditions and lower CCN activity at supersaturation (Biskos et al., 2009; Massling et al., 2023). This is likely the primary source of the discrepancy.

(2) Persistent role of the nano size effect: While it may not explain the difference of 10 nm SA particles directly, the nano size effect is a critical factor that systematically lowers the κ values across our entire measured size range (3-10 nm) compared to theoretical values for larger particles. Its influence is integral to understanding why our entire dataset is shifted to lower values.

(3) Synergistic effect and measurement scarcity: We think that the magnitude of the difference maybe due to a synergistic combination of the above factors. Furthermore, we highlight that the direct measurements in this size range are exceptionally rare. For SA particles, only Kim et al. (2016) reported directly measured κ values as far as we know. The lack of a benchmark makes cross-technique comparisons challenging. This means that the discrepancies observed here hard to attribute to reasons other than instrument differences.

We have emphasized the method difference between this work and Kim et al. (2016) and provided further discussion on the nano-size effect and the potential contamination of NH_3 in Section 3.1:

“Hygroscopicity of SA particles also revealed a consistent decrease with rising RH: at RH = 80%, κ values declined to 0.361 ± 0.013 for 3 nm and 0.171 ± 0.011 for 10 nm particles, decreasing 13% and 18% compared to RH = 20%. This demonstrates that SA particles exhibit reduced hygroscopicity under higher humidity conditions. Although bases such as ammonia/amine could in principle suppress the hygroscopicity of SA particles (Yishake et al., 2025), the κ of an SA-ammonia/amine mixture would be expected to increase with RH, because a higher SA fraction (more acidic) is expected at higher RH (Chen et al., 2018). This κ-RH dependence is opposite to the trend observed in our study. Moreover, there was no identified source of bases in our system, so ammonia contamination can largely be ruled out. Furthermore, previous studies have shown that the average number of water molecules hydrating each H_2SO_4 molecule increases with RH (Kurtén et al., 2007; Temelso et al., 2012; Zollner et al., 2012). Therefore, the observed decrease in hygroscopicity can be attributed to the particles already containing more water at higher RH, resulting in a reduced capacity for additional water uptake.

The κ values reported in previous studies are summarized in Table 1. The measured hygroscopicity results in this work are much lower than those reported in previous studies (0.68-0.9, Petters and Kreidenweis, 2007; Shantz et al., 2008; Sullivan et al., 2010), which predicted by thermodynamic model in 30-80 nm based on the model parameters provided by Clegg et al. (1998). The hygroscopicity of newly formed sulfuric acid nanoparticles in CLOUD chamber was examined by a nano hygroscopicity tandem differential mobility analyser (nano-HTDMA) and the reported κ values were 0.64 ± 0.02 and 0.52 ± 0.02 for 10 nm and 15 nm, respectively (Kim et al., 2016). The reported variation trend in particle size aligns with our findings but the κ values were much larger than that in this work. While both Kim et al. (2016) and our study report κ values of the oxidation products of SO_2, the measurement methods used are fundamentally different. Kim et al. (2016) employed a nano-HTDMA, which measures hygroscopic growth under subsaturated conditions. In contrast, our SFCPC method derives κ values by activating particles under supersaturated conditions. As discussed in previous studies, the measurement condition can induce inherently different κ values (Biskos et al., 2009; Massling et al., 2023). Specifically, SA particles are expected to exhibit comparably higher hygroscopic growth under subsaturated conditions and lower CCN activity at supersaturation. Therefore, this methodological difference is likely the primary factor contributing to this discrepancy in κ values. In addition, for sub-10 nm particles, the enhanced Kelvin effect (compared to that for larger CCN-size particles) dramatically raises the energy barrier for vapor condensation, directly contributing to suppressed hygroscopicity. Furthermore, the potential size-dependent influence on phase state may reflect a tendency for nanoparticles to remain in a liquid or mixed phase (Cheng et al., 2015). These nano-size effects on the thermodynamic and physical properties of aerosol particles are likely significant contributing factors in explaining the distinctively lower κ values observed in our study. As far as we know, direct measurements of the κ of sulfuric acid particles remain limited in the literature, and our results is the first measurement under supersaturation condition in 3-10 nm range."

2. Comments and suggestions:

Can there be ammonia and/or amine contamination in your system? If yes, how would that affect the results and would that be constant with RH?

Responses and Revisions:

We thank the reviewer for raising this important point regarding potential ammonia/amine contamination and its influence. The possibility and implications have been carefully considered. Indeed, if present, ammonia (or amines) could affect our results by partially neutralizing the sulfuric acid (H_2SO_4, SA) particles, as acid-base reactions can alter aerosol hygroscopicity. Literature suggests that for mixtures like SA-ammonia, the measured hygroscopic growth would be lower than the theoretical prediction for pure SA but higher than that of ammonium sulfate (Yishake et al., 2025). However, we argue that ammonia/amine contamination is unlikely to be the primary factor driving the observed decreasing hygroscopicity trend with increasing RH in our experiments, for the following reasons:

(1) Controlled experimental system: There was no deliberate or identified source of ammonia in the experimental setup. Most notably, the quartz flow tube was replaced for every experimental group to eliminate potential cross-contamination between runs. This practice significantly reduces the possibility of persistent ammonia residues affecting the results.

(2) Acidic nature of particles under trace contamination: Even if trace amounts of ammonia were present, the SA concentration in our system was overwhelmingly higher than of any potential ammonia contaminant. Previous study indicates that for sub-10 nm particles formed from SA with bases, the particles remain highly acidic when the ammonia is in substantial excess (Chen et al., 2018). Therefore, the potential minor contamination would likely result in particles whose composition and properties are still dominated by acidic SA rather than neutral salts.

(3) Inconsistency with expected RH dependence: This is the most critical point. If ammonia contamination were significant and driving the measured hygroscopicity suppression, one would expect the effective hygroscopicity parameter (κ) of the resulting partially neutralized particles to increase with increasing RH. This is because higher fraction of SA (more acidic) is expected at higher RH as discussed above, typically enhancing the hygroscopic response of SA-ammonia mixture. However, our observations show the opposite trend: a clear decrease in κ with increasing RH, where this discrepancy suggests that the dominant mechanism causing the RH-dependent decrease in κ in our data is unlikely to be an artifact of neutralization by base.

In conclusion, while we acknowledge the reviewer's valid hypothesis, the combination of our controlled experimental setup, the expected persistence of highly acidic particles, and—most decisively—the opposite RH trend compared to what a significant ammonia influence would predict, leads us to cautiously conclude that ammonia/amine contamination is not the main factor responsible for the observed decrease in particle hygroscopicity with increasing RH in this study.

We have added a brief sentence in the revised manuscript (Section 3.1):

"Although bases such as ammonia/amine could in principle suppress the hygroscopicity of SA particles (Yishake et al., 2025), the κ of an SA-ammonia/amine mixture would be expected to increase with RH, because a higher SA fraction (more acidic) is expected at higher RH (Chen et al., 2018). This κ-RH dependence is opposite to the trend observed in our study. Moreover, there was no identified source of bases in our system, so ammonia contamination can largely be ruled out."

3. Comments and suggestions:

In row 138 you mention "the mass spectrometry" which was not discussed anywhere else. What mass spectrometer was used and for which part of the experiment?

Responses and Revisions:

We thank the reviewer for pointing out the need for clarification. The mass spectrometry analysis was not a core component of the main experiment but was employed as a preliminary, auxiliary measurement to rule out potential interference from organic compounds in the observed hygroscopic behavior of sulfuric acid. Specifically, an iodide chemical ionization mass spectrometer (Vocus AIM) was used to characterize the composition of gaseous oxidation products prior to conducting the core experiments. The corresponding results are now provided as Figure S2 in the Supplementary Information. The results confirmed the absence of significant organic signals, supporting the conclusion that organic contamination did not drive the decreasing trend mentioned in the text. We have accordingly revised the manuscript in Section 3.1 to ensure clarity:

"Moreover, prior to the hygroscopicity measurements, the oxidation products of SO_2 were characterized using an iodide chemical ionization mass spectrometry (Vocus AIM), which detected no significant organic compound signals in the gas phase (Figure S2). Therefore, this decreasing trend cannot be attributed to organic contamination."

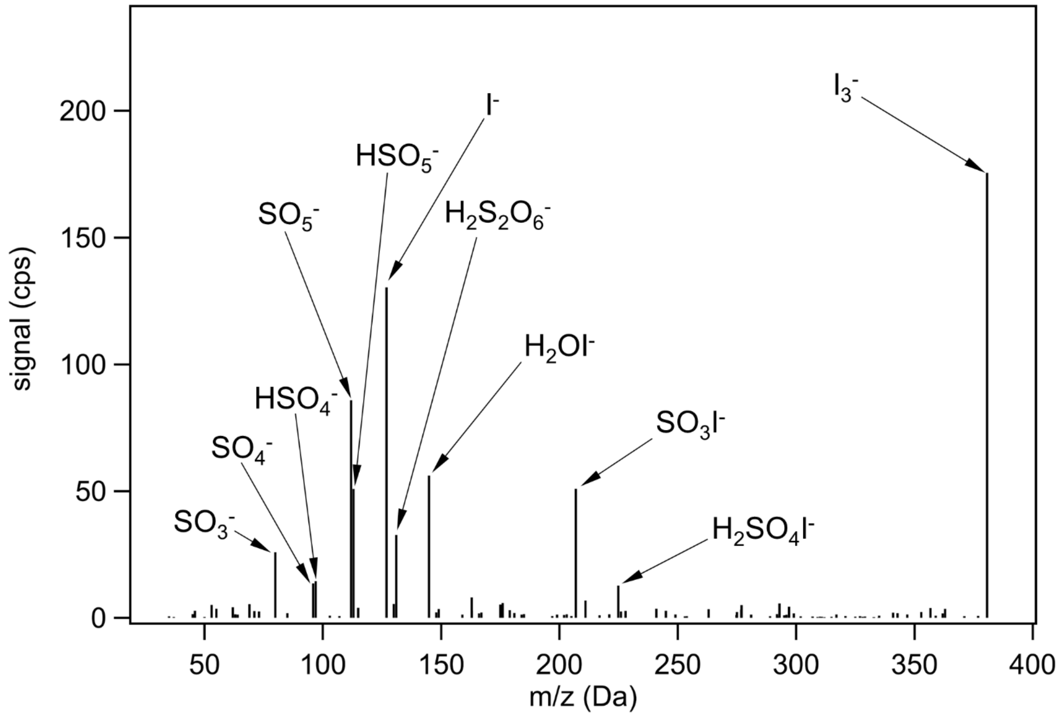

Figure S2. Representative Vocus AIM negative ion mass spectra of the oxidation products of SO_2.

Minor comments

4. Comments and suggestions:
What is the RH of the DMA sheat flow?

Responses and Revisions:

We sincerely thank the reviewer for raising this important point. In the present study, the RH of the DMA sheath flow was not measured. As the reviewer rightly implies, this parameter is critically important in HTDMA-based hygroscopicity measurements, where precise control of the sheath flow RH is essential for accurate determination of the particle growth factor. However, for measurement techniques analogous to ours, which utilize CCNC and determine hygroscopicity by activating particles under supersaturation conditions, the RH of DMA sheath flow is generally not monitored or reported (Roberts and Nenes, 2005; Rose et al., 2008; Wang et al., 2015). Therefore, in line with this established methodology, our experimental design did not specifically focus on the RH of the DMA sheath flow. Nonetheless, we fully agree with the reviewer that direct measurement of this parameter could provide valuable additional information and further improve the reliability of particle sizing, particularly in ensuring the consistency of the dry diameter selection. In future work, we will incorporate in situ RH monitoring of the sheath flow to enable more precise characterization and enhance methodological rigor. Thank you again for this valuable and constructive suggestion.

5. Comments and suggestions:

Abstract, row 21: more pronounced compared to what?

Responses and Revisions:

We sincerely apologize for this unclear expression. We have revised it more clearly:

"Compared to 3-5 nm, this enhancement was more pronounced for 5-10 nm particles associated with the incorporation of increased yields of more volatile oxidation products and Kelvin effect."

Refences:

Biskos, G., Buseck, P. R., and Martin, S. T.: Hygroscopic growth of nucleation-mode acidic sulfate particles, J. Aerosol Sci., 40, 338–347, https://doi.org/10.1016/j.jaerosci.2008.12.003, 2009.

Chen, H., Chee, S., Lawler, M. J., Barsanti, K. C., Wong, B. M., and Smith, J. N.: Size resolved chemical composition of nanoparticles from reactions of sulfuric acid with ammonia and dimethylamine, Aerosol Sci. Technol., 52, 1120–1133, https://doi.org/10.1080/02786826.2018.1490005, 2018.

Cheng, Y., Su, H., Koop, T., Mikhailov, E., and Pöschl, U.: Size dependence of phase transitions in aerosol nanoparticles, Nat. Commun., 6, 5923, https://doi.org/10.1038/ncomms6923, 2015.

Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic Model of the System $H^+ - NH_4^+ - Na^+ - SO_4^{2-} - NO_3^- - Cl^- - H_2O$ at 298.15 K, J. Phys. Chem. A, 102, 2155–2171, https://doi.org/10.1021/jp973043j, 1998.

Kim, J., Ahlm, L., Yli-Juuti, T., Lawler, M., Keskinen, H., Tröstl, J., Schobesberger, S., Duplissy, J., Amorim, A., Bianchi, F., Donahue, N. M., Flagan, R. C., Hakala, J., Heinritzi, M., Jokinen, T., Kürten, A., Laaksonen, A., Lehtipalo, K., Miettinen, P., Petäjä, T., Rissanen, M. P., Rondo, L., Sengupta, K., Simon, M., Tomé, A., Williamson, C., Wimmer, D., Winkler, P. M., Ehrhart, S., Ye, P., Kirkby, J., Curtius, J., Baltensperger, U., Kulmala, M., Lehtinen, K. E. J., Smith, J. N., Riipinen, I., and Virtanen, A.: Hygroscopicity of nanoparticles produced from homogeneous nucleation in the CLOUD experiments, Atmos. Chem. Phys., 16, 293–304, https://doi.org/10.5194/acp-16-293-2016, 2016.

Kurtén, T., Noppel, M., Vehkamäki, H., Salonen, M., and Kulmala, M.: Quantum chemical studies of hydrate formation of H2SO4 and HSO4– - ProQuest, Boreal Environ. Res., 2007.

Massling, A., Lange, R., Pernov, J. B., Gosewinkel, U., Sørensen, L.-L., and Skov, H.: Measurement report: High arctic aerosol hygroscopicity at sub- and supersaturated conditions during spring and summer, Atmos. Chem. Phys., 23, 4931–4953, https://doi.org/10.5194/acp-23-4931-2023, 2023.

Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, Atmos. Chem. Phys., 7, 1961–1971, https://doi.org/10.5194/acp-7-1961-2007, 2007.

Roberts, G. C. and Nenes, A.: A continuous-flow streamwise thermal-gradient CCN chamber for atmospheric measurements, Aerosol Science and Technology, 39, 206–221, https://doi.org/10.1080/027868290913988, 2005.

Rose, D., Gunthe, S. S., Mikhailov, E., Frank, G. P., Dusek, U., Andreae, M. O., and Pöschl, U.: Calibration and measurement uncertainties of a continuous-flow cloud condensation nuclei counter (DMT-CCNC): CCN activation of ammonium sulfate and sodium chloride aerosol particles in theory and experiment, Atmos. Chem. Phys., 8, 1153–1179, https://doi.org/10.5194/acp-8-1153-2008, 2008.

Shantz, N. C., Leaitch, W. R., Phinney, L., Mozurkewich, M., and Toom-Sauntry, D.: The effect of organic compounds on the growth rate of cloud droplets in marine and forest settings, Atmos. Chem. Phys., 8, 5869–5887, https://doi.org/10.5194/acp-8-5869-2008, 2008.

Sullivan, R. C., Petters, M. D., DeMott, P. J., Kreidenweis, S. M., Wex, H., Niedermeier, D., Hartmann, S., Clauss, T., Stratmann, F., Reitz, P., Schneider, J., and Sierau, B.: Irreversible loss of ice nucleation active sites in mineral dust particles caused by sulphuric acid condensation, Atmos. Chem. Phys., 10, 11471–11487, https://doi.org/10.5194/acp-10-11471-2010, 2010.

Temelso, B., Morrell, T. E., Shields, R. M., Allodi, M. A., Wood, E. K., Kirschner, K. N., Castonguay, T. C., Archer, K. A., and Shields, G. C.: Quantum mechanical study of sulfuric acid hydration: Atmospheric implications, J. Phys. Chem. A, 116, 2209–2224, https://doi.org/10.1021/jp2119026, 2012.

Wang, Z., Su, H., Wang, X., Ma, N., Wiedensohler, A., Pöschl, U., and Cheng, Y.: Scanning supersaturation condensation particle counter applied as a nano-CCN counter for size-resolved analysis of the hygroscopicity and chemical composition of nanoparticles, Atmos. Meas. Tech., 8, 2161–2172, https://doi.org/10.5194/amt-8-2161-2015, 2015.

Yishake, J., Zang, H., Tan, R., Yao, L., Guo, S., Zhao, Y., and Li, C.: Size- and Composition-Dependent Hygroscopic Growth of Sub-20 nm Atmospherically Relevant Particles: Implications for New Particle Survival, Environ. Sci. Technol., acs.est.5c00068, https://doi.org/10.1021/acs.est.5c00068, 2025.

Zollner, J. H., Glasoe, W. A., Panta, B., Carlson, K. K., McMurry, P. H., and Hanson, D. R.: Sulfuric acid nucleation: Power dependencies, variation with relative humidity, and effect of bases, Atmos. Chem. Phys., 12, 4399–4411, https://doi.org/10.5194/acp-12-4399-2012, 2012.