Response to Referee #2

Dear Editor and Referee #2,

Thank you very much for your time and effort in reviewing our manuscript ***"Trifluoroacetic acid enhances sulfuric acid–ammonia nucleation in the cold atmosphere: Molecular mechanism and atmospheric implications"*** (MS No.: egusphere-2026-2877). Our point-by-point responses are given below.

Referee's general assessment: This study investigates the potential role of trifluoroacetic acid (TFA), a representative perfluorocarboxylic acid (PFCA), in atmospheric new particle formation by combining quantum chemical calculations combined with Atmospheric Cluster Dynamics Code (ACDC) simulations. The potential involvement of persistent fluorinated organic acids in atmospheric nucleation has received increasing attention. However, their roles in molecular clustering and early-stage particle formation remain poorly constrained. This work provides molecular-level insights into TFA-containing sulfuric acid–ammonia (SA–NH_3) clusters and their potential influence of these clusters on nucleation processes under cold atmospheric conditions. The combination of quantum chemical calculations and kinetic cluster simulations provides an appropriate framework for linking molecular-scale interactions with atmospheric nucleation processes. The analyses of cluster structures, thermodynamic properties, kinetic behavior, and formation pathways contribute to a better understanding of TFA-assisted nucleation mechanisms. Taken together, the findings provide valuable molecular-scale insights into the potential role of fluorinated organic acids in atmospheric nucleation chemistry. The manuscript would be suitable for publication after the authors carefully consider and address the following comments.

Response: We sincerely thank the referee for the positive evaluation of our work. Corresponding revisions have been made to the manuscript as suggested.

Specific comments

Comment 1. The authors investigate hydrated clusters and assess the influence of relative humidity on cluster stability. Because water molecules can significantly affect hydrogen-bonding networks and the thermodynamic properties of atmospheric clusters, the structural and energetic information of these hydrated clusters is important for evaluating the calculated results. The authors should provide the Gibbs free energies of formation and optimized Cartesian coordinates of the studied hydration clusters in the Supplement. Including these data would improve the reproducibility of the calculations and allow more detailed evaluation of the hydration effects discussed in the manuscript.

Response: We thank the referee for this valuable suggestion. Following the referee's suggestion, we have added the Gibbs free energies of formation (Table S4) and the optimized Cartesian coordinates (Table S1) of the studied hydrated clusters, $(SA)_1 \cdot (NH_3)_y \cdot (TFA)_1 \cdot (H_2O)_n$ (y = 1–2 and n = 1–3), to the revised Supplement. A corresponding statement has also been added to Section S8 of the revised Supplement as: "The addition of water molecules can increase the number of hydrogen bonds, and these processes are thermodynamically favorable."

Comment 2. The reliability of the predicted nucleation enhancement depends strongly on the completeness of conformational sampling. The authors should provide additional details on the sampling strategy and clarify whether selecting 100 low-energy structures after PM7 optimization is sufficient to identify the global minimum structures of the investigated clusters.

Response: We thank the referee for this important comment. According to the suggestion, we have revised the manuscript to clarify this limitation and avoid implying complete conformational coverage in lines 97-101:

"Although we retained a large number of low-energy structures (usually 1,000 from CHARMM36 and 100 from PM7) at the above two stages, selecting a subset of 100 low-energy structures after PM7 optimization may be not sufficient to identify the true global minimum, as this subset may still exclude it. In addition, several chemically plausible candidate structures with multiple hydrogen- and halogen-bonding interactions were manually constructed based on chemical intuition."

Comment 3. Since UFF may not accurately capture proton transfer or bond rearrangement, the authors should clarify whether ionic configurations or structures involving proton transfer were considered during the initial sampling. This information is important for assessing the reliability of the predicted cluster structures and subsequent nucleation simulations.

Response: We thank the referee for this comment. Because proton transfer is not explicitly described by the CHARMM36 force field, ionic monomers with different protonation states were included in the configurational sampling. We also manually constructed several chemically plausible structures featuring multiple hydrogen- and halogen-bonding interactions. The corresponding statement has been added to the revised manuscript in Section 2 as follows:

"Because the CHARMM36 force field cannot explicitly describe proton transfer, ionic species with different protonation states were included in the configurational search. The species considered were HSO_4^-, SO_4^{2-}, CF_3COO^-, and NH_4^+."

Comment 4. The authors should further justify the boundary conditions used in the ACDC simulations and discuss their atmospheric representativeness. Since simulated nucleation rates are sensitive to precursor concentrations and environmental parameters, the basis for selecting the concentrations of sulfuric acid, ammonia, and TFA, as well as temperature and relative humidity, should be clarified. This information would help evaluate the relevance of the predicted nucleation enhancement under different atmospheric conditions.

Response: We thank the referee for this valuable suggestion. According to the referee's suggestion, we have stated in the Section S5 of the revised Supplement as follows:

"Therefore, $(SA)_3{\cdot}(NH_3)_3{\cdot}(TFA)_1$ and $(SA)_4{\cdot}(NH_3)_3$ clusters were set as the boundary of the following ACDC simulation at 220-240 K, [SA] = 7.0×10^5–1.0×10^7 molecules cm^{-3}, $[NH_3] = 1.0 \times 10^8$–1.0×10^{11} molecules cm^{-3}, and [TFA] = 1.0×10^6–1.0×10^8 molecules cm^{-3}."

Comment 5. The relevant statement should be further specified to better reflect the atmospheric conditions under which the conclusion applies. For example, the statement that "the SA–NH_3–TFA ternary mechanism emerges as a particularly critical contributor to the clustering process" could be revised to "the SA–NH_3–TFA ternary mechanism emerges as a critical contributor to the clustering process under cold atmospheric conditions."

Response: We thank the referee for this suggestion. According to the suggestion, we have revised the statement in the Conclusions as follows: "Hence, beyond the SA–NH_3 binary nucleation mechanism, the SA–NH_3–TFA ternary mechanism emerges as a critical contributor to the clustering process under cold atmospheric conditions."

Comment 6. The caption of Fig. 5 should clearly indicate that pathways contributing less than 5% to the total flux are excluded from the pathway analysis.

Response: We thank the referee for this suggestion. According to the suggestion, we have added the statement in the caption of Fig. 5 as follows: "Pathways contributing less than 5% of the total flux are not shown in panel (a), the TFA-free contribution below 5% is retained in panel (c) to illustrate its temperature dependence."

Comment 7. The manuscript compares the roles of TFA and nitric acid in SA–NH_3. A quantitative comparison would strengthen the mechanistic interpretation of the proposed analogy. For example, differences in cluster formation free energies, evaporation rates, and collision coefficients between TFA- and HNO_3-containing clusters could provide further insight into their respective thermodynamic and kinetic effects on nucleation.

Response: We thank the referee for this suggestion. According to the referee's suggestion, we have provided a quantitative comparison in Tables S14 and S15 of the revised Supplement.

We have stated in Section 3.6 of the revised manuscript as follows:

"The comparison of stability between SA–NH_3–TFA based clusters and SA–NH_3–NA based clusters is shown in the Section S9 of the Supplement."

We have stated in the Section S9 of the Supplement as follows:

"For most corresponding ternary compositions, TFA-containing clusters have more favorable formation free energies and lower total monomer evaporation coefficients ($\Sigma\gamma$), whereas the collision coefficients (β) are comparable between the two systems. Consequently, most of the tabulated ternary-cluster growth steps have higher collision-to-evaporation ratios ($\beta C/\Sigma\gamma$) in the TFA system at the stated concentrations. These trends support favorable competition between growth and evaporation for TFA-containing clusters, although they do not directly establish the relative overall particle formation rates. The particle formation rate also depends on the relative concentration between TFA and NA.

Fig. 6(b) shows that the SA–NH_3–NA system has moderately higher particle formation rates at lower [NH_3]. As [NH_3] increases, the rates of the SA–NH_3–TFA system approach those of the NA system at [TFA] = 2.0×10^7 molecules cm^{-3} and exceed them at [TFA] = 1.0×10^8 molecules cm^{-3}. Overall, the two systems exhibit comparable particle formation rates under the conditions shown. Taken together, the cluster-level comparison and simulated rates indicate that TFA can compete with NA in promoting SA–NH_3 cluster formation under the investigated cold conditions, with its contribution becoming particularly competitive at elevated [NH_3]."

Comment 8. The treatment of the sticking coefficient in the ACDC simulations should be clarified. Since the sticking coefficient can influence cluster formation kinetics and the resulting particle formation rates, a brief discussion of its uncertainty and potential impact on the simulated results would be helpful.

Response: We thank the referee for this suggestion. According to the referee's suggestion, we have tested the influence of the sticking coefficient on the particle formation rate (J) and the enhancement of TFA on the J (Fig. S7), and stated in the Section S2 of the revised Supplement that "Previous studies using a sticking coefficient of α = 0.5 have reported good agreement between simulated SA–DMA–TFA cluster concentrations and field measurements in Shanghai (Lu et al., 2020), as well as reasonable agreement between simulated SA–NH_3–HNO_3 particle formation rates and CLOUD chamber measurements (Liu et

al., 2021). These comparisons indicate that α = 0.5 is a reasonable choice for the present analysis, and we therefore adopted this value in our ACDC simulations. To further evaluate the influence of the sticking coefficient, we performed a sensitivity analysis with α = 1, 0.5, and 0.1. The results are presented in Fig. S7 of the Supplement. Decreasing α reduces the particle formation rate J, but increases the TFA enhancement factor. Thus, both the absolute formation rates and the enhancement depend on α, whereas the promoting effect of TFA persists across all three tested values."

Technical issues

Comment T1. The description should be made more precise in terms of terminology. The statement that "SA, NH_3, and TFA can form cage-like clusters stabilized by the hydrogen-bond network" should be revised to "SA, NH_3, and TFA can form cage-like structures stabilized by the hydrogen-bond network."

Response: We thank the referee for this correction. We have replaced "cage-like clusters" with "cage-like structures" in the corresponding structural description in Section 3.1, Abstract, and Conclusions.

Comment T2. The terms "nucleation rate" and "cluster formation rate" should be used consistently throughout the manuscript.

Response: We thank the referee for this suggestion. We have standardized the terminology throughout the manuscript and Supplement, including the main text, section headings, figure captions, and supplementary text and captions, by consistently using the term "particle formation rate".

We thank the referee again for the careful and constructive comments.

Sincerely,

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Reference

Liu, L., Yu, F., Du, L., Yang, Z., Francisco, J. S., and Zhang, X.: Rapid sulfuric acid–dimethylamine nucleation enhanced by nitric acid in polluted regions, Proc. Natl. Acad. Sci. U.S.A., 118, e2108384118, https://doi.org/10.1073/pnas.2108384118, 2021.

Lu, Y., Liu, L., Ning, A., Yang, G., Liu, Y., Kurtén, T., Vehkamäki, H., Zhang, X., and Wang, L.: Atmospheric sulfuric acid–dimethylamine nucleation enhanced by trifluoroacetic acid, Geophys. Res. Lett., 47, e2019GL085627, https://doi.org/10.1029/2019GL085627, 2020.