## *Response to Referee #3*

### *General Comments*

*Zhang et al measured the hygroscopicity of aerosol particles containing sulfuric acid (SA), α-pinene-derived oxygenated organic molecules (OOMs), and their mixture in the size range of 3-10 nm. The measurement was conducted using a custom-designed scanning flow condensation particle counter (SFCPC). By doing this, the organic mass fraction for the mixture particle can be derived for the SA-OOM mixture particles that were generated at different SA/α-pinene ratios and humidity. The main claim is that OOMs' contribution to the particle phase becomes increasingly important as particle size increases. When the motivation of the study and the use of language are overall good, the current level of analysis is not convincing enough to back up the main claim. If the following comments could be adequately addressed, I would suggest considering the work for publication.*

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:*

*Novelty of the work: The SFCPC has been used to study the CCN activity of nanoparticles several times before. The authors must provide a summary of their previous work (Wang et al., 2015; Zhang et al., 2023; Zhang et al., 2025) based on the SFCPC in the introduction. Unfortunately, the authors barely mention their previous work using SFCPC, and therefore, readers most likely have no clue about the novelty of the current work.*

**Responses and Revisions:**

We thank the reviewer for the constructive suggestions and comments. This study marks the first application of the SFCPC to infer the chemical composition of mixtures containing unknown components. Our previous works (Wang et al., 2015; Zhang et al., 2023, 2025) focused on the development and characterization of novel instrumental methods, along with the assessment of associated uncertainties, and did not encompassed investigations into the generation and growth of new particles. The novelty of this work and its distinct differences from our previous studies are summarized as follows:

(1) Wang et al. (2015) and Zhang et al. (2023) developed and characterized the nano-CCNC and SFCPC, respectively, where the major difference between these two studies is the method used to alter the inner supersaturation. The linear relationship of $\kappa$-$f_{\mathrm{org}}$ were established between ammonium sulphate (AS) and levoglucosan/sucrose generated by Electrospray from solutions with known mixing ratios, to demonstrate its ability to infer chemical composition.

(2) Zhang et al. (2025) focused on the modelling studies of exemplary substances to assess uncertainties arising from the dependence of $\kappa$ on particle size and thermodynamic models. Although it discussed chemical composition inference (Section 3.4), its primary focus was on verifying the linear relationship of $\kappa$-$f_{\mathrm{org}}$ and assessing the associated uncertainties. More critically, that work also utilized particles generated via Electrospray from solutions of AS and *cis*-pinonic acid. This experimental approach, particularly the use of Electrospray to generate particles from solution, could not directly represent the gas-phase precursor mechanisms that govern atmospheric nucleation and growth processes.

(3) The present study, by contrast, is designed to directly probe NPF and subsequent growth by simulating atmospheric processes. Utilizing a flow tube reactor, we introduced gas-phase precursors ($SO_2$ and α-pinene) to study nucleation and particle growth under controlled conditions. This methodology enables us to demonstrate the role of their oxidation products in the growth process. Thus, our work provides valuable and novel physical and chemical results of nanoparticle down to 3 nm that have not been previously reported, thereby yielding critical implications for understanding atmospheric particle formation and growth.

We agree with the reviewer that highlighting the distinction between this work and our previous studies is crucial for underscoring its novelty. We acknowledge that our initial manuscript did not sufficiently articulate this progression. The differences in research objectives and contents (applied compositional analysis vs. instrumental development and characterization) led us to primarily cite prior work in the Introduction and Methods sections as foundational references, rather than providing a focused comparative discussion in the Results section. Accordingly, in the revised manuscript, we have added relevant text to summary our previous work (Section 2.3):

"Our previous work extended the linear relationship between $\kappa$ and $f_{\mathrm{org}}$ to 3-10 nm size range for AS and levoglucosan/sucrose mixed particles, which were generated via

Electrospray from solutions with known mixing ratios (Wang et al., 2015; Zhang et al., 2023). Zhang et al. (2025) assessed the uncertainty arising from the dependence of $\kappa$ on particle size, also based on Electrospray-generated particles (AS and *cis*-pinonic acid). In this work, we introduced $\kappa$-$f_{\mathrm{org}}$ linear relationship into the mixing products from flow tube—a setup designed to simulate atmospheric processes—in order to explore the organic content in the particulate phase. Furthermore, we established size-resolved $\kappa$-$f_{\mathrm{org}}$ linear relationship to eliminate the mentioned uncertainty. The application of the $\kappa$-$f_{\mathrm{org}}$ linear relationship relies on the assumption of ideal internal mixing within the particles. Under our experimental conditions, for in situ freshly formed 3-10 nm particles, the characteristic mixing times are short, and organic-inorganic mixtures are likely to remain liquid and well-mixed (Cheng et al., 2015). Therefore, the ideal internal mixing assumption is reasonable. For SA-OOMs mixture, we use the $\kappa$ values of pure organic (OOMs) and inorganic (SA) experiment groups to represent the hygroscopicity of the organic and inorganic component in the mixture particles, respectively. Although the organic and inorganic components in mixture may not be identical to those in pure organic and inorganic particles of the same size under the same RH due to the potential change of oxidation processes, this simplification is a necessary given the current inability to directly measure the composition and component-specific hygroscopicity of particles in the 3-10 nm size range. To further reduce uncertainties associated with the linear relationship, the $\kappa$ values of pure organic and inorganic particles were taken from the fitted lines to serve as a reference baseline, as shown in Figure S1. Based on the size-resolved $\kappa$-$f_{\mathrm{org}}$ linear relationship (colored solid lines) and the measured $\kappa$ values (grey dashed line) of the SA-OOMs mixture, the corresponding $f_{\mathrm{org}}$ values (colored dashed lines) for particles generated in the flow tube reactor were derived using Eq. 1"

***2. Comments and suggestions:***

*Aerosol Generation: There are a couple of questions that need clarification with support from compositional measurement and/or modelling.*

We sincerely appreciate the reviewer's constructive comments regarding the aerosol generation. Our responses to each sub-point are provided below.

**2.1** *What was the estimated OH concentration in the flow tube per experiment?*

**Responses and Revisions:**

Thank you for your comment. Hydroxyl radicals (OH·) would participate in the oxidation processes of both $SO_2$ and α-pinene, but its concentration was not estimated in the present experimental setup. In this study, we focus primarily on the apparent hygroscopicity ($\kappa$) and organic mass fraction ($f_{org}$) of the formed particles, rather than on molecular-level details or specific chemical pathways. Moreover, in the mixed $SO_2$/α-pinene system used here, determining the OH· concentration for each experiment is particularly complex. Although our current experimental setup and instrumentation do not allow for reliable estimation of OH· concentrations, this limitation does not affect the measurement of apparent hygroscopicity or the subsequent determination of organic content for the newly formed particles, which are the central objectives of the present work.

We have added the following explicit statement in Section 2.1:

"While the present study did not estimate the OH· concentration and further elucidate specific mechanistic pathways, this simplification is justified because, to the best of our knowledge, no existing studies have clearly demonstrated significant differences in the hygroscopic performance of pure OOMs derived from different α-pinene oxidation pathways."

**2.2** *How was α-pinene consumed via ozonolysis and OH oxidation pathways?*

**Responses and Revisions:**

We thank the Referee for this insightful comment. As noted in the original manuscript, α-pinene was simultaneously exposed to $O_3$ and OH· radicals due to the inevitable production of OH· from $O_3$ photolysis and subsequent reactions.

The two oxidation pathways are generally understood as follows: (1) The gas-phase ozonolysis of α-pinene proceeds via the formation of Criegee intermediates (carbonyl oxides; CI), which undergo rapid unimolecular reactions to form vinyl hydroperoxides (VHP) and subsequently different peroxy radical ($RO_2$) isomers, leading to low-volatility oxygenated organic molecules (OOMs) (Iyer et al., 2021; Yang et al., 2025). (2) $O_3$ undergoes photolysis to produce $O(^1D)$ atoms, which then react with water vapor to generate OH· radicals. OH-initiated oxidation of α-pinene proceeds mainly via OH· addition to the double bond, forming peroxy radicals ($RO_2$) (Berndt et al., 2016; Kang et al., 2025). These $RO_2$ radicals undergo autoxidation and $HO_2$ cycling, producing OOMs that could contribute to the growth of particles.

The present study, however, primarily focuses on the bulk physicochemical properties (hygroscopicity and organic fraction) of the 3-10 nm particles generated under known oxidation conditions, rather than on elucidating specific mechanistic pathways. Furthermore, to the best of our knowledge, no existing studies have clearly indicated significant differences in the hygroscopicity of pure OOMs derived from different α-pinene oxidation pathways. The methods employed in this study do not provide molecular composition information, which would be required for pathway assignment. Should future techniques enable molecular speciation of such small particles, this would greatly advance our understanding of nucleation and growth mechanisms. We appreciate the reviewer's comment, which has helped us to clarify the scope of our work.

In response to this comment, we have added the following explicit statement in Section 2.1:

"For pure organic experimental groups, OOMs were produced from organic peroxides formed from oxidation reactions of α-pinene (Kirkby et al., 2016; Lee et al., 2019). α-pinene was exposed to ozone and also to hydroxyl radicals (OH·) due to the unavoidable production of OH· from ozone photolysis and secondary reactions. Although detailed molecular composition information could not obtained in our work, the ozonolysis pathway is generally understood to proceed via Criegee intermediates, leading to various peroxy radicals and subsequent low-volatility products (Iyer et al., 2021; Yang et al., 2025). Similarly, OH-initiated oxidation proceeds mainly via OH· addition, forming peroxy radicals that further react to produce condensable organic species (Berndt et al., 2016; Kang et al., 2025). While the present study did not estimate the OH· concentration and further elucidate specific mechanistic pathways, this simplification is justified because, to the best of our knowledge, no existing studies have clearly demonstrated significant differences in the hygroscopic performance of pure OOMs derived from different α-pinene oxidation pathways."

***2.3*** *Was the composition of OOM comparable between different sizes for the OOM-only particles?*

**Responses and Revisions:**

We thank the reviewer for raising this insightful and important question regarding the potential size-dependent composition of the nanoparticles formed from oxidation products of α-pinene.

Based on the governing physical principles of gas-to-particle partitioning, the chemical composition of OOMs particles formed from α-pinene oxidation products is not expected to be strictly identical across different sizes. The partitioning of organic vapors into the particle phase is influenced by their volatility and the Kelvin effect (Stolzenburg et al., 2023), which becomes increasingly significant for smaller particles, potentially altering the species participating in nanoparticle growth. Therefore, some size-dependent variation in the detailed chemical composition is likely. Despite this expected variation, current analytical techniques also pose limitations for obtaining the exact composition of newly formed 3-10 nm particles (Smith et al., 2021; Zhang et al., 2022).

Meanwhile, our key experimental observation is that the $\kappa$ of these pure OOMs particles showed no significant dependence on particle size within the 3-10 nm range (as shown in Figure 2b). This suggests that the effective average hygroscopicity of the mixture of OOMs condensing onto particles in this size range remains relatively constant. This finding is consistent with the observation by Frosch et al. (2011) of an almost constant $\kappa$ for 50-150 nm particles from α-pinene oxidation. It seems to indicate that either the composition shifts involve compounds with similar $\kappa$ values, or that the net effect of compositional changes on the bulk hygroscopicity is minor within this specific diameter range. To our knowledge, no studies have specifically examined the particle size dependence of hygroscopicity for 3-10 nm particles from α-pinene oxidation. In our analysis, we have incorporated the potential size-dependent variation in chemical composition by establishing independent linear relationships for each particle diameter, thereby eliminating potential uncertainties in the inferred organic mass fraction arising from size-dependent differences.

We have therefore revised the manuscript to include this point explicitly in the Section 3.1:

"Different from the SA results, the OOMs particles formed by the oxidation products of α-pinene have almost constant $\kappa$ values in the 3-10 nm diameter range. As shown in Figure 2(b), $\kappa$ of the pure organic group under 20% RH is ~0.065. This result indicates that the OOMs particles exhibit non-hygroscopicity compared to SA particles and its hygroscopicity has no significant dependence on particle diameter. While the detailed chemical composition of OOMs in these nanoparticles may vary with size due to volatility-dependent partitioning and the Kelvin effect, the observed constancy in $\kappa$ suggests that the effective hygroscopic properties of the condensing mixture do not change significantly within this size range. This finding is consistent with Frosch et al. (2011), who also observed almost constant $\kappa$ values (0.11 ± 0.02) for 50-150 nm particles from α-pinene oxidation. However, to our knowledge, research on particle size dependence is very rare, and no studies have specifically examined the hygroscopicity of α-pinene oxidation particles in the 3-10 nm size range. Alfarra et al. (2013) measured the hygroscopicity of particles formed from α-pinene oxidation via both OH radicals and $O_3$ using CCNC. Our results align closely with their reported $\kappa$ values (0.1-0.16), which were also observed under supersaturation conditions. Furthermore, numerous studies have investigated the hygroscopicity of α-pinene oxidation products using CCNC or HTDMA, reporting a wide range of $\kappa$ values (0.03-0.19, Cain et al., 2021; Duplissy et al., 2011; Engelhart et al., 2008; Massoli et al., 2010; Razafindrambinina et al., 2022; Wang et al., 2019; Zhao et al., 2016). All experimental results reported here fall within the established range of values found in existing publications."

***2.4** How can the authors be sure the composition of OOM was the same between the OOM-only particles and SA-OOM particles for a specific size under the same RH?*

**Responses and Revisions:**

We thank the reviewer for raising this important point regarding the compositional consistency of the OOMs in different experimental groups. We fully agree that this is an important assumption in our analysis, and we appreciate the opportunity to clarify our rationale.

In this study, we aimed to derive insights into the organic contribution to the initial particle growth in 3-10 nm size range by utilizing the reported linear relationship between hygroscopicity ($\kappa$) and the organic mass fraction ($f_{org}$), where direct measurement of particulate-phase composition is extremely challenging. When applying this $\kappa$-$f_{org}$ linear relationship to infer the organic fraction in SA-OOMs particles, a representative hygroscopicity parameter for the organic component ($\kappa_{org}$) is required. In the absence of direct measurements of $\kappa$ for the organics in the mixed SA-OOMs particles, we used the $\kappa$ value measured for pure OOMs particles as the best available value for $\kappa_{org}$ in the mixtures.

We acknowledge that the organic composition in mixed SA-OOMs particles may not be identical to that in pure OOMs particles for the same particle size under the same RH. The presence of $SO_2$ and sulfuric acid (SA) could potentially alter the oxidation and condensation pathways. However, it is currently unclear how it affects the composition of organic composition and the hygroscopic performance of organic parts in such small particles. Moreover, the direct measurement of the separate $\kappa$ values of organics in mixture particles is not currently feasible. Therefore, using the measured $\kappa$ of pure OOMs particles represents the most reasonable and practical approximation available to apply the $\kappa$-$f_{org}$ linear relationship to our mixed system. This approach allows us to provide valuable, albeit indirectly-informed, insights into the early growth of atmospheric nanoparticles.

We agree that future measurements capable of characterizing the detailed molecular composition and component-specific hygroscopicity of nanoparticles in this size range would be invaluable. Such data would significantly advance the understanding of the nanoparticle growth and refine the application of hygroscopicity-based approach. We have added related text in the revised manuscript to highlight this point and the associated assumption more explicitly:

Section 2.3: "For SA-OOMs mixture, we use the $\kappa$ values of pure organic (OOMs) and inorganic (SA) experiment groups to represent the hygroscopicity of the organic and inorganic component in the mixture particles, respectively. Although the organic and inorganic components in mixture may not be identical to those in pure organic and inorganic particles of the same size under the same RH due to the potential change of oxidation processes, this simplification is a necessary given the current inability to directly measure the composition and component-specific hygroscopicity of particles in the 3-10 nm size range."

***3. Comments and suggestions:***

*Determination of forg: It looks like the eq (1) is based on the assumption of ideal mixing of SA and OOM. If so, can you discuss the uncertainty regarding this assumption and how it will impact the determination of forg?*

**Responses and Revisions:**

We thank the reviewer for raising this critical point regarding the assumption underlying Eq. (1). We fully agree that the $\kappa$-$f_{org}$ linear relationship is based on the assumption of ideal internal mixing between sulfuric acid (SA) and oxidized organic molecules (OOMs). Below, we discuss the potential uncertainties associated with this assumption and their impact on the $f_{org}$ determination.

As the reviewer rightly noted, deviations from ideal internal mixing—such as external mixing, core-shell morphology, or liquid-liquid phase separation (LLPS)—could cause the linear mixing rule to break down. In an extreme core-shell scenario where a pure SA core is fully coated by OOMs, the overall particle hygroscopicity would be governed primarily by the organic shell. Consequently, the measured $\kappa_{mix}$ of SA-OOMs would approach the value of $\kappa_{org}$, leading to a substantial overestimation of $f_{org}$ (approaching ~100%, in contrast to the actual organic fraction of SA-OOMs). While we recognize these potential biases, quantitatively describing the $\kappa$-$f_{org}$ relationship under every possible non-ideal mixing state remains challenging, due to the absence of a generalized theoretical framework and direct observational constraints for particles in this size range.

Nevertheless, we argue that the ideal internal mixing assumption is reasonable for our experimental conditions (in situ freshly formed 3-10 nm particles). For nanoparticles of this scale, characteristic mixing times are short, and organic-inorganic mixtures are likely to remain liquid and well-mixed (Cheng et al., 2015), thereby minimizing the prevalence of phase-separated or core-shell structures. Thus, although we cannot fully exclude morphological uncertainties, the $\kappa$-$f_{org}$ linear relationship provides a well-established approach to estimate composition from hygroscopicity in such systems (Dusek et al., 2010; Pöhlker et al., 2023; Vogel et al., 2016; Zhou et al., 2024).

To ensure clarity, we have revised the manuscript (Section 2.3) to explicitly state this key assumption:

"In this work, we introduced $\kappa$-$f_{org}$ linear relationship into the mixing products from flow tube—a setup designed to simulate atmospheric processes—in order to explore the organic content in the particulate phase. Furthermore, we established size-resolved $\kappa$-$f_{org}$ linear relationship to eliminate the mentioned uncertainty. The application of the $\kappa$-$f_{org}$ linear relationship relies on the assumption of ideal internal mixing within the particles. Under our experimental conditions, for in situ freshly formed 3-10 nm particles, the characteristic mixing times are short, and organic-inorganic mixtures are likely to remain liquid and well-mixed (Cheng et al., 2015). Therefore, the ideal internal mixing assumption is reasonable."

## *Minor comments*

### *4. Comments and suggestions:*

*Lines 114 – 116: The description for the use of the electrometer needs to be clarified. Was it used to count total particle concentrations?*

**Responses and Revisions:**

We thank the reviewer for this helpful comment. Yes, the electrometer was used to measure the total particle concentration ($N_{total}$) in our experimental setup. To clarify this in the text, we have revised the description in Section 2.2 accordingly. The revised text now explicitly states that the electrometer was operated in parallel to obtain $N_{total}$, which serves as the reference for calculating the counting efficiency:

"SFCPC, which was improved from a water-based condensation particle counter (WCPC, TSI model 3788) and could change the supersaturation fast by altering the sample flow, was deployed to count the activated particle concentration ($N$). And an electrometer (EM, TSI model 3068B) was operated in parallel to measure the total particle concentration ($N_{total}$), where the counting efficiency of sampled particles ($f_{count}$) in different supersaturation ($S$) conditions could be obtained by $N/N_{total}$."

### *5. Comments and suggestions:*

*Line 138: Where is the mass spectrometry data?*

**Responses and Revisions:**

Thank you for your comment. The mass spectrometry data from the iodide chemical ionization mass spectrometry (Vocus AIM) are now provided as Figure S2 in the Supplementary Information, and we have added the corresponding citation in the revised manuscript. These data were obtained prior to the main experiments as an auxiliary characterization to confirm the absence of significant organic compound signals in the gas phase, thereby excluding organic contamination as a driver for the observed trend. The revised text in Section 3.1 is as follows:

"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."

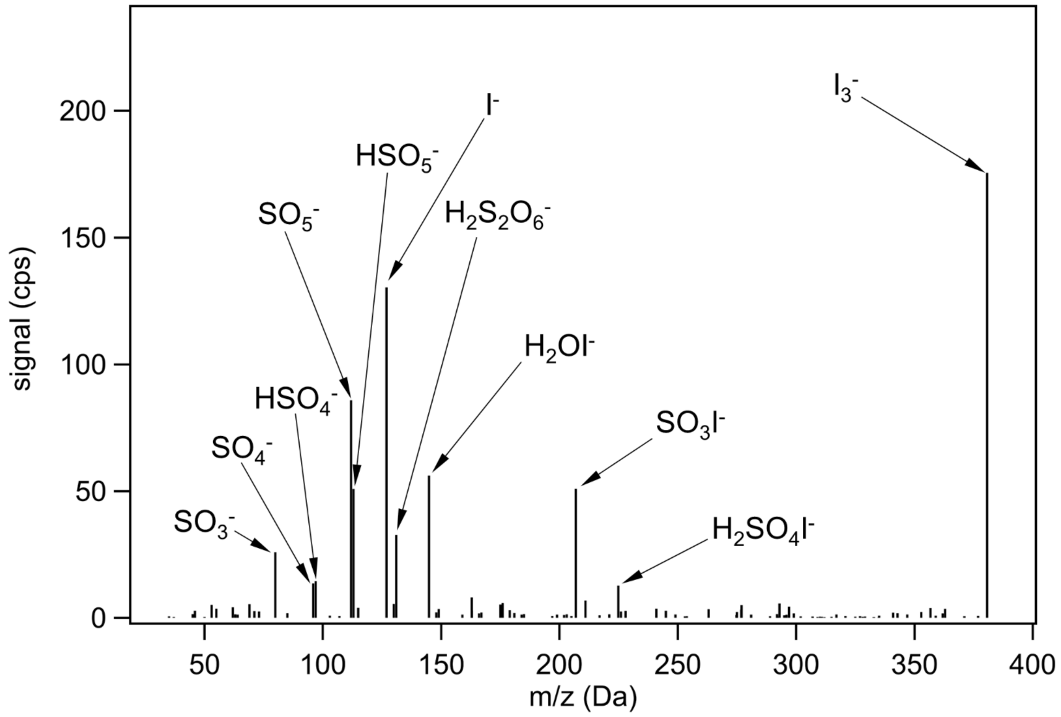

Figure S2. Representative Vocus AIM negative ion mass spectra of the oxidation products of $SO_2$.

***6. Comments and suggestions:***

*Line 144: If SA exist in the form as (H2SO4)m-(H2O)n, how will the m and n change regarding particle size and the presence of OOM?*

**Responses and Revisions:**

We thank the reviewer for raising this important point regarding the evolution of the composition, expressed as the stoichiometric coefficients m and n in $(H_2SO_4)_m$-$(H_2O)_n$, with particle size and in the presence of OOMs. Our response addresses each aspect below:

(1) Dependence of m/n on particle size: As discussed in the manuscript, the sulfuric acid and water binary nucleation is the basic mechanism for the SA particle

formation, the water molecules play a significant role through hydration (Kulmala et al., 1998; Lee et al., 2019; Stolzenburg et al., 2023; Yu et al., 2017). The initial formation of $H_2SO_4 \cdot H_2O$ molecular clusters is followed by rapid addition of further $H_2O$ molecules and these stepwise hydrates process ultimately leads to particles covered with water during growth (Couling et al., 2003; Matsubara et al., 2009), this mean the m/n would decrease with the increasing size. However, we are unable to determine specific m or n values through experiments, and we have not found data of them for 3-10 nm sulfuric acid particles in the literature.

(2) Influence of OOMs on m and n: OOMs, formed from α-pinene oxidation, may influence SA particle formation through several ways, such as participating in cluster/particle formation themselves or altering the oxidative environment for $SO_2$ (e.g., via Criegee intermediates or OH radical). While these interactions would potentially affect the overall composition and growth dynamics of the mixed SA-OOMs particles, molecular-level quantification of the particle composition or determination of m and n values in $(H_2SO_4)_m$-$(H_2O)_n$ remains a significant experimental challenge for both our approach and other analytical methods.

(3) Rationale for our analytical approach: Given the above constraint, a core assumption in our analysis is necessary: we use the hygroscopicity derived from the pure inorganic system (SA from $SO_2$ oxidation) as a proxy for the hygroscopicity of the inorganic fraction within the mixed SA-OOMs particles. This implies that, we assume the effective m and n of the $(H_2SO_4)_m$-$(H_2O)_n$ component are similar in both pure and mixed systems with same particle size. This assumption allows us to quantify the organic mass fraction ($f_{org}$) of overall particle and the contribution of organics to the particle initial growth, which is a primary objective of this work.

We fully agree with the reviewer that determining how m and n values of $(H_2SO_4)_m$-$(H_2O)_n$ evolve under various atmospheric conditions, including in complex mixtures with organics, is crucial for a mechanistic understanding of new particle growth. Advanced mass spectrometric techniques and coupled theoretical modeling focused on multicomponent clusters are needed to address this challenge. Insights from such future studies would greatly refine growth models and our ability to predict aerosol climate impacts.

We have added related text in the revised manuscript to highlight this simplification more explicitly:

Section 2.3: "For SA-OOMs mixture, we use the $\kappa$ values of pure organic (OOMs) and inorganic (SA) experiment groups to represent the hygroscopicity of the organic and inorganic component in the mixture particles, respectively. Although the organic and inorganic components in mixture may not be identical to those in pure organic and inorganic particles of the same size under the same RH due to the potential change of oxidation processes, this simplification is a necessary given the current inability to directly measure the composition and component-specific hygroscopicity of particles in the 3-10 nm size range."

## *Technical comments*

***7. Comments and suggestions:***

*Was a double-charge correction applied when deriving S from the measurement data?*

**Responses and Revisions:**

Thank you for raising this point. As noted in previous studies (Fuchs, 1963; Wiedensohler et al., 1986; Wiedensohler and Fissan, 1988), the probability of double-charge is extremely low for sub-20 nm particles and can be considered negligible. In our experiments, the calibration aerosols did not exceed 20 nm, and the size range of interest (3-10 nm) lies well within this limit. Therefore, we think that the influence of double-charge on the derived results is negligible. For clarity, a brief statement has been added in the revised manuscript (Section 2.2) indicating that no double-charge correction was applied for the studied size range.

"The aerosol particles were passed through a neutralizer (X-ray, TSI model 3080), and a nano-differential mobility analyzer (nano-DMA, TSI model 3086) was used to select charged monodisperse particles in diameter range of 3-10 nm (with intervals of 0.2 nm in the 3-4 nm range and intervals of 0.5 nm in the 4-10 nm range). Considering the negligible probability of double-charge for particles below 20 nm (Fuchs, 1963; Wiedensohler et al., 1986; Wiedensohler and Fissan, 1988), no double-charge correction was applied in the studied size range."

***8. Comments and suggestions:***

*What was the value for surface tension used in the equation to derive kappa?*

**Responses and Revisions:**

We thank the reviewer for this question. The $\kappa$-Köhler equation was applied following the specific implementation described by Equation 2 in Zhang et al. (2023). In the application, the value used for surface tension is that of pure water, 0.072 N $m^{-1}$. This has been explicitly clarified in the revised manuscript (Section 2.2):

"Then the $\kappa$ values could be obtained from dry diameter ($D_d$) and its corresponding $S$ based on $\kappa$-Köhler equation (Petters and Kreidenweis, 2007). The equation was applied following Equation 2 in Zhang et al. (2023), in which the surface tension of water (0.072 N $m^{-1}$) was used."

***9. Comments and suggestions:***

*Line 161: Please clarify what the nano-size effect is.*

**Responses and Revisions:**

We thank the reviewer for raising this important question. In the context of our study, the "nano-size effect" specifically refers to the profound changes in particle behavior within the 3-10 nm size range, which is the focus of our work. These changes, driven by the reduction in particle size, primarily manifest as an enhanced Kelvin effect and potential alterations in phase state, both of which could influence hygroscopicity.

(1) The enhanced Kelvin effect: This is a fundamental thermodynamic principle wherein the equilibrium vapor pressure over a curved surface increases exponentially with its curvature. For nanoparticles (<10 nm), the extreme curvature dramatically elevates the energy barrier for vapor condensation. This directly suppresses water uptake, leading to a lower measured hygroscopicity parameter ($\kappa$).

(2) The size-dependent influence on phase state: particle size can fundamentally impact phase state, exhibiting a tendency of nanoparticles for staying in liquid and mixed phase. This potential liquid state can significantly alter physicochemical properties relevant to hygroscopicity, such as surface tension, viscosity, and solute dissolution kinetics, thereby further modifying the water uptake behavior.

Therefore, in our study, the term "nano-size effect" encapsulates the combined action of these two factors. Together, they provide a coherent explanation for the distinctively lower $\kappa$ we observed.

We have revised the relevant discussion in section 3.1 to incorporate this clarified of the nano-size effect:

"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 $\kappa$ values observed in our study."

## Refences:

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