Responses to Referee #3'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 #3's comments are summarized below:

This manuscript examines how gas–liquid interfacial reactions of higher iodine oxide (I_2O_5) influence the formation of marine iodine aerosols using molecular dynamics simulations. The authors elucidate the I_2O_5 heterogeneous hydrolysis mechanism, emphasizing the catalytic effects of atmospheric chemicals. These mechanisms are likely to provide evidence for the extensive presence of iodate in aqueous aerosols, offering guidance for refining atmospheric models of aerosol burden and radiative forcing. As a well-designed theoretical study with atmospheric implications, I recommend this work for publication, subject to my comments being addressed.

Response: Thanks for the review's valuable comments and suggestions on our manuscript. The comments have greatly helped us improve the quality of the paper. We have responded to each point carefully and revised the manuscript accordingly.

The authors suggest that iodine-mediated reactions are more likely to play an important role in pristine environments, whereas pollutant-mediated reactions dominate in polluted marine environments. These heterogeneous mechanisms may have significant atmospheric impacts and need to be evaluated by embedding them into atmospheric models. What challenges do the authors foresee in implementing this cross-scale simulation?

Response: The reviewer's valuable comment has prompted us to consider how to effectively connect microscopic mechanisms with macroscopic environmental impacts. For heterogeneous reaction kinetics, obtaining reaction rates under different environmental conditions remains highly challenging, because the concentrations of I_2O_5 in the air or aerosols are largely uncertain. Moreover, the coupled effects of temperature, humidity, aerosol size, pH, aging, ions, and other components remain unknown. For atmospheric modeling, it is challenging to obtain a reliable and comprehensive emission inventory and, based on this, to construct a simulation of the physicochemical transformations from source species to the reactive components of interest. This is followed by the additional difficulty of calibrating the simulated concentrations against field measurements. In summary, the lack of data on heterogeneous reaction kinetics and atmospheric modeling renders cross-scale studies linking interfacial reaction mechanisms to environmental impacts highly challenging.

Line 11: I am not quite sure whether the expression 'higher iodine oxides' is widely used and easily understood, and the authors should check this.

Response: The reviewer's comment is quite thorough. In fact, this expression, referring to $I_2O_{3\text{-}5}$, appears in many iodine-related studies (Huang et al., 2022; Kaltsoyannis and Plane, 2008; Lewis et al., 2020; Ning et al., 2024; Pound et al., 2024). Many researchers favor higher iodine oxides, while others prefer 'higher-order' (Gómez Martín et al., 2022; Lewis et al., 2020). Considering that 'higher-order' better represents the higher oxidation state of I, we ultimately chose 'higher-order iodine oxides'. We have changed 'higher iodine oxides' into 'higher-order iodine oxides' in the revised manuscript (Page 1, line 11; page 11, line 277).

Line 20: I suggest that the authors moderate some of their conclusions, as this study does not quantify the rates of the relevant chemical processes. Expressions such as "highly effective" should therefore be toned down. More generally, conclusions should avoid absolute or overly strong wording unless supported by quantitative data.

Response: The reviewer's suggestion is crucial for improving the rigor of the summary and abstract. As the theoretical findings in this manuscript focus on reaction mechanisms rather than quantitative rate information, terms such as "highly" are inappropriate. we have softened the overstrong statements in the manuscript, with the specific changes detailed as follows: we have changed "highly effective" into "relatively effective" (Page 1, line 20) and "a critical step" into "an unheeded step" (Page 1, line 22).

Line 31: The reference to Barnes et al. lacks bibliographic details—specifically the year of publication—and similar issues should be checked throughout the reference list. In addition, many studies have examined DMS-derived sulfur and its relation to aerosols; citing only two papers is insufficient. Please include more primary studies and relevant reviews to support the claim.

Response: We appreciate the reviewer's careful review. We have supplemented the bibliographic details of the reference to Barnes et al., and have confirmed the reference list. As suggested by the reviewer, historically, extensive studies have investigated DMS-driven sulfur, particularly the role of methanesulfonic acid (MSA) in aerosol nucleation; thus, the current citations are insufficient to support this point. To address this, we have supplemented more references to enrich the studies for DMS-derived sulfur and its relation to aerosols (Li et al., 2024; Ning and Zhang, 2022; Shen et al., 2020; Zhang et al., 2022, 2024).

Line 38: In the section addressing the uncertain fate of I_xO_y, the authors should consider citing the experimental study by Finkenzeller et al. (*Nat. Chem*., 2023, 15, 129). They argued that stable I_2O_3 should be observable, but it was not, which also highlights the uncertainty in the fate of I_xO_y and supports the view of an unclear I_xO_y sink.

Response: We admire the reviewer's thorough knowledge of the field. The study by Finkenzeller et al. (2023) provides a complete evolution pathway for iodine oxides. Accordingly, we have supplemented this reference in the introduction as suggested.

Line 44: "…particles through the reaction (R1: $2HIO_3 \rightarrow I_2O_5 + H_2O$)" should be revised to the more accurate wording "…particles through the dehydration reaction (R1: $2HIO_3 \rightarrow I_2O_5 + H_2O$)."

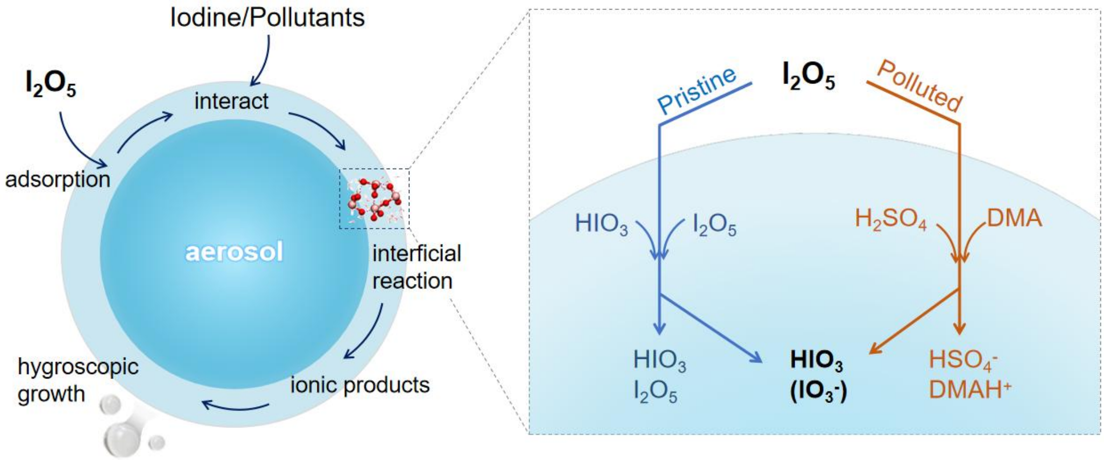
Response: According to the reviewer's suggestion, the sentence "…particles through the reaction (R1: $2HIO_3 \rightarrow I_2O_5 + H_2O$)" has been corrected to "…particles through the dehydration reaction (R1: $2HIO_3 \rightarrow I_2O_5 + H_2O$)" in the revised manuscript (Page 2, line 44).

Line 64: Iodate, rather than HIO_3, is likely abundant in the aerosol; therefore, the statement should be revised to 'HIO_3 (detected as IO_3^-)'."

Response: Line 64 "HIO_3" is revised to "HIO_3 (detected as IO_3^-)".

Line 262: In Scheme 1, according to the caption, the figure is supposed to illustrate the mechanism. However, it actually lacks many details and resembles more of a TOC-style figure. I suggest that the authors replace it with a figure that presents a more detailed depiction of the heterogeneous mechanism.

Response: We appreciate the reviewer's constructive comments. We have provided a detailed explanation of this issue in our response to Reviewer 2 and included the revised figure. The latest version of the figure has been updated in the revised manuscript.



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.

Reference:

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