Response to Referee #1

Dear Editor and Referee #1,

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: The authors report a molecular-level investigation of how trifluoroacetic acid (TFA), used as a model perfluorocarboxylic acid with long lifetime and widespread distribution, enhances sulfuric acid (SA)–ammonia (NH_3) nucleation under cold atmospheric conditions, using quantum chemical calculations combined with Atmospheric Cluster Dynamics Code simulations. The results show that TFA can form stable cage-like SA–NH_3–TFA clusters through strong hydrogen-bond networks and proton-transfer-induced electrostatic interactions. Thermodynamic and kinetic analyses further indicate that these clusters become increasingly stable at lower temperatures. The simulated particle formation rates and cluster concentrations are enhanced by TFA, particularly under low-SA, high-NH_3, high-TFA, and low-temperature conditions, and the pathway analysis suggests that TFA-containing growth routes can dominate the simulated clustering flux under favorable cold conditions. Importantly, the authors appropriately frame the atmospheric relevance of this mechanism differently for the cold boundary layer and the upper troposphere: the former is better supported by existing TFA observations, whereas the latter remains an exploratory sensitivity scenario due to the lack of direct gas-phase TFA measurements aloft. The calculations are performed at an adequate computational level, and the mechanistic analysis is generally thorough. The work addresses acid-assisted atmospheric nucleation involving halogenated organic acids and provides molecular-level insight into a potentially important pathway for new particle formation in cold environments, while appropriately acknowledging the need for further observational constraints. Overall, this study falls within the scope of Atmospheric Chemistry and Physics. I recommend publication after the authors adequately address the following comments.

Response: We sincerely thank the referee for the positive assessment. Our responses are provided below.

Scientific issues

Comment S1. The manuscript uses TFA as a "model PFCA" to explore the general role of perfluorocarboxylic acids in atmospheric nucleation. The authors emphasize that TFA is the shortest-chain and most abundant PFCA and possesses strong acidity and hydrogen-bonding ability. However, it remains unclear whether the observed enhancement originates from general PFCA characteristics or from unique properties of TFA. A more cautious statement is recommended in the manuscript.

Response: We thank the referee for this important comment. We agree that our results should not be interpreted as implying that all PFCAs exhibit the same nucleation-enhancing efficiency as TFA. TFA was selected as a model PFCA because it shares key structural features with other PFCAs, particularly the carboxylic acid group and the electron-withdrawing perfluoroalkyl moiety, which are relevant to hydrogen-bonding and proton transfer ability. Thus, the molecular interactions identified for TFA can provide mechanistic insight into the potential involvement of other PFCAs in SA–NH_3 cluster stabilization. However, individual PFCAs differ in molecular size, perfluoroalkyl chain length, volatility, atmospheric abundance, transport, and thermodynamic properties, and therefore their quantitative effects may differ from those of TFA.

Accordingly, we have added the following statement to the **Introduction** as follows:

"Because the characteristic carboxylic acid group and electron-withdrawing perfluoroalkyl moiety are shared across PFCAs, the molecular interactions identified for TFA may provide mechanistic insight into the potential involvement of other PFCAs in SA–NH_3 cluster stabilization, although their quantitative effects may vary among individual species."

We have also revised the corresponding statement in the **Conclusions** as follows:

"TFA is used here as a representative model PFCA to probe a possible cluster-stabilization mechanism associated with structural features common to PFCAs, rather than as a quantitative proxy for the entire PFCA class. Individual PFCAs differ in molecular size, perfluoroalkyl chain length, volatility, atmospheric abundance, transport, and thermodynamic properties, and may therefore exert different quantitative effects on cluster formation. Consequently, the atmospheric contribution of PFCAs to cluster formation may reflect the combined effects of multiple PFCA species rather than TFA alone."

Comment S2. The simulations consider TFA concentrations ranging from 1.0×10^6 to 1.0×10^8 molecules cm^{-3}. Since the predicted enhancement reaches nearly three orders of magnitude at high TFA abundance, the atmospheric importance depends critically on whether such concentrations occur frequently. The authors state that these values are based on boundary-layer observations. However, under what environments were these measurements obtained should be more clarified.

Response: We thank the referee for this professional comment. According to the suggestion, we have added the statement in lines 186-187 of the revised manuscript as: "The TFA concentrations adopted here (1.0×10^6 to 1.0×10^8 molecules cm^{-3}) are based on field measurements in the boundary layer, especially in polluted urban atmosphere".

Comment S3. The authors focus on clusters containing up to six molecules. Please clarify why clusters larger than six molecules were not considered and whether the selected cluster size is sufficient to capture the nucleation enhancement. A brief discussion based on computational limitations and previous ACDC studies would improve transparency.

Response: We thank the referee for this professional comment. According to the suggestion, we have added a brief explanation of this choice to the Section S5 of the revised Supplement as follows:

"The cluster system was limited to six molecules based on cluster size, kinetic stability, and computational cost. First, the six-molecule clusters reach a size of up to 1.5 nm, which is comparable to the typical size range of critical atmospheric clusters. Second, the largest six-molecule clusters, $(SA)_3 \cdot (NH_3)_3$ and $(SA)_2 \cdot (NH_3)_3 \cdot (TFA)_1$, have collision-to-evaporation ratios close to or above unity under the investigated conditions, indicating that further growth is comparable to or more favorable than monomer evaporation. Therefore, extending the cluster size beyond six molecules is unlikely to alter the qualitative conclusions while substantially increasing the computational cost."

Comment S4. The manuscript appropriately acknowledges that direct gas-phase TFA measurements in the upper troposphere are unavailable. However, some statements still imply that TFA may represent an important upper tropospheric nucleation pathway. Given that the UT simulations are based on assumed TFA concentrations rather than observational constraints, the authors should consistently describe these results as "potential mechanistic scenarios" rather than "atmospherically relevant pathways". The conclusion should clearly separate: (1) observationally supported cold boundary-layer implications. (2)

hypothetical upper tropospheric sensitivity tests.

Response: We thank the referee for this professional comment. Accordingly, we have revised the relevant statements throughout the manuscript to consistently distinguish between the observationally supported cold boundary-layer implications and the UT sensitivity analysis. In particular, the prescribed TFA concentrations used in the UT simulations are now explicitly described as exploratory sensitivity conditions rather than observationally constrained atmospheric abundances.

To further clarify this distinction, we have revised the corresponding statement in the revised manuscript as follows:

Abstract: "its role serves as a critical low-temperature mechanistic insight, pending direct observations of gas-phase TFA aloft" has been revised as "its role serves as a potentially critical low-temperature mechanistic insight, pending direct observations of gas-phase TFA aloft".

Introduction: "the present study provides molecular-level insight into how TFA, as a model PFCA, influences the SA–NH_3 nucleation process under cold conditions, encompassing both of the cold boundary layer and the upper troposphere." has been revised as "the present study provides molecular-level insight into TFA-assisted SA–NH_3 nucleation, with direct atmospheric implications for the cold boundary layer and exploratory low-temperature sensitivity tests for the upper troposphere".

Conclusions: "The mechanism has different levels of atmospheric support in different cold atmospheric environments. It is directly relevant in the cold boundary layer, where TFA has been observed. In the upper troposphere, the results represent robust mechanistic low-temperature sensitivity tests that demonstrates how strongly low temperatures amplify TFA-assisted nucleation, should TFA be present aloft" has been revised as "In the cold boundary layer, where TFA has been observed, the results provide observationally supported implications for TFA-assisted cluster formation. In the upper troposphere, where gas-phase TFA concentrations remain unconstrained, the calculations should be regarded as potential mechanistic scenarios and exploratory low-temperature sensitivity tests rather than as evidence for an established atmospheric nucleation pathway."

Comment S5. The introduction explains that nitric acid enhances SA–NH_3 nucleation under cold conditions. However, the logical transition from nitric acid to TFA is somewhat abrupt. The authors should explain why TFA is expected to behave similarly to nitric acid considering molecular properties and atmospheric concentrations. This would make the hypothesis more scientifically grounded.

Response: We thank the referee for this professional comment. Accordingly, we have strengthened the transition in the Introduction of the revised manuscript by adding the following statement:

"In this respect, PFCAs share with NA several molecular properties relevant to acid-assisted SA–NH_3 stabilization, particularly strong acidity and hydrogen-bonding capability, suggesting that they may provide a related stabilization mechanism under cold conditions".

Comment S6. The manuscript defines the enhancement factors only in figure captions. This definition should be introduced in the main text before discussing enhancement values.

Response: We thank the referee for this helpful suggestion. Accordingly, we have added the definitions of the particle formation rate enhancement factor (R_J), and the cluster concentration enhancement factor (R_C), at their first occurrence in Sections 3.3 and 3.4, respectively, as follows:

Section 3.3: "The J of SA–NH_3–TFA nucleation mechanism and the enhancement (R_J) of SA–NH_3 nucleation by TFA" has been revised as "The J of SA–NH_3–TFA nucleation mechanism and the enhancement (R_J, $R_J = J_{SA\text{-}NH3\text{-}TFA}/J_{SA\text{-}NH3}$) of SA–$NH_3$ nucleation by TFA".

Section 3.4: "TFA participation substantially enhances cluster concentrations, with the enhancement (R_C) showing …" has been revised as "TFA participation substantially enhances cluster concentrations, with the enhancement (R_C, $R_C = C_{SA\text{-}NH3\text{-}TFA}/C_{SA\text{-}NH3}$) showing …".

Technical issues

Comment T1. "enhances SA–NH_3 nucleation by up to 950-fold" in the Abstract should be changed to "enhances the simulated particle formation rate by up to 950-fold" because nucleation itself is not directly measured.

Response: We thank the referee for this correction. "enhances SA–NH_3 nucleation by up to 950-fold" has been corrected as "enhances the simulated SA–NH_3 particle formation rate by up to 950-fold."

Comment T2. Line 42. "… Wang et al., 2023; Zhang et al., 2018b) However, …" should be corrected as "… Wang et al., 2023; Zhang et al., 2018b). However, …"

Response: The missing period after the closing parenthesis has been added.

Comment T3. Page 3: "upper tropospheric sensitivity tests" should be used consistently instead of "upper tropospheric conditions".

Response: "upper tropospheric conditions" has been revised to "upper tropospheric sensitivity tests" on Page 11 of the revised manuscript.

Comment T4.

"3.1 Cluster Structures and Intermolecular Interactions" should be corrected as "3.1 Cluster structures and intermolecular interactions".

"3.2 Thermodynamic and Kinetic Stability of Clusters" should be corrected as "3.2 Thermodynamic and kinetic stability of clusters".

"3.3 Particle Formation Rates Enhanced by TFA" should be corrected as "3.3 Particle formation rates enhanced by TFA".

"3.4 Cluster Concentrations and Enhancement" should be corrected as "3.4 Cluster concentrations and enhancement".

"3.5 Dominant Cluster Formation Pathways" should be corrected as "3.5 Dominant cluster formation pathways".

Response: The titles of Sections 3.1–3.5 have been revised according to the referee's suggestions.

Comment T5. Reference "Wang, M., Xiao, M., Bertozzi, B., Marie, G., Rörup, B., Schulze, B., and Bardakov, R.: Synergistic HNO_3-H_2SO_4-NH_3 upper tropospheric particle formation, Nature, 605, 483–489, https://doi.org/10.1101/pdb.caut449, 2022." should be "Wang, M., Xiao, M., Bertozzi, B., Marie, G., Rörup, B., Schulze, B., and Bardakov, R.: Synergistic HNO_3-H_2SO_4-NH_3 upper tropospheric particle formation, Nature, 605, 483–489, https://doi.org/10.1038/s41586-022-04605-4, 2022."

Response: Reference "Wang, M., Xiao, M., Bertozzi, B., Marie, G., Rörup, B., Schulze, B., and Bardakov, R.: Synergistic HNO_3-H_2SO_4-NH_3 upper tropospheric particle formation, Nature, 605, 483–489,

https://doi.org/10.1101/pdb.caut449, 2022." has been corrected to "Wang, M., Xiao, M., Bertozzi, B., Marie, G., Rörup, B., Schulze, B., and Bardakov, R.: Synergistic HNO_3-H_2SO_4-NH_3 upper tropospheric particle formation, Nature, 605, 483–489, https://doi.org/10.1038/s41586-022-04605-4, 2022."

Comment T6. Reference "Stewart, *J. J.* P.: MOPAC2016, Stewart Computational Chemistry: Colorado Springs, n.d." should be "Stewart, *J. J.* P.: MOPAC2016, Stewart Computational Chemistry: Colorado Springs, 2016."

Response: The publication year for MOPAC2016 has been corrected from "n.d." to "2016".

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

Sincerely,

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