Responses to Referee #2's comments

We are grateful to the reviewers for their professional and helpful comments on our manuscript "**Mechanistic Insights into I_2O_5 Heterogeneous Hydrolysis and Its Role in Iodine Aerosol Growth in Pristine and Polluted Atmospheres**" (MS No.: egusphere-2025-3770). Accordingly, we have carefully revised the manuscript. The point-to-point responses to the Referee #2's comments are summarized below:

The manuscript by Deng et al. adopted first-principles molecular dynamics to examine the heterogeneous hydrolysis of I_2O_5 and its role in aerosol growth. The study identifies interfacial mechanisms driven by iodic species in pristine conditions and by acid/base pollutants in polluted environments. These findings emphasize the importance of reactive atmospheric components in I_2O_5 hydrolysis and provide a mechanistic explanation for its sink and the observed I_2O_5-to-HIO_3 conversion. This topic is timely and relevant to Atmos. Chem. Phys., given its focus on aerosol formation process. The manuscript is overall well presented, with sound methodology and adequate supporting evidence. Nevertheless, I suggest that the authors consider my comments and perform the minor revisions before the manuscript can be recommended for publication.

Response: We appreciate the insightful and constructive suggestions. According to these comments, we have responded and revised the manuscript as follows.

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1. In conducting the metadynamics simulations, the authors appear to have employed SMS-MetaD rather than the more widely used MetaD approach. I am curious about the rationale behind this choice. The authors should explain the advantages of this method in the Methods section. Furthermore, to substantiate its feasibility, some successful case studies along with appropriate references should be provided, which would make the presented results more convincing and reliable.

Response: This is a helpful point in demonstrating the reliability of the adopted method; thank you for raising it. The SMS-MetaD was chosen for this study for two reasons: *i*) By partitioning the reaction potential energy surface (PES), the SMS-MetaD method allows a more efficient exploration of the free energy landscape of the reaction process, avoiding excessive time being wasted in overly deep wells around the stable minima of reactants and products; *ii*) The SMS-MetaD is well-suited for effectively modeling chemical systems with complex PES, such as chemical reactions at the air–water interface. Prof. Zhu's group provides more detailed explanations of SMS-MetaD (Fang et al., 2022). This method has already been successfully employed for several theoretical studies, especially investigations into the chemical reaction at the air-water interface (Fang et al., 2024a, b; Tang et al., 2024; Wan et al., 2023). Accordingly, we have added the explanation for selecting SMS-MetaD approach in the Methods section in revised manuscript as follows (Page 4, line 117):

"The SMS-MetaD method is well-suited for effectively modeling chemical systems with complex potential energy surface, especially at the air-water interface (Fang et al., 2022), which has already been successfully employed in the studies of heterogeneous reactions (Fang et al., 2024a, b; Tang et al., 2024; Wan et al., 2023)."

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2. Beyond iodic acid, other iodine oxoacids such as HIO_2 and HOI also exist, along with various iodine oxides. In addition, there are many more pollutants, for instance, nitric acid and fluorinated carboxylic acids. Could these species also have an impact? Of course, I am not suggesting that additional calculations be included in this work, but at the very least, the manuscript should address the current limitations of the study and outline potential directions for future improvement.

Response: We thank the reviewer for this insightful comment highlighting the limitations of our manuscript. We agree with the reviewer that other species may also influence this reaction to some extent and should be investigated in future work. The scope of this study does not exclude these possibilities; rather, we focus here on the effects of representative chemical species. A more detailed discussion has been provided in our response to Reviewer 1, and corresponding clarifications have also been added to the revised manuscript (Page 12, Line 304), as follows: "The real atmosphere is chemically complex, including iodine species (e.g. HOI, HIO_2, HIO_3, I_2O_3, I_2O_4, and I_2O_5) and atmospheric pollutants (e.g. H_2SO_4, HNO_3, organic acids, and ammonia), which are likely to influence the heterogeneous hydrolysis of I_2O_5. In future work, we intend to confirm the impacts from other atmospheric components."

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3. In Fig. 6, the process of a gas-phase DMA approaching the interfacial I_2O_5 is presented. However, conversely, would a gas-phase I_2O_5 approaching the interfacial DMA also lead to a reaction? Why was this scenario not considered?

Response: We appreciate the reviewer's keen observation and thoughtful comment, which highlights an important aspect of the reaction dynamics at the interface. Indeed, the mutual approach of the two species could give rise to the two scenarios mentioned by the reviewer. However, since aerosols are generally acidic, the base DMA is unlikely to persist for long and would be protonated to $DMAH^+$, occupying its reactive site and preventing participation in subsequent I_2O_5 hydrolysis. Therefore, in this study, we only considered the approach of gas-phase DMA toward interfacial I_2O_5.

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4. In the supporting information, some figure annotations or captions should be more detailed. For example, in Fig. S14, the arrows appear to indicate the ESP maxima or minima of the product molecule. Although I can make an educated guess, the authors should provide clearer labels or explanatory notes.

Response: Thank reviewer for the perfection of our figures. The explanation of the figure appears only in the caption; there remains a gap between the figure's details and what we intend to convey. We have supplemented the explanatory notes for the arrows, ESP maxima and minima as following,

"The yellow sites indicate" have been changed into "The yellow sites (pointed by yellow arrows) indicate" and "The cyan sites indicate" have been changed into "The cyan sites (pointed by cyan arrows) indicate".

In addition, we have confirmed that the remaining figures are free of similar issues.

(a) $HIO_3 + IO_3^- + MAH^+$ **(b)** $HIO_3 + IO_3^- + DMAH^+$ **(c)** $HIO_3 + IO_3^- + TMAH^+$

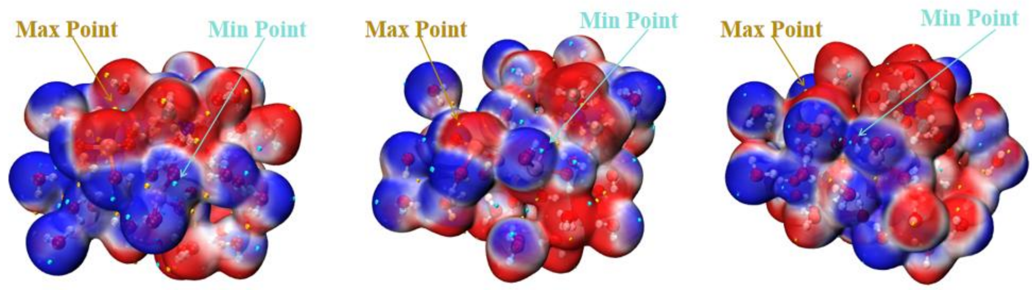

Figure S17. The electrostatic potential (ESP)-mapped molecular vdW surfaces of the interfacial reaction products mediated by (a) MA, (b) DMA, and (c) TMA. The red regions are electron-deficient, and the blue regions are electron-rich. The yellow sites (pointed by yellow arrows) indicate the points of local ESP maximum; the cyan sites (pointed by cyan arrows) indicate the points of local ESP minimum.

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5. For the ELF results shown in Fig. S15, the meaning of the different colored regions should be clarified, as many readers may not be specialists in theoretical studies. For the other figures and captions, I will not list further examples. However, I suggest that the authors carefully re-examine whether the information provided is sufficiently detailed, and consider it from the perspective of a non-specialist reader.

Response: We appreciate the reviewer's comment, which enables us to refine our work from the reader's perspective. A corresponding color bar is shown on the right side of each figure, indicating the color scale from high to low (red-green-blue) for the ELF values. We have emphasized the color bar mapping to electron-density magnitude and added explanations of the colored regions in the figure annotation in the Supporting Information as follows:

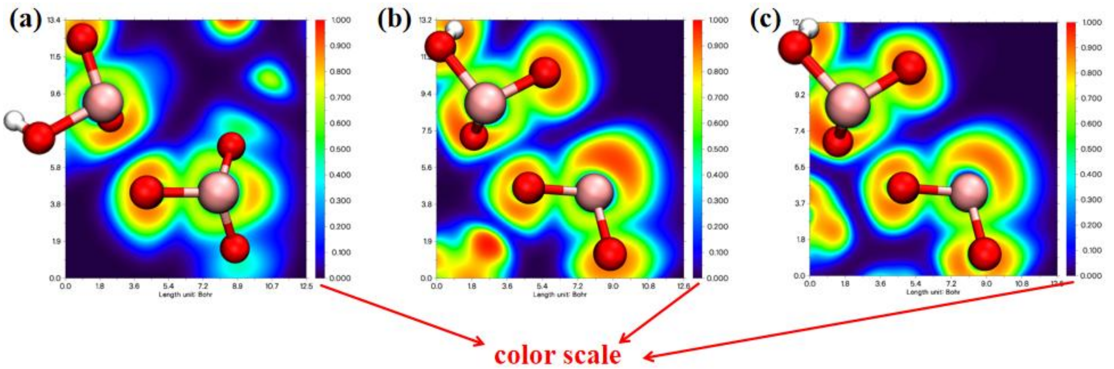

Figure S18. Color-mapped ELF for the iodine products (IO_3^- and HIO_3) of I_2O_5 hydrolysis mediated by (a) MA, (b) DMA, and (c) TMA. The ELF values (1 to 0) are mapped on a red-green-blue color scale indicated on the right of each subplot.

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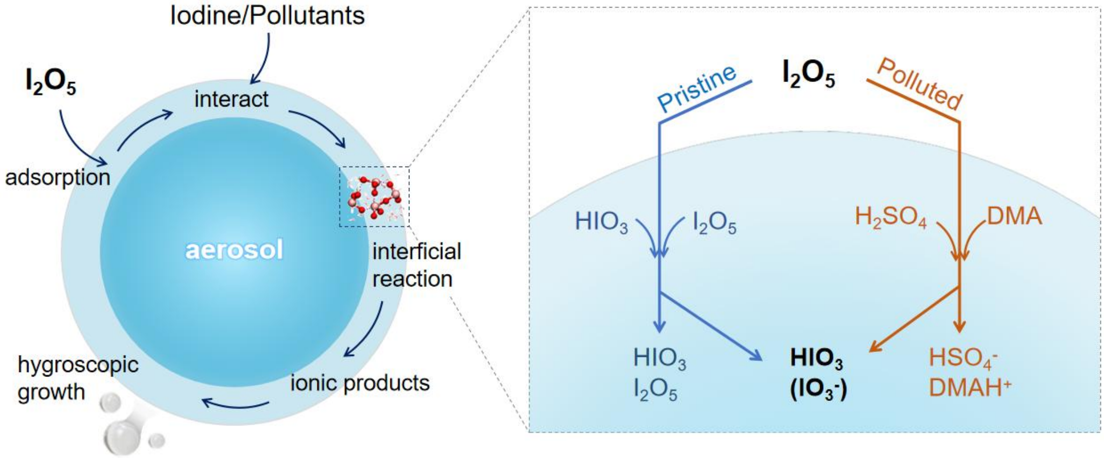
6. It may be helpful to revise Scheme 1 to more clearly reflect the key ideas presented in the manuscript. For example, the ionic products that contribute to enhanced hygroscopicity are mentioned in the text but are not explicitly shown in the current scheme. In addition, specifying the molecular pairs responsible for hydrogen and halogen bonding would improve clarity; iodic acid, for instance, may engage in both hydrogen bonding and halogen bonding with water. The central label of "low volatility" could also be made more explicit by indicating the specific species it refers to.

Response: Thanks for the reviewer's valuable comments. The Scheme 1 was intended to overview and summarize the Conclusions section by highlighting several representative species to convey the main idea. Consequently, mechanistic details were largely absent. We have reconsidered the role of the scheme in the manuscript and agree with the reviewer's suggestion; accordingly, we have redrawn Scheme 1 to present the complete mechanism and to include the information missing from the earlier figure.



Scheme 1. Illustration of aerosol growth driven by I_2O_5 hydrolysis at the air-water interface, highlighting the potential reaction pathways and resulting products in pristine and polluted environments.

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7. The mechanism mediated by DMA in Fig. 6 would be better presented in a manner consistent with the others, and I recommend that the corresponding reaction equation be included for completeness.

Response: Thank the reviewer for careful attention to the figure details. Indeed, amine-mediated mechanisms (MA, DMA, and TMA) were examined via unbiased BOMD simulations, whereas other species were studied using the SMS-MetaD approach. As these methods provide different types of insights—BOMD and SMS-MetaD simulations focus on the time evolution and free energy changes of key structures in the reaction process, respectively, which leads to slightly different presentations. To enhance consistency in data presentation, we have added the corresponding reaction equation in Figures 6 and S5-6.

Suggested corrections

Line 40: Should “a typical higher $I_2O_{2\text{-}5}$” be “one of the highest iodine oxides”?

Line 48: “More recently, the experimental evidence” --> “A most recent experimental evidence”

Line 51: “found the direct” --> “found that the direct”

Line 63: “HIO_3 abundant” --> “HIO_3 is abundant”

Line 93: Check the word “consisting”

Page 11: Make sure Scheme 1 is clear enough.

Response: According to the reviewer’s suggestions, we have completed all corresponding revisions.

Reference:

Fang, Y.-G., Li, X., Gao, Y., Cui, Y.-H., Francisco, J. S., Zhu, C., and Fang, W.-H.: Efficient exploration of complex free energy landscapes by stepwise multi-subphase space metadynamics, J. Chem. Phys., 157, 214111, https://doi.org/10.1063/5.0098269, 2022.

Fang, Y.-G., Tang, B., Yuan, C., Wan, Z., Zhao, L., Zhu, S., Francisco, J. S., Zhu, C., and Fang, W.-H.: Mechanistic insight into the competition between interfacial and bulk reactions in microdroplets through N_2O_5 ammonolysis and hydrolysis, Nat. Commun., 15, 2347, https://doi.org/10.1038/s41467-024-46674-1, 2024a.

Fang, Y.-G., Wei, L., Francisco, J. S., Zhu, C., and Fang, W.-H.: Mechanistic Insights into Chloric Acid Production by Hydrolysis of Chlorine Trioxide at an Air–Water Interface, J. Am. Chem. Soc., 146, 21052–21060, https://doi.org/10.1021/jacs.4c06269, 2024b.

Tang, B., Bai, Q., Fang, Y.-G., Francisco, J. S., Zhu, C., and Fang, W.-H.: Mechanistic Insights into N_2O_5-Halide Ions Chemistry at the Air–Water Interface, J. Am. Chem. Soc., 146, 21742–21751, https://doi.org/10.1021/jacs.4c05850, 2024.

Wan, Z., Fang, Y., Liu, Z., Francisco, J. S., and Zhu, C.: Mechanistic Insights into the Reactive Uptake of Chlorine Nitrate at the Air–Water Interface, J. Am. Chem. Soc., 145, 944–952, https://doi.org/10.1021/jacs.2c09837, 2023.