Dear Editor,

Thanks sincerely for your handling our manuscript "**Molecular-level study on the role of methanesulfonic acid in iodine oxoacids nucleation**" (MS No.: egusphere-2023-2084). According to reviewer's professional and helpful comments, we have further revised the manuscript carefully. Additionally, we have included Dr. Biwu Chu in the author list, owing to his significant contribution in the uncertainty analysis section. The point-to-point responses to the Referee #4's comments are listed as below:

Referee comments:

The authors have addressed most of my concerns, but minor revision is still required before the manuscript can be published.

Response: We appreciate the valuable suggestions and positive feedback provided by the reviewer, which is helpful for further refining our manuscript and even holds significant guidance for our future research endeavors.

Comments:

1. The authors have made a mistake in connecting J1.2 and J1.5. When the cited formula is used, CS should have the unit of m^-2 instead of s^-1 (i.e., the value 0.002 s-1 should be converted to an area). Please refer to this paper: Analytical formulae connecting the "real" and the "apparent" nucleation rate and the nuclei number concentration for atmospheric nucleation events.

Response: This is a key and helpful point – thanks for bringing it up. This expert advice is beneficial for improving the accuracy of comparing the ACDC simulation with the field observations. According to the study of Kerminena and Kulmalab (2002), we have converted the CS value to CS' by the following equation (Kerminena and Kulmalab 2002):

$$CS = 4\pi D_i CS'$$

where D_i is the diffusion coefficient of the condensing vapor, usually assumed to be sulfuric

acid (0.08 cm^{-2} s^{-1}) (Kulmala et al. 2012). When the CS value is 0.002 s^{-1}, the CS' value is 18 m^{-2}.

Therefore, the relationship between the formation rates of simulated clusters ($J_{1.2}$) and observed clusters ($J_{1.5}$) can be written as (Kulmala et al. 2012):

$$J_{1.2} = J_{1.5} \exp\left\{0.23 \times \left(\frac{1}{1.2} - \frac{1}{1.5}\right) \frac{CS'}{GR}\right\},$$

where GR was measured to be 3.2 – 4.4 $nm \cdot h^{-1}$ in the 1.1 – 2.0 nm size range during three observed events, and CS' was 18 m^{-2}. Accordingly, the calculated $J_{1.2}$ is 1.1 – 1.2 times of $J_{1.5}$. The observed cluster formation rates for 1.5 nm clusters can be converted to the simulated $J_{1.2}$.

Thanks again for the reviewer's professional review. We have revised all the relevant figures (Figs. 6 and S14) and text (Lines 254, 256, 260 and 265) in the revised manuscript and supporting file.

2. In performing the uncertainty analysis with respect to deltaG, it is my understanding that the authors have added 1 kcal/mol to (or subtracted 1 kcal/mol from) the calculated deltaG of all clusters. I'm not sure if the values of all cluster energies should move in the same direction. If this is indeed the case, can the authors explain why?

An alternate method to calculate the overall uncertainties is to do a Monte Carlo uncertainty analysis by doing many calculations. In each calculation, the deltaG of each cluster is randomly assigned a value within an uncertainty range. With J values from many of such calculations, an overall uncertainty can be derived.

Response: Thanks for this insightful suggestion from the reviewer, which is important for refining the uncertainty analysis. Indeed, as the reviewer mentioned, the potential deltaG energy bias of all clusters may not move towards the same direction. Hence, we have further performed a new uncertainty analysis based on the reviewer's advice. Accordingly, we have randomly assigned the ΔG bias of each cluster at 278 K in each calculation within the uncertainty range of -1 to 1 kcal mol^{-1} (Almeida et al. 2013), then performed 500 ACDC calculations to obtain the cluster formation rates (J) based on the newly assigned ΔG values (Fig. S17).

For the convenience of the review, we have copied the added Fig. S17 and the corresponding analysis (in the revised supporting file) as following: "Furthermore, given that

the potential bias of all clusters may not move in the same direction, we have further randomly assigned ΔG value of each cluster (ΔG_{rand} at 278 K) within its uncertainty range (ΔG_{ref} – 1 kcal mol^{-1} < ΔG_{rand} < ΔG_{ref} + 1 kcal mol^{-1}), where ΔG_{ref} indicates the results from the current quantum chemical calculations. Using the newly assigned ΔG_{rand}, we have further performed the ACDC simulations to calculate the cluster formation rate (J). Figure S17 presents the results of 500 calculations. The results do not alter the overall trend of the rate variation, and the resulting principal conclusions of this study."

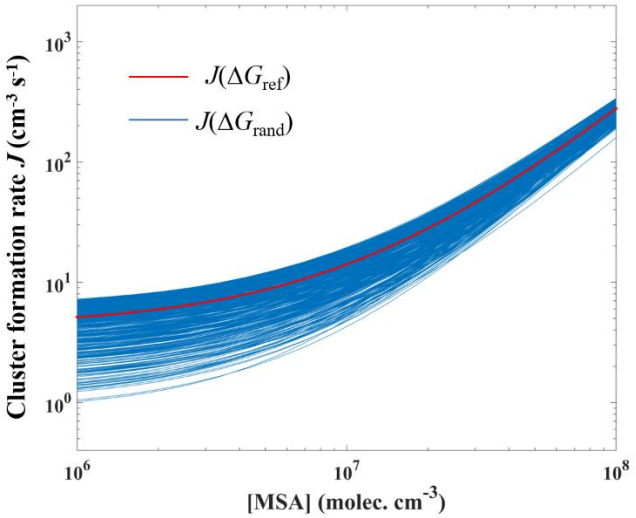

Figure S17. Cluster formation rate J (cm^{-3} s^{-1}) as a function of [MSA] = 10^6 – 10^8 molec. cm^{-3}, with different energy of ΔG_{ref} (red line, reference condition), ΔG_{rand} (blue line, randomly assigned ΔG values of all clusters within the potential bias between -1 and 1 kcal mol^{-1}), at T = 278 K, CS = 2.0 × 10^{-3} s^{-1}, [HIO_3] = 10^7, [HIO_2] = 2.0 × 10^5 molec. cm^{-3}.

Minor:

1. For the pseudo color plots (or heat map), the contour lines should be a bit thicker to improve their visibility.

Response: Thanks for the reviewer's careful reading. We have thickened the contour lines of all the heat maps in the revised manuscript (Fig. 5) and supporting file (Figs. S10 and S11).

2. Some of the wording in manuscript are a bit awkward. I suggest the authors do one more round of language editing.

Response: According to the reviewer's valuable comments, we have re-edited the language of the article. The specific modifications are as follows:

Lines 15-17: The sentence 'The results show that MSA can form stable molecular clusters with HIO_3 and HIO_2 jointly via hydrogen and halogen bonds, as well as electrostatic attraction after proton transfer to HIO_2' has been changed to 'Our results show that MSA can form stable molecular clusters with HIO_3 and HIO_2 jointed via hydrogen bond, halogen bond, and electrostatic attraction after proton transfer to HIO_2'.

Lines 18-20: The sentence 'Furthermore, adding MSA significantly enhance the rate of HIO_3-HIO_2-based cluster formation, even up to 10^4-fold at cold marine regions with rich MSA and scarce iodine, such as polar Ny-Ålesund and Marambio' has been changed to 'Furthermore, our results show that considering MSA will significantly enhance the calculated rate of HIO_3-HIO_2-based cluster formation, with up to 10^4-fold at cold marine regions containing rich MSA and scarce iodine, such as polar Ny-Ålesund and Marambio'.

Line 22: The word 'burst' has been changed to 'bursts'.

Lines 24-25: The sentence 'Marine aerosol, the primary natural aerosol, significantly impact global climate, radiation balance, and even human health' has been changed to 'Marine aerosol, which is the primary natural aerosol, has a significant impact on global climate, radiation balance, and even human health'.

Line 25: The word 'main' has been changed to 'primary'.

Line 27: The word 'And' has been changed to 'Moreover'.

Line 40: The word 'real' has been changed to 'authentic'.

Lines 84-85: The sentence 'To probe the binding nature within molecular clusters, wavefunction analysis was conducted using Multiwfn 3.7' has been changed to 'Wavefunction analysis was carried out using Multiwfn 3.7 to investigate the binding nature within molecular clusters'.

Line 108: The word 'are' has been changed to 'is'.

Line 109: Added the sentence '(Table S8 and Figs. S15, S16 and S17)'.

Line 130: The word ‘greater’ has been changed to ‘stronger’.

Line 151: The word ‘affect’ has been changed to ‘affects’.

Line 167: The sentence ‘through the collision of’ has been changed to ‘by colliding’.

Lines 217-218: The sentence ‘In fact, apart from atmospheric temperature, precursor concentrations may vary regionally or seasonally, further affecting nucleation’ has been changed to ‘It’s worth noting that apart from atmospheric temperature, precursor concentrations might also vary regionally or seasonally, which can further affect nucleation’.

Line 283: The sentence ‘Compared to previously the reported HIO_3-HIO_2 system’ has been changed to ‘Compared to the HIO_3-HIO_2 system reported previously’.

Lines 286-289: The sentence ‘Further comparison with field observations indicates that the HIO_3-HIO_2-MSA synergistic nucleation plays a limited role in the mid-latitude oceans, particularly with abundant iodine (e.g., Mace Head), but an important role in the colder polar regions (e.g., Ny-Ålesund and Marambio)’ has been changed to ‘Further comparison with field observations indicates that the HIO_3-HIO_2-MSA synergistic nucleation plays a limited role in mid-latitude ocean regions, particularly in regions with abundant iodine (e.g., Mace Head), but a potential role in colder polar regions (e.g., Ny-Ålesund and Marambio)’.

Line 288: The sentence ‘In addition to MSA, given the complex oceanic atmosphere, other potential nucleation precursors, such as sulfuric acid and amines, may also affect the HIO_3-HIO_2 nucleation process, further contributing to the formation of marine iodine particles, which deserves future studies’ has been changed to ‘Given the complex oceanic atmosphere, other potential nucleation precursors beyond MSA, such as sulfuric acid and amines, may also affect the HIO_3-HIO_2 nucleation process and further contribute to the formation of marine iodine particles, which deserves future investigations’.

Thanks again for the reviewers’ professional and valuable suggestions, we have done our best to refine our manuscript.

Reference:

Kerminena, V.-M. & M. Kulmalab 2002 Analytical formulae connecting the “real” and the “apparent” nucleation rate and the nuclei number concentration for atmospheric nucleation events. *Aerosol Science,* 33**,** 609-622.

Kulmala, M., T. Petäjä, T. Nieminen, M. Sipilä, H. E. Manninen, K. Lehtipalo, M. Dal Maso, P. P. Aalto, H. Junninen, P. Paasonen, I. Riipinen, K. E. J. Lehtinen, A. Laaksonen & V.-M. Kerminen 2012 Measurement of the nucleation of atmospheric aerosol particles. *Nature Protocols,* 7**,** 1651-1667.

Almeida, J., S. Schobesberger, A. Kürten, I. K. Ortega, O. Kupiainen-Määttä, A. P. Praplan, A. Adamov, A. Amorim, F. Bianchi, M. Breitenlechner, A. David, J. Dommen, N. M. Donahue, A. Downard, E. Dunne, J. Duplissy, S. Ehrhart, R. C. Flagan, A. Franchin, R. Guida, J. Hakala, A. Hansel, M. Heinritzi, H. Henschel, T. Jokinen, H. Junninen, M. Kajos, J. Kangasluoma, H. Keskinen, A. Kupc, T. Kurtén, A. N. Kvashin, A. Laaksonen, K. Lehtipalo, M. Leiminger, J. Leppä, V. Loukonen, V. Makhmutov, S. Mathot, M. J. McGrath, T. Nieminen, T. Olenius, A. Onnela, T. Petäjä, F. Riccobono, I. Riipinen, M. Rissanen, L. Rondo, T. Ruuskanen, F. D. Santos, N. Sarnela, S. Schallhart, R. Schnitzhofer, J. H. Seinfeld, M. Simon, M. Sipilä, Y. Stozhkov, F. Stratmann, A. Tomé, J. Tröstl, G. Tsagkogeorgas, P. Vaattovaara, Y. Viisanen, A. Virtanen, A. Vrtala, P. E. Wagner, E. Weingartner, H. Wex, C. Williamson, D. Wimmer, P. Ye, T. Yli-Juuti, K. S. Carslaw, M. Kulmala, J. Curtius, U. Baltensperger, D. R. Worsnop, H. Vehkamäki & J. Kirkby 2013 Molecular understanding of sulphuric acid–amine particle nucleation in the atmosphere. *Nature,* 502**,** 359-363.