Response to Referee #1

Dear Editor and Referee #1,

Thank you so much for your time and effort in handling our manuscript *"**Altitude-Dependent Role of Nitric Acid in Iodic Acid–Iodous Acid Nucleation: From Marine Boundary Layer Catalyst to Upper Troposphere Core Component**"* (MS No.: egusphere-2026-1771). We are grateful to the referee for the positive assessment and the constructive comments, which have been very helpful in improving our manuscript. We have revised the manuscript carefully, and our point-by-point responses are summarized below.

Referee's general assessment: "The authors integrate high-level quantum chemical calculations with Atmospheric Cluster Dynamics Code simulations to systematically investigate how HNO_3 influences HIO_3–HIO_2 nucleation across the troposphere. The results reveal that HNO_3 can undergo a functional transition from a nucleation catalyst in the warm marine boundary layer (MBL) to a core structural component of nucleating clusters in the cold upper troposphere (UT). This conclusion is particularly important given declining global sulfur emissions, rising marine iodine emissions, and the well-recognized significance of upper tropospheric new particle formation for the global cloud condensation nuclei budget. The manuscript is clearly written and employs state-of-the-art computational methodologies for atmospheric cluster nucleation research, while its altitude-resolved mechanistic analysis provides a valuable, novel perspective to the field. Overall, this work is logically structured and easy to follow, with a topic that aligns closely with the scope of *Atmospheric Chemistry and Physics*. I recommend this work for publication following the adequate addressing of the comments below."

Response: We sincerely thank the referee for the valuable evaluation. We have addressed every point as detailed below, with revised text highlighted in the manuscript.

Scientific issues

Comment S1. Figure 2(b) shows boundary clusters determined at 228, 248, 268, and 288 K. However, the ACDC simulations cover 204–288 K (Fig. 4a), yet boundary clusters are not provided for the remaining temperatures. Boundary clusters should be provided for all the studied temperatures.

Response: We thank the referee for this professional comment. The four temperatures (228, 248, 268, and 288 K) in Figure 2(b) were chosen as representative altitude markers (UT, FT, polar boundary layer, and MBL). Figure 2(b) documents how $c_{boundary}$ is obtained from the temperature-dependent collision and evaporation coefficients, after which the boundary clusters at any given monomer concentration can be determined. For the simulations at different altitudes in Figure 4, however, 141 distinct temperatures are required (204–288 K in 0.6 K increments), which cannot be conveniently tabulated. To ensure full reproducibility, we have therefore uploaded the full set of corresponding boundary condition files to a public repository, accessible at:

https://doi.org/10.5281/zenodo.20712556.

The repository contains the resulting $c_{boundary}$ values at every simulated temperature across 204–288 K. A corresponding sentence and citation of the repository have been added to Figure S4 of the revised SI. Additionally, we have added the representative boundary conditions to Table S3.

Comment S2. The introduction briefly notes that HNO_3 stabilizes sulfuric acid-based clusters, without explicitly extending this established behavior to iodine oxoacid systems. A clear logical bridge is missing: if HNO_3 enhances sulfuric acid nucleation via hydrogen bonding and proton transfer, it is reasonable to hypothesize a stabilizing effect in iodine oxoacid systems, given their ability to form hydrogen-bond and halogen-bond networks. Adding this analogy would strengthen the motivation for investigating HNO_3 in iodine-driven nucleation, making the hypothesis less speculative and better grounded in existing knowledge.

Response: We thank the referee for this valuable suggestion. We have linked the analogy to the existing iodine-nucleation literature, which already indicates that additional acidic/basic species participate in iodine oxoacid clustering. The added content in lines 50–54 of the revised manuscript frames HNO_3 as the natural candidate:

"Previous studies have confirmed that HNO_3 stabilizes atmospheric molecular clusters via hydrogen bonds and proton transfer-driven electrostatic interactions in both H_2SO_4–dimethylamine (DMA) (Liu et al., 2021) and H_2SO_4–NH_3 (Liu et al., 2018) nucleation systems, and since iodine oxoacids readily form hydrogen- and halogen-bond networks (Ma et al., 2023; Zu et al., 2023, 2024), the ubiquitous and co-located HNO_3 is a strong candidate for the additional species that promotes iodine-driven nucleation."

Comment S3. In Section 2.1, the cluster composition is defined as $(HNO_3)_x(HIO_3)_y(HIO_2)_z$ with $1 \le x \le 3$, but no justification is provided for limiting the number of HNO_3 molecules to three. This arbitrary cutoff lacks chemical or kinetic rationale. A brief explanation (e.g., thermodynamic or kinetic stability) should be added to clarify this constraint.

Response: We thank the referee and have added a brief explanation. Two complementary lines of evidence support the choice of $1 \le x \le 3$.

First, our calculations show that HNO_3 exhibits substantially weaker self-binding than HIO_3. As reported in Table S1, the pure-acid trimer of HNO_3 is thermodynamically unfavorable (ΔG at 268 K = + 3.9 kcal mol^{-1} for $(HNO_3)_3$), whereas the pure-acid trimer of HIO_3 is strongly favorable (ΔG at 268 K = − 23.8 kcal mol^{-1} for $(HIO_3)_3$). HNO_3 therefore cannot self-cluster effectively and must rely on participation of the base HIO_2 to form stable clusters, which limits its incorporation in nucleation.

Second, the most stable clusters in this system follow a 1:1 acid-to-base ratio, in which HNO_3 and HIO_3 act as acids and HIO_2 is the only base (Fig. 2(a)). For the studied clusters ($2 \le x + y + z \le 6$), a 1:1 acid:base composition allows at most three acid molecules, so $x \le 3$ already spans the entire thermodynamically favorable composition space. This rationale has been added to Section 2.1, lines 77–78, of the revised manuscript, as follows:

"The constraint of $1 \le x \le 3$ is applied because HNO_3 exhibits relatively weak self-binding ability (Liu et al., 2021; Zu et al., 2023), meaning HNO_3 relies on HIO_2 to form thermodynamically stable clusters."

Comment S4. In Section 2.3, the kinetic criterion $\beta c/\sum\gamma > 1$ defines stable clusters, but the monomer concentration c is not clearly specified. Given that HNO_3, HIO_3, and HIO_2 concentrations differ by orders of magnitude, an ambiguous c undermines the criterion. Please clarify whether c refers to the dominant precursor concentration or an equivalent concentration.

Response: We apologize for the ambiguity. In the criterion $\beta c/\sum\gamma > 1$, c denotes the gas-phase concentration of the specific monomer involved in the collision being evaluated; that is, each collision pathway uses the

ambient concentration of the colliding species (HNO_3, HIO_3, or HIO_2) rather than a single value. We have revised Section 2.4, line 136-137 of the revised manuscript, to state this explicitly, as below:

"Here, *c* denotes the gas-phase concentration of the actual colliding species (HNO_3, HIO_3, or HIO_2)."

To illustrate this with a concrete example: in Figure 2(b), the reported $c_{boundary}$ is the minimum HNO_3 concentration at which an HNO_3-containing cluster reaches kinetic stability against evaporation. Once [HNO_3] exceeds the $c_{boundary}$ of, for example, the $(HNO_3)_1(HIO_3)_2(HIO_2)_3$ cluster, this cluster can successfully collide with another HNO_3 monomer to grow into $(HNO_3)_2(HIO_3)_2(HIO_2)_3$, exceeding the simulation box. The corresponding $c_{boundary}$ criteria for [HIO_3] and [HIO_2] collisions are presented in Figure S4, ensuring that each colliding species is evaluated against its own ambient concentration.

Comment S5. A previous study has shown that HIO_3–HIO_2–DMA nucleation (*Atmos. Chem. Phys.*, 24, 5823–5835, 2024) plays an important role in the marine boundary layer. This nucleation mechanism is also relevant to the Zhejiang and Mace Head cases, where DMA is abundant. To better illustrate the practical atmospheric significance of the proposed HIO_3–HIO_2–HNO_3 nucleation pathway, a direct comparison with the well-documented HIO_3–HIO_2–DMA nucleation mechanism should be included.

Response: We thank the referee for this valuable suggestion. To keep the main text focused, we have provided this direct comparison as a new figure in the revised SI (Figure S7).

At Zhejiang (288 K, high-DMA conditions, [DMA] = 1×10^8 molecules cm^{-3}) and Mace Head (288 K, [DMA] = 5×10^6 molecules cm^{-3}), we compared the cluster formation rates of the HIO_3–HIO_2–HNO_3 and HIO_3–HIO_2–DMA mechanisms across the relevant range of iodine oxoacid concentrations. The results show that at low HIO_3 concentrations (~5×10^6 molecules cm^{-3}), HIO_3–HIO_2–DMA remains the more effective pathway, whereas as HIO_3 concentrations increase, the HNO_3–HIO_3–HIO_2 mechanism takes the lead. This comparison is presented in Figure S7 of the revised SI, with the caption below:

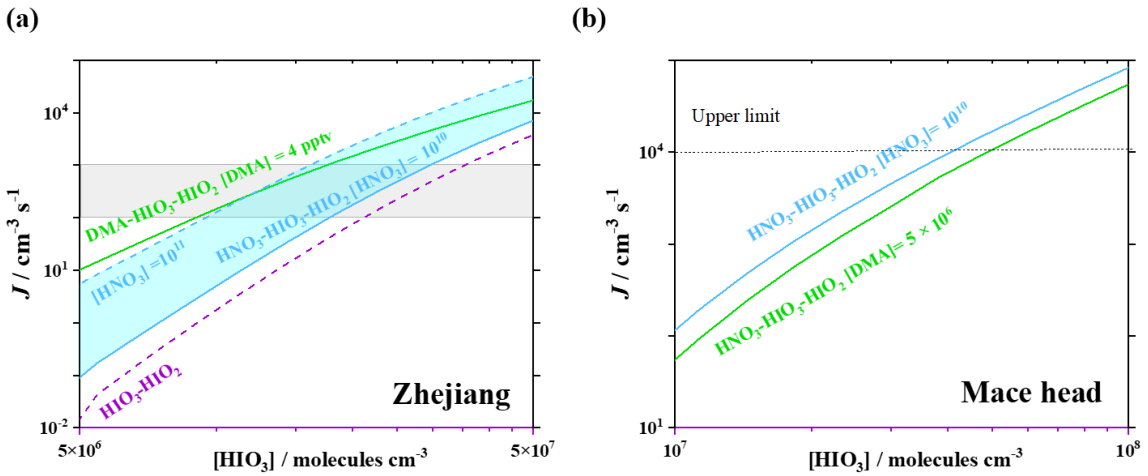

Figure S7. Cluster formation rates (*J*, cm^{-3} s^{-1}) for the HIO_3–HIO_2 (purple dashed line), HNO_3–HIO_3–HIO_2 (blue) and HIO_3–HIO_2–DMA (green) systems under the corresponding atmospheric conditions of (a) Zhejiang, where gray shaded areas represent locally observed cluster formation rates (Yu et al., 2019); and (b) Mace Head, where the dashed line marks the upper limit of cluster formation rates reported in field

observations (Sipilä et al., 2016).

Comment S6. The conclusion links Arctic NPF enhancement to anthropogenic nitrogen emissions but does not explain how elevated HNO_3 interacts with iodine species under the cold, low-condensation-sink Arctic conditions. This weakens the causal link. Additional environmental and mechanistic context should be provided.

Response: We thank the referee for this valuable comment. We have expanded the conclusion to provide the missing mechanistic and environmental context. Specifically, we now explain how cold temperatures and a low condensation sink act together to amplify the role of HNO_3 in stabilizing iodine clusters. We have added the following explanation to lines 358–361 of the revised manuscript:

"Under cold Arctic conditions with a low condensation sink, cluster evaporation and scavenging losses are strongly suppressed, allowing HNO_3 to participate more effectively in cluster stabilization. Consequently, modest increases in HNO_3 concentrations from rising shipping NO_x emissions translate directly into substantial enhancements in the cluster formation rate."

Technical issues

We thank the reviewer for the careful reading. All listed technical corrections have been made, and similar errors found elsewhere in the manuscript have been corrected accordingly. Item-by-item responses follow.

Line 19. "200-fold enhancement in nucleation" should be "in the cluster formation rate".

Response: "200-fold enhancement in nucleation" has been corrected as "…driving a 200-fold enhancement in the cluster formation rate."

Line 48. "proton transfer-driven electrostatic interactions" should be "proton-transfer driven electrostatic interactions".

Response: "proton transfer-driven electrostatic interactions" has been corrected as "proton-transfer driven electrostatic interactions".

Line 165. Inconsistent unit notation: "molecules/cm^3" here vs. "molecules cm^{-3}" elsewhere.

Response: "molecules/cm^3" has been corrected as "molecules cm^{-3}", and we have checked the whole manuscript and SI.

Line 196. "…minimizes scavenging of nascent clusters This enhancement…" is missing a period.

Response: "…minimizes scavenging of nascent clusters This enhancement…" has been corrected as "…minimizes scavenging of nascent clusters. This enhancement…".

Line 209. The caption refers to "Heatmaps of (a) cluster formation rates" but only one panel is labelled.

Response: Since the figure presents a single class of heatmap (a grid over *T* and CS), we have removed the "(a)".

Line 329. "solidifying HIO_3's role as a UT nucleation core component" should be "solidifying HNO_3's role…".

Response: "solidifying HIO_3's role as a UT nucleation core component" has been corrected as "…solidifying HNO_3's role as a UT nucleation core component."

Line 540. The reference Jones et al. (*Atmos. Chem. Phys.*, 2014, 14, 11843–11851) is listed but not cited in the main text.

Response: Thanks for pointing this out. We have cited Jones et al. (2014) where polar/Arctic HNO_3 is discussed.

Lines 590–595. "Li, J., Ning, A., Liu, L., and Zhang, X. … 2024a" and "… 2024b" are identical references (same title, journal, DOI).

Response: These are indeed duplicates. We have merged them into a single entry.

We have tried our best to address all of the reviewer's comments, and we believe the manuscript has been substantially improved. All major changes are highlighted in the revised manuscript. We thank the reviewer again for the valuable and constructive feedback.

Sincerely,

Xiuhui Zhang
Key Laboratory of Cluster Science, Ministry of Education of China
School of Chemistry and Chemical Engineering, Beijing Institute of Technology
Beijing 100081, P. R. China
Email: zhangxiuhui@bit.edu.cn

References

Liu, L., Li, H., Zhang, H., Zhong, J., Bai, Y., Ge, M., Li, Z., Chen, Y., and Zhang, X.: The role of nitric acid in atmospheric new particle formation†, Phys. Chem. Chem. Phys., https://doi.org/10.1039/c8cp02719f, 2018.

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.

Ma, F., Xie, H.-B., Zhang, R., Su, L., Jiang, Q., Tang, W., Chen, J., Engsvang, M., Elm, J., and He, X.-C.: Enhancement of Atmospheric Nucleation Precursors on Iodic Acid-Induced Nucleation: Predictive Model and Mechanism, Environ. Sci. Technol., 57, 6944–6954, https://doi.org/10.1021/acs.est.3c01034, 2023.

Sipilä, M., Sarnela, N., Jokinen, T., Henschel, H., Junninen, H., Kontkanen, J., Richters, S., Kangasluoma, J., Franchin, A., Peräkylä, O., Rissanen, M. P., Ehn, M., Vehkamäki, H., Kurten, T., Berndt, T., Petäjä, T., Worsnop, D., Ceburnis, D., Kerminen, V.-M., Kulmala, M., and O'Dowd, C.: Molecular-scale evidence of aerosol particle formation via sequential addition of HIO_3, Nature, 537, 532–534, https://doi.org/10.1038/nature19314, 2016.

Yu, H., Ren, L., Huang, X., Xie, M., He, J., and Xiao, H.: Iodine speciation and size distribution in ambient aerosols at a coastal new particle formation hotspot in China, Atmos. Chem. Phys., 19, 4025–4039, https://doi.org/10.5194/acp-19-4025-2019, 2019.

Zu, H., Zhang, S., Liu, L., and Zhang, X.: The vital role of sulfuric acid in iodine oxoacids nucleation: impacts of urban pollutants on marine atmosphere, Environ. Res. Lett., https://doi.org/10.1088/1748-9326/ad193f, 2023.

Zu, H., Chu, B., Lu, Y., Liu, L., and Zhang, X.: Rapid iodine oxoacid nucleation enhanced by dimethylamine in broad marine regions, Atmos. Chem. Phys., 24, 5823–5835, https://doi.org/10.5194/acp-24-5823-2024, 2024.