Responses to Referee #2's comments

We are grateful to the reviewers for their valuable and helpful comments on our manuscript "**Molecular-level study on the role of methanesulfonic acid in iodine oxoacids nucleation**" (MS No.: egusphere-2023-2084). We have revised the manuscript carefully according to reviewers' comments. The point-to-point responses to the Referee #2's comments are summarized below:

Referee comments:

Jing Li et al. reports a theoretical study on the iodic acid (HIO_3) – iodous acid (HIO_2) based nucleating process enhanced by methanesulfonic acid (MSA) by quantum chemical calculation and cluster dynamic simulation. They found that the MSA can enhance the HIO_3-HIO_2-based nucleation, especially in polar oceanic regions. This manuscript has systematically studied the HIO_3-HIO_2-MSA ternary nucleation system, covering cluster stability, thermodynamic/kinetic analysis, and molecular-level mechanism. These interesting findings show the significance of sulfur and iodine synergistic nucleation, providing deeper insights into marine secondary particle formation, given chemical complexity of real atmosphere. This well-written manuscript has important atmospheric implications, such as in the studies of marine aerosol formation and the sulfur/iodine cycling. Hence, I recommend the publication of this study in *Atmospheric Chemistry and Physics* after considering my comments listed below.

Response: We appreciate the reviewer for dedicating time to assess our manuscript and providing valuable comments and positive feedback.

General comments:

Comment 1: Although the authors have provided sufficient computational details, it would be better to add the grid settings for DFT calculations and the optimization convergence in method section of the main text.

Response: Based on the reviewer's suggestion, we have added the adopted grid settings (FineGrid) of DFT calculations in Section 2.1 in the main text. Accordingly, the corresponding sentence in Lines 64-65 of page 3 has been restructured as follows: "All density functional

theory (DFT) calculations were carried out using the Gaussian 09 package (Frisch et al., 2009), where FineGrid and tight convergence were employed."

Comment 2: In general, the nucleation process involves competition between cluster collision and its evaporation processes. In the ACDC simulations presented in this manuscript, could the authors specify which types of collision and evaporation processes considered? If possible, these details would be better to added in the ACDC methodology section.

Response: Thanks. The reviewer's professional comment is beneficial in enhancing the readers' understanding of more simulation details. Accordingly, the detailed settings about the collision and evaporation processes in ACDC simulations have been added in the revised manuscript (Lines 100-102, page 4) as follows: "In the performed ACDC simulations, all possible collision and evaporation processes, including monomer-monomer, monomer-cluster, cluster-cluster collisions, as well as the decomposition of parent clusters into monomers and clusters, or into two smaller clusters, were taken into account."

Comment 3: In this work, the authors systematically investigated the HIO_3-HIO_2-MSA ternary nucleation process, where HIO_2 appears to play a crucial role in all clustering pathways. How should this be interpreted?

Response: Thanks. It is indeed an important query. As expertly suggested by the reviewer, HIO_2 appears to play a crucial role in all clustering pathways of HIO_3-HIO_2-MSA nucleation. This is mainly because HIO_2, when interacting with acidic HIO_3 or MSA, behaves like base molecules[1-3]. Specifically, it can serve as a proton acceptor, being protonated by HIO_3 or MSA, leading to the formation of stable acid-base ion pairs. Once HIO_2 is missing, the acid-base reaction between HIO_3 and MSA cannot occur. Thus, HIO_2-induced acid-base reactions with MSA and HIO_3 yield ion pairs whose electrostatic interactions enhance the stability of the formed cluster.

Comment 4: For the formed HIO_3-HIO_2-MSA clusters, especially large-sized clusters, are there any unoccupied binding sites that can enable further molecular binding and cluster growth?

The authors would better provide theoretical evidence by quantum chemical calculations, such as using wave function analysis, or others. If done, this will provide the readers with an intuitive understanding of the growth potential of the cluster.

Response: Following the professional advice of the reviewer, we have performed the electrostatic potential (ESP) analysis for the vacant sites of the stable large-size structure cluster in the revised manuscript. The results of ESP analysis are presented in Fig. S2 below. The red localizations with maximum ESP at the end of the iodine and hydrogen atoms within HIO_3 and HIO_2 along the O–I and O–H direction, which can act as XB or HB donor sites. While the blue regions with minimum ESP of the terminal oxygen atoms have strong nucleophilicity as the HB or XB acceptors.

Herein, we have added the ESP results and analysis to the revised manuscript, and for the convenience of the review, we have copied Figure S2 and the corresponding analysis (Lines 129-132, page 5) as following: "Additionally, taking the $(HIO_3)_1(HIO_2)_3(MSA)_1$ cluster for example, there are still some potential remaining unoccupied binding sites as shown in Fig. S2. It suggests that the studied large-size clusters still have unoccupied HB and XB sites that can potentially facilitate the condensation of precursors in the atmosphere, enhancing further growth of marine aerosols."

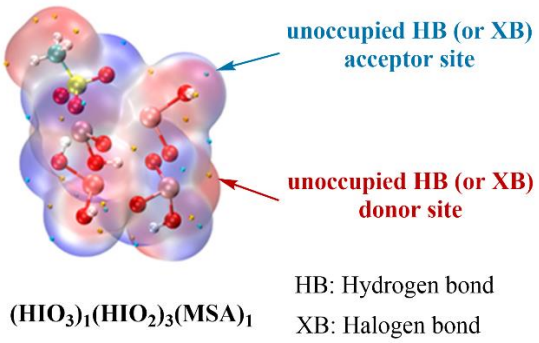

Figure S2. The ESP-mapped molecular vdW surfaces of the $(HIO_3)_1(HIO_2)_3(MSA)_1$ cluster. The red region is the electron-deficient region, and the blue region is the electron-rich region.

Specific comments:

Comment 5.

Page 3-4, Line 76 and 91: In the equation (2) and (3), the operator $\sum_{i=1}^{n} N_i$, $\sum_{j<i} \beta$ should be change to:

$$\sum_{i=1}^{n} N_i \quad , \qquad \sum_{j<i} \beta$$

Response: The operators in the equation (2) and (3) have been corrected accordingly as suggested by the reviewer.

Comment 6.

Page 4, Line 96: Please provide more details of the calculations of the volume of cluster *i* (V_i).

Response: According to the reviewer's suggestion, the details of the calculations of the volume of cluster *i* (V_i) have been added in Lines 95-96 (page 4) of the revised manuscript as follows: "And $V_i = 3/4 \times \pi \times (d_i/2)^3$, where the diameter d_i of cluster *i* is derived from the cluster volume V_i calculated by Multiwfn 3.7."

Comment 7.

Page 5, Figure 1: The authors seem to have forgotten to plot the hydrogen and halogen bonds with dotted lines in Fig. 1(d), please correct it.

Response: Thanks for the reviewer's carefulness. We have added the dotted lines indicating hydrogen and halogen bonds in Fig. 1(d) in the revised manuscript.

Comment 8.

Page 6, Line 141: In the sentence, 'Here, the condensation sink (CS) coefficient is set to be 2.0 × 10^{-3}', there is a missing unit after the CS value.

Response: Thanks for the reviewer's careful reading. We have added the missing unit 's^{-1}' after the CS value in the revised manuscript (Line 152, page 6).

Comment 9.

Page 7, Figure 3: To enhance data clarity for readers, consider enlarging the font size in Fig. 3, which appears relatively small.

Response: Based on the reviewer's suggestion, we have adjusted the small font in Fig. 3 in the revised manuscript to enhance content clarity.

Comment 10.

Page 12, Line 252: The word ‘play’ should be ‘plays’.

Response: Accordingly, the word ‘play’ has been changed to ‘plays’ in Line 280 of the revised manuscript.

Reference:

[1] L. Liu, S. Li, H. Zu, X. Zhang, Unexpectedly significant stabilizing mechanism of iodous acid on iodic acid nucleation under different atmospheric conditions, Sci. Total Environ. 859 (2023) 159832.
[2] S. Zhang, S. Li, A. Ning, L. Liu, X. Zhang, Iodous acid - a more efficient nucleation precursor than iodic acid, Phys. Chem. Chem. Phys. 24 (2022) 13651–13660.
[3] R. Zhang, H.B. Xie, F. Ma, J. Chen, S. Iyer, M. Simon, M. Heinritzi, J. Shen, Y.J. Tham, T. Kurtén, D.R. Worsnop, J. Kirkby, J. Curtius, M. Sipilä, M. Kulmala, X.C. He, Critical Role of Iodous Acid in Neutral Iodine Oxoacid Nucleation, Environ. Sci. Technol. 56 (2022) 14166–14177.