Responses to Referee #2's comments

We are grateful to the reviewers for their valuable and helpful comments on our manuscript "Unexpected enhancement of new particle formation by lactic acid sulfate resulting from SO_3 loss in forested and agricultural regions" (Manuscript ID: egusphere-2025-4894). We have revised the manuscript carefully according to reviewers' comments. The point-to-point responses to the Referee #2's comments are summarized below:

Referee Comments:

Wang et al. utilized quantum chemical calculations, master equation analysis, and Atmospheric Clusters Dynamic Code kinetic model to systematically investigate the formation mechanism of lactic acid sulfate (LAS) and its enhancing effect on sulfuric acid (SA)-NH_3(A) nucleation. Particular attention is given to the reaction between lactic acid and SO_3, the catalytic effects of H_2O/SA, and the dual role played by LAS in the SA-A-LAS ternary system (both as a participant and as a catalyst). The topic is novel, the methodology is sound, and the work provides an important-yet previously underappreciated-mechanistic explanation for the unusually high NPF rates observed in forested and agricultural regions. Most of this manuscript is well written and will be of broad interest to the readers of Atmospheric Chemistry and Physics. I recommend its publication in the journal, provided that the following comments are addressed.

Response: We would like to thank the reviewer for the positive and valuable comments, and we have revised our manuscript accordingly.

Specific Comments:

Comment 1:

The results indicate that the barriers to the reaction between lactic acid and SO_3 are substantially reduced with the addition of SA. However, the underlying mechanism driving SA's pronounced catalytic effect has not been adequately addressed. Providing one or two specific structural characteristics, such as the lengths of critical hydrogen bonds or specific geometric changes in transition states, would clarify why SA exhibits higher catalytic efficiency than H_2O, thereby allowing readers to fully comprehend the mechanism driving the "barrier reduction".

Response: Thank you for your valuable comments. According to your suggestion, the geometrical

structure of the eight-membered ring transition state TS_{SA} has been compared with that of the six-membered ring transition state TS_{WM}. In Lines 199-202 Page 8 of the revised manuscript, this comparison is presented as follows: "As compared with six-membered ring transition state TS_{WM}, the transition state TS_{SA} shows eight-membered ring structure, which reduces the ring tension greatly. So, from an energetic point of view, SA lowers the Gibbs free energy barrier to 3.5 kcal·mol^{-1}, 4.3 kcal·mol^{-1} lower than the barrier observed for the H_2O-catalyzed pathway.".

Comment 2:

The authors' calculations reveal that the dominant nucleation pathways shift with temperature, however, the manuscript does not adequately explain why the contribution of LAS-related pathways increases with increasing temperature. Further clarification of the underlying mechanism is required, such as whether this behavior is associated with variations in collision frequency or the fact that LAS exhibits a relatively weak temperature dependence in its evaporation rate. Incorporating such an explanation would greatly enhance the interpretability of the trend presented in Fig. 5 of the manuscript.

Response: Thanks for your valuable comments. According to the reviewer's suggestion, the reason for the variation of LAS-related pathways with temperature has been added. The corresponding changes are as follows.

(a) In Lines 285-287 Page 10 of the revised manuscript, the reason for the increasing influence of LAS-involved pathways with rising temperature is added and organized as " As temperature increases, the influence of LAS-involved pathways becomes progressively more dominant, due to the elevated vapor pressure of LAS raises its gas-phase concentration, thereby promoting further cluster formation.".

(b) In Lines 288-290 Page 11 of the revised manuscript, at lower temperatures, the reason for the modest contribution of LAS-involved pathways is presented and organized as " At lower temperatures (238.15 and 258.15 K), SA-A clustering remains the dominant process, accounting for 73% of nucleation events, while LAS-involved pathways contribute a modest 21%, because of the reduced collision frequency of LAS.".

Comment 3:

The manuscript proposes that LAS may function either as a "participant" or as a "catalyst-like promoter," which is an interesting and meaningful finding. At present, the distinction between these

two roles is mainly inferred from the ACDC pathways in Fig. 5 (i.e., whether LAS ultimately remains in the cluster), whereas Fig. 6 and Fig. 7 primarily illustrate how the contribution of LAS varies with temperature and precursor concentrations. Their connection to the role distinction is not explicitly established. To make the origin of this "dual role" clearer, a brief clarification in the discussion section would help enhance the manuscript's logical coherence assist readers in better understanding how LAS behaves under different conditions.

Response: Thanks for your valuable comments. Specifically, we highlight that the dual role of LAS is determined by its behavior in the cluster formation pathway, as illustrated in Fig. 5. When LAS functions as a 'catalyst', it temporarily participates in the cluster formation but evaporates after facilitating the growth process. In contrast, when LAS acts as a 'participant', it remains within the cluster throughout the entire nucleation process. To make the origin of this 'dual role' clearer, the corresponding changes are as follows.

(a) In Lines 331-332 Page 12 of the revised manuscript, an example illustrating the role of LAS as a catalyst has been added and organized as "While LAS contributes to the initial stages of cluster formation, it subsequently evaporates from the pre-nucleation cluster, ultimately functioning in a catalyst-like capacity (Fig. S16).".

(b) In Lines 335-338 Page 12 of the revised manuscript, an example illustrating the role of LAS as a participant has been added and organized as "At high [LAS], as observed in the Centreville, Alabama (1.77×10^6 molecules·cm^{-3}) (Hettiyadura et al., 2017), LAS-driven nucleation becomes dominant, resulting in a 'participant' synergistic nucleation mechanism that works like 'hand in hand' (Fig. S17), contributing up to 97 % of the total nucleation rate.".

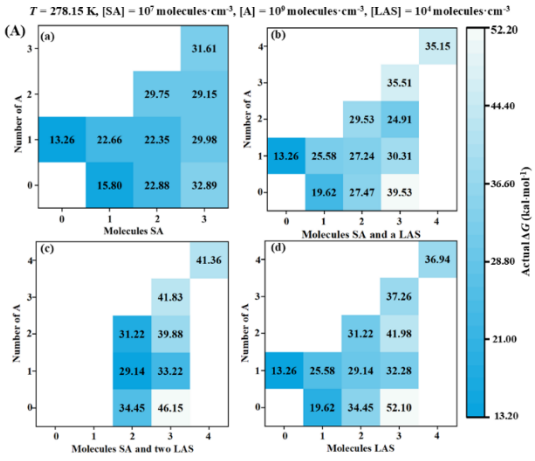
Comment 4:

I suggest the authors explicitly outline how boundary conditions were set in their ACDC simulations, along with justifying the maximum cluster size they selected. Nucleation rates are often sensitive to the choice of boundary conditions. Accordingly, it is essential to clarify why setting the maximum cluster size at $x + y + z \leq 3$ was adequate for their simulations, or alternatively, to discuss the implications of extending this boundary to larger clusters. Even a short, targeted explanation would greatly enhance the clarity and reproducibility of the methodology.

Response: Thanks for your valuable comments. For reviewers' comments, the corresponding revision has been made as follows.

(a) In ACDC simulations, boundary clusters are those allowed to flux out of the simulation box for further growth. Consequently, the smallest clusters outside the simulated system must be sufficiently stable to prevent immediate evaporation back into the system. In addition, considering the formation Gibbs free energy (Table S7) and evaporation rates (Table S9), the clusters $(LAS)_4(A)_3$, $(LAS)_4(A)_4$, $(LAS)_2(SA)_2(A)_3$, $(LAS)_2(SA)_2(A)_4$, $(LAS)(SA)_3(A)_3$, $(LAS)(SA)_3(A)_4$, $(SA)_4(A)_3$ and $(SA)_4(A)_4$ clusters are selected as the boundary clusters for LAS-SA-A system. Based on the above analysis, in Lines 158-160 Page 6 of the revised manuscript, the relevant information about boundary clusters have been added and organized as "Additionally, $(LAS)_4(A)_3$, $(LAS)_4(A)_4$, $(LAS)_2(SA)_2(A)_3$, $(LAS)_2(SA)_2(A)_4$, $(LAS)(SA)_3(A)_3$, $(LAS)(SA)_3(A)_4$, $(SA)_4(A)_3$ and $(SA)_4(A)_4$ clusters are acting as boundary clusters for LAS-SA-A system.".

(b) As reported by Besel et al. (*J. Phys. Chem. A*, 2020, 124(28), 5931-5943), the explicitly simulated set of clusters should always include the "critical cluster". Usually, the highest barrier on the lowest-energy path connecting the monomers to the outgrowing clusters (a saddle point on the actual ΔG surface) represents the "critical cluster". So, at 278.15 K (Fig. S4), the actual ΔG of $(A)_y(LAS)_z$ ($0 \le y \le z \le 4$), $(SA)_x(A)_y$ ($0 \le y \le x \le 3$), $(SA)_x(A)_y(LAS)_1$ ($0 \le y \le 4$, $0 \le x \le 3$), and $(SA)_x(A)_y(LAS)_2$ ($0 \le y \le 4$, $0 \le x \le 2$) clusters were calculated to verify that the 3 × 3 systems adequately capture the influence of LAS on SA-A nucleation. As seen in Fig. S4, the actual ΔG surface represented that the simulated set of clusters always included the critical cluster. So, we conclude that, in atmospherically relevant conditions, a 3 × 3 cluster set is adequate for predicting the particle formation in the SA-A system.



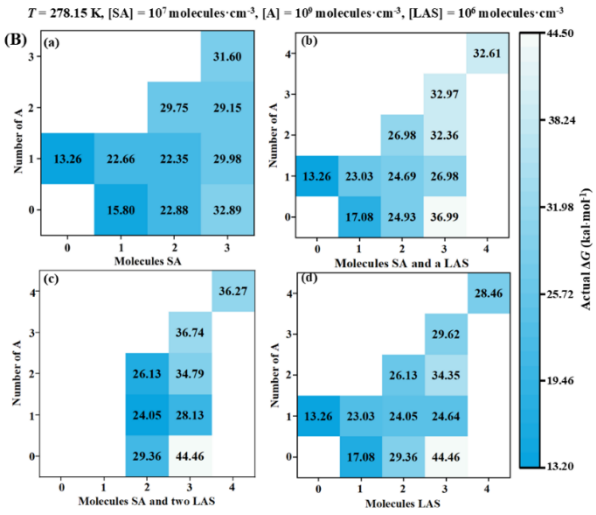


Fig. S4 A typical actual Δ*G* surface at 278.15 K. [SA] is the concentration of sulfuric acid monomers, [A] the concentration of ammonia monomers and [LAS] is lactic acid sulfate

Comment 5:

A single value of 2.6 × 10^{-3} s^{-1} was adopted for the condensation sink in the ACDC kinetics simulation under different atmospheric conditions of agricultural and forested regions (Figure 6), without addressing whether this parameter is representative of such diverse conditions. In practice, condensation sinks can vary by orders of magnitude depending on aerosol loading. Hence, the manuscript ought to explain the rationale for using a single Cs value across all cases, or discuss the uncertainties associated with this choice for the cluster formation rates or pathways. Including such justification would greatly enhance the credibility of the modeled nucleation rates.

Response: We sincerely appreciate the reviewer's careful reading of our manuscript. As the reviewer pointed out, the condensation sink (Cs) coefficients vary significantly across regions. According to previous reports (Jayaratne et al., 2017; Qi et al., 2015; Shen et al., 2020), the effect of Cs on results was examined, by additional runs with various values covering cases of clean and haze days (6 × 10^{-4} to 6 × 10^{-2} s^{-1}). To further evaluate the influence of Cs values on cluster formation rates, two additional sets of ACDC simulations were performed using different Cs values (Fig. S11). The results indicate that varying Cs value settings (6 × 10^{-4} ~ 6 × 10^{-2} s^{-1}) does not affect the main conclusions of this study (Fig. S11). Thus, a representative Cs value of 2.6 × 10^{-3} s^{-1}, was adopted as the sink term in the ACDC simulations. Following the reviewer's suggestion, in Lines 155-158 Page 6 of the revised manuscript, the sentence of "Here, the condensation sink coefficient was assigned 2.6 × 10^{-3}." has been changed as "Sensitivity tests were conducted by varying the

condensation sink (Cs) from $6 \times 10^{-4} \sim 6 \times 10^{-2}$ s^{-1}, indicating that the Cs exerted minimal influence on the main conclusions (Fig. S11). Therefore, the Cs was set to a representative value of 2.6×10^{-3} for all subsequent calculations (Liu et al., 2021).".

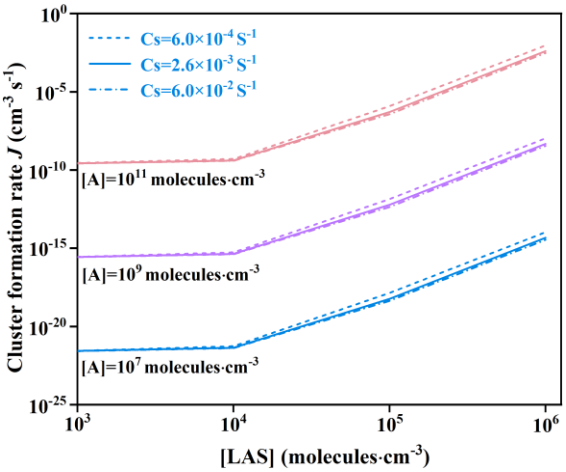


Fig. S11 The formation rate J (cm^{-3} s^{-1}) of LAS at varying consentrations of A and different condensation sink (Cs) values in the SA-A-LAS-based system where T = 278.15 K, [SA] = 10^5 molecules cm^{-3}, [LAS] = $10^3 \sim 10^6$ molecules cm^{-3}. Cs = 6×10^{-4} s^{-1} (dotted lines), 2.6×10^{-3} s^{-1} (solid lines) and 6×10^{-2} s^{-1} (dash-dotted lines)

References

Jayaratne, R., Pushpawela, B., He, C., Li, H., Gao, J., Chai, F., and Morawska, L.: Observations of particles at their formation sizes in Beijing, China, Atmos. Chem. Phys., 17, 8825-8835, 2017.

Qi, X. M., Ding, A. J., Nie, W., Petäjä, T., Kerminen, V. M., Herrmann, E., Xie, Y. N., Zheng, L. F., Manninen, H., Aalto, P., Sun, J. N., Xu, Z. N., Chi, X. G., Huang, X., Boy, M., Virkkula, A., Yang, X. Q., Fu, C. B., and Kulmala, M.: Aerosol size distribution and new particle formation in the western Yangtze River Delta of China: 2 years of measurements at the SORPES station, Atmos. Chem. Phys., 15, 12445-12464, 2015.

Shen, J., Elm, J., Xie, H. B., Chen, J., Niu, J., and Vehkamäki, H.: Structural effects of amines in enhancing methanesulfonic acid-driven new particle formation, Environ. Sci. Technol., 54, 13498-13508, 2020.

Comment 6:

Technical corrections:

Page 6 line 161: "In the direct cycloaddition pathway (Channel LAS) illsutrated in Fig. 1"

The word "illsutrated" should be corrected to "illustrated". In addition, there is a spelling error in the caption of Fig. 4, where "nunber" should be corrected to "number."

Page 5 line 114: "To identity the global minimum energy configurations of …"

The word "identity" should be corrected to "identify".

Page 10 line 278: "… the contributions of LAS to the SA-A nucleation process was examined, …"

The word "was" should be corrected to "were".

Page 12 lines 325-326: "LAS-driven nucleation becomes dominate, …"

The word "dominate" should be corrected to "dominant".

Page 21 lines 665-672: In the reference list, Yin et al., 2021a and Yin et al., 2021b share the same title and page numbers (Acid-base clusters during atmospheric new particle formation in urban Beijing" Environ. Sci. Technol., 55, 10994-11005). Please remove the duplicate references and update the citation numbers in the main text.

Response: Thanks to the reviewer's insightful comment, we are sorry for the trouble we have caused by oversight. In order to improve the accuracy of the expression, the corresponding main revision has been made as follows:

(a) In Line 164 Page 6 of the revised manuscript, "illsutrated" has been corrected to "illustrated".

(b) In Fig. 4, the "nunber" has been corrected to "number". The newly revised Fig. 4 is shown below.

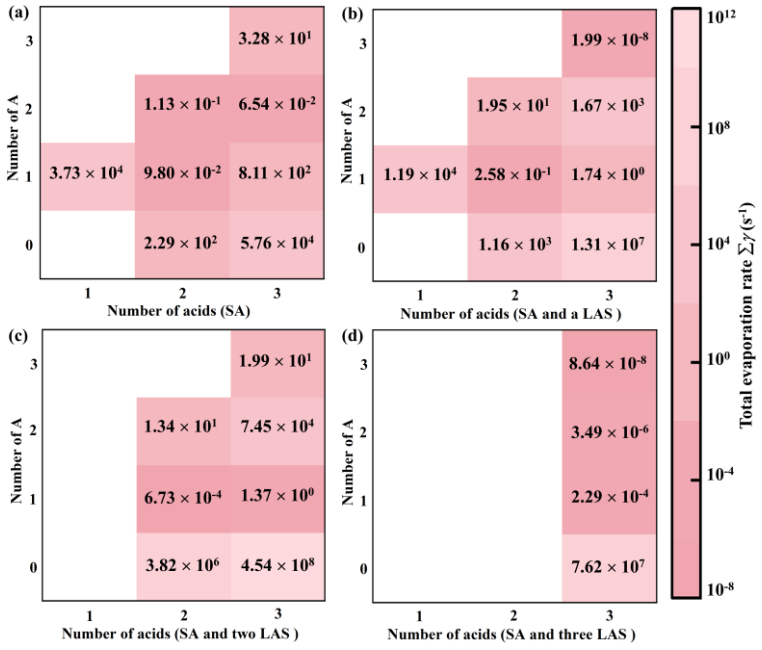


Fig. 4 The total evaporation rates ($\sum\gamma$) (s^{-1}) of $(SA)_x(A)_y(LAS)_z$ ($y \leq x + z \leq 3$) clusters at 278.15 K and 1 atm calculated at the M06-2X/6-311++G(2*df*, 2*pd*) level of theory. (a) without LAS monomer, (b) containing 1 LAS monomer, (c) containing 2 LAS monomers, and (d) containing 3 LAS monomers

(c) In Line 112 Page 4 of the revised manuscript, "identity" has been corrected to "identify".

(d) In Line 283 Page 10 of the revised manuscript, “was” has been corrected to “were”.

(e) In Line 337 Page 12 of the revised manuscript, “dominate” has been corrected to “dominant”.

(f) In Line 57 Page 3 of the revised manuscript, we have removed the duplicate reference and updated all corresponding citation numbers throughout the manuscript accordingly.