Responses to Referee #4's comments

We sincerely appreciate the reviewer's 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 reviewer's comments. The point-to-point responses to the Referee #4's comments are summarized below:

Referee comments:

This manuscript explores the enhancement effects of MSA on the HIO_3-HIO_2 system through DFT calculations and kinetic analysis. It is found that adding MSA significantly enhances the nucleation rate, especially in colder regions. The calculations are also compared with observations and in general the MSA-HIO_3-HIO_2 nucleation better explains the results than the binary HIO_3-HIO_2 nucleation. Overall, I find this manuscript clearly written and it is a nice contribution to the literature. The manuscript can be published after the following comments are addressed.

Response: We would like to thank the reviewer for taking the time to review our manuscript and for providing the professional comments and positive feedback.

Major comments:

Comment 1: What is the criterion for stable clusters (based on which nucleation rates can be defined)? Are they determined based on the growth rate/dissociation rate ratio? A clear definition should be given in the main text.

Response: Indeed, as expertly suggested by the reviewer, whether a cluster is stable or not is determined based on the cluster growth rate/dissociation rate ratio. In ACDC simulations[1], stable clusters are those in which collisions with molecules can be assumed to dominate over cluster evaporation.

According to the reviewer's helpful suggestions, the corresponding definition has been added in the main text of the revised manuscript (Lines 102-103, Page 4) as follows: "Additionally, whether the clusters in the simulated system are stable depends on whether the rate of collision frequencies exceeds the total evaporation rate coefficients ($\beta C/\Sigma\gamma > 1$) (Table

S4)."

Comment 2: Section 3.4: how *J* is defined/calculated in the measurements should be discussed here, since I assume it is different from the definition used in the simulation. In other words, more justification of why the simulated rates and observed rates are directly comparable should be provided.

Response: This is a very helpful point – thanks for bringing it up. In the ACDC simulation, nucleation generally refers to the formation of relatively stable clusters for which collisions with molecules can be assumed to dominate over cluster evaporation. Accordingly, the cluster formation rate (J) indicates the particle flux out of the studied system. In this case, it is the rate of clusters forming at some specific size (*i.e.* the net flux into the size from all other sizes)[2]. In field observation, the formation rates ($J_{1.5}$) were measured by instruments, such as nitrate chemical ionization atmospheric pressure interface Time-Of-Flight mass spectrometer (CI-APi-TOF)[3], differential mobility particle sizer (DMPS) and neutral cluster and air ion spectrometer (NAIS)[4].

According to the Kerminen-Kulmala equation [5], cluster formation rates for d_2 nm clusters (J_{d_2}) relate to those for d_1 nm clusters (J_{d_1}) by

$$J_{d_1} = J_{d_2} \exp\left\{\gamma\left(\frac{1}{d_1} - \frac{1}{d_2}\right)\frac{\mathrm{CS}}{\mathrm{GR}_{d_2\text{-}d_1}}\right\},$$

where the $\mathrm{GR}_{d_2\text{-}d_1}$ is the initial cluster growth rate from d_1 to d_2 nm, and CS represents condensation sink of clusters by preexisting particles. The parameter γ depends on many factors but can usually be approximated by assuming it to be equal to 0.23 $\mathrm{nm^2\ m^2\ h^{-1}}$.

In this study, the relationship between the formation rates of simulated clusters ($J_{1.2}$) and that of observed clusters ($J_{1.5}$) can be written as:

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

where GR was measured to be 3.2 – 4.4 $\mathrm{nm \cdot h^{-1}}$ in the 1.1 – 2.0 nm size range during three observed events[6, 7], and CS was 0.002 $\mathrm{s^{-1}}$. $J_{1.2}$ was then calculated to be 1.00001 – 1.00002 times of $J_{1.5}$. Thus, the observed cluster formation rates for 1.5 nm clusters can be directly comparable with the simulated $J_{1.2}$.

We have included corresponding justification in Section 3.4 of the revised manuscript

(Lines 242-243, Page 11) and supporting file as follows: "Subsequently, we compared these simulation results with observed nucleation rates and the definition of cluster formation rate was detailed in Supporting Information (SI)."

Comment 3: I suggest the authors do two types of calculations corresponding to polluted (CS larger than 0.002/s) and relatively clean environments. This could benefit future research in more polluted coastal regions.

Response: Thanks, these suggestions from the reviewer are very important for improving the environmental impacts of the HIO_3-MSA-HIO_2 nucleation. Accordingly, we have performed additional ACDC simulations with CS values of 1.0×10^{-2} s^{-1} and 1.0×10^{-4} s^{-1} corresponding to polluted and relatively clean environments, respectively. The figures below present the results of the simulated cluster formation rates J (Figures S8-S9) and enhancement strength R of MSA (Figures S10-S11).

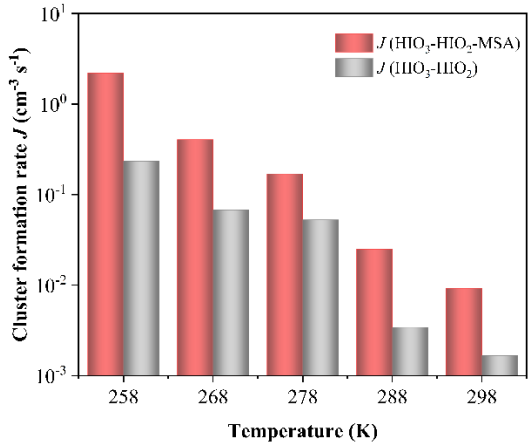

Figure S8. Simulated cluster formation rates J (cm^{-3} s^{-1}) against varying atmospheric temperatures (T = 258 – 298 K), CS = 1.0×10^{-2} s^{-1}, [HIO_3] = 1.0×10^7, [HIO_2] = 2.0×10^5, and [MSA] = 1.0×10^7 molec. cm^{-3}.

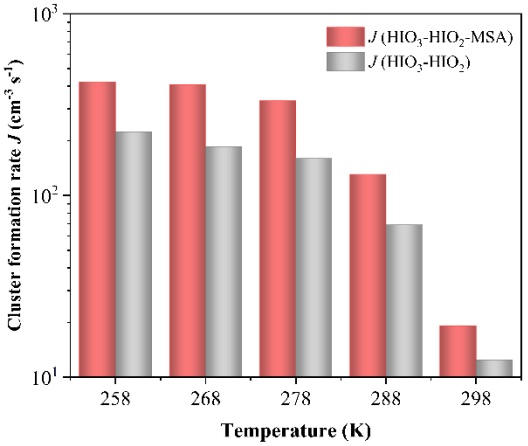

Figure S9. Simulated cluster formation rates J (cm^{-3} s^{-1}) against varying atmospheric temperatures (T = 258 – 298 K), CS = 1.0×10^{-4} s^{-1}, $[HIO_3] = 1.0 \times 10^7$, $[HIO_2] = 2.0 \times 10^5$, and [MSA] = 1.0×10^7 molec. cm^{-3}.

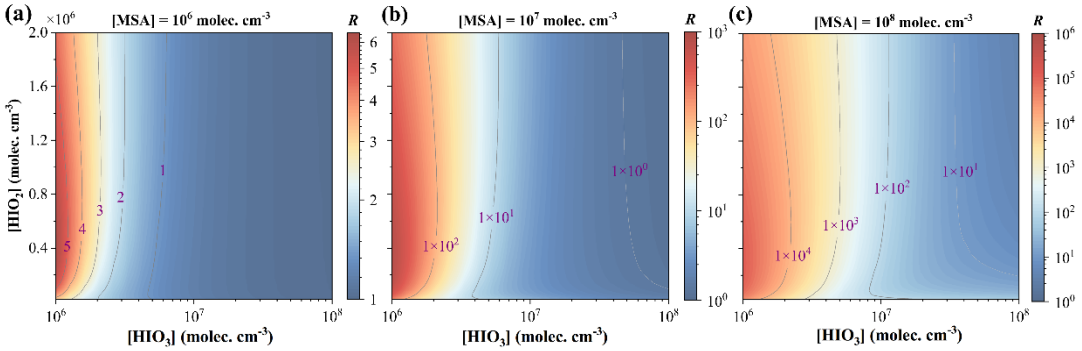

Figure S10. Enhancement strength R of MSA on cluster formation rates at varying precursor concentrations: $[HIO_3] = 10^6 – 10^8$, $[HIO_2] = 2.0 \times 10^4 – 2.0 \times 10^6$ molec. cm^{-3}, **(a)** [MSA] = 1.0×10^6 molec. cm^{-3}, **(b)** [MSA] = 1.0×10^7 molec. cm^{-3}, and **(c)** [MSA] = 1.0×10^8 molec. cm^{-3}, T = 278 K, CS = 1.0×10^{-2} s^{-1}.

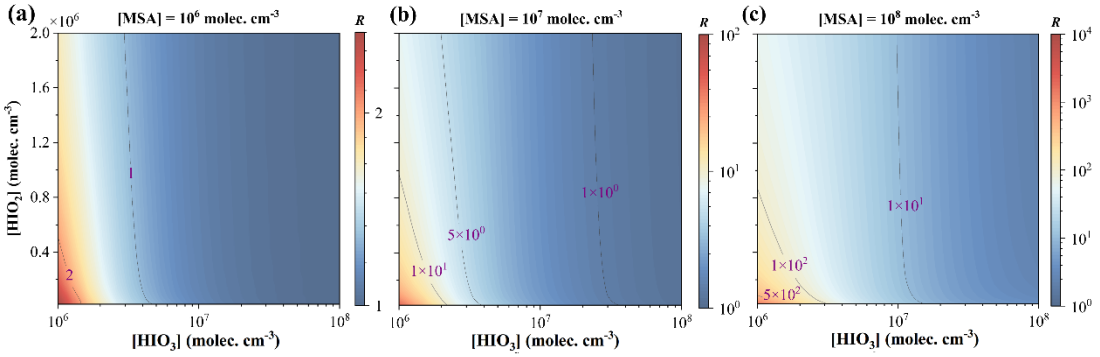

Figure S11. Enhancement strength R of MSA on cluster formation rates at varying precursor

concentrations: [HIO_3] = 10^6 – 10^8, [HIO_2] = 2.0 × 10^4 – 2.0 × 10^6 molec. cm^{-3}, **(a)** [MSA] = 1.0 × 10^6 molec. cm^{-3}, **(b)** [MSA] = 1.0 × 10^7 molec. cm^{-3}, and **(c)** [MSA] = 1.0 × 10^8 molec. cm^{-3}, T = 278 K, CS = 1.0 × 10^{-4} s^{-1}.

Herein, we have added the simulated J and R results, along with their analysis, in the revised supporting file (Figures S8 – S11). For the convenience of the review, we have copied the corresponding analysis (Lines 233-235, Page 10) as following: "In addition, we also examined the conditions in relatively polluted (CS = 1.0 × 10^{-2} s^{-1}) and clean environments (CS = 1.0 × 10^{-4} s^{-1}) and found that, similar to the environment with CS value of 2.0 × 10^{-3} s^{-1}, MSA exhibits significant promoting effects on iodine particle formation (Figs. S8-S11)."

Comment 4: Figure 6. I believe the blue line should be an area as the other two. Also, how does the rates differ if the uncertainties of the DFT calculations for key clusters are considered? A table might be provided for this uncertainty analysis.

Response: We appreciate the insightful and rigorous comments from the reviewer. These suggestions can enhance the robustness of the simulation results. The blue line in Fig. 6 depicts HIO_3-HIO_2 nucleation rate, and since the ratio [HIO_3]/[HIO_2] is held constant (50) according to the measured ratio HIO_3/HIO_2 from Sipilä et al. 2016[8], resulting in a line increasing with HIO_3 concentration. We have added description of the relationship between [HIO_3] and [HIO_2] to the caption of Figure 6 as: "[HIO_3]/[HIO_2] is a constant". Therefore, as [HIO_3] increases, the J(HIO_3-HIO_2) does change as a line.

In addition, following the expert advice of the reviewer, we examined the effects of DFT computational uncertainty for key clusters on the rate as well as on the enhancement R of MSA. The uncertainties of the DFT calculations ultimately manifested in the calculated ΔG values. As reported by Kupiainen[9] et al. (2012), the differences between the computational (DFT//RI-CC2 method) and experimental ΔG values are about 1 kcal mol^{-1} or less[10]. Accordingly, Almedia[11] et al. (2013) calculated the uncertainty range of ACDC simulated cluster formation resulting from QC calculations by adjusting the binding energy (±1 kcal mol^{-1}). Further given the consistency of our research framework (DFT//RI-CC2 + ACDC) with Almedia et al. (2013), herein we have performed the uncertainty analysis of R_{MSA} caused by QC calculations through adding or subtracting 1 kcal mol^{-1} from the ΔG (using ΔG_{278K} as a reference). The table and

figure below present the uncertainty analysis results of J and R_{MSA} at T = 278 K, CS = 2.0 × 10^{-3} s^{-1}, [HIO_3] = 10^7, [HIO_2] = 2.0 × 10^5, [MSA] = 10^6 – 10^8 molec. cm^{-3}.

Table S8. Cluster formation rate J of HIO_3-HIO_2-MSA system under different Gibbs free energy (ΔG_{278K}, ΔG_{278K} + 1, ΔG_{278K} - 1) at T = 278 K, CS = 2.0 × 10^{-3} s^{-1}, [HIO_3] = 10^7, [HIO_2] = 2.0 × 10^5, [MSA] = 10^6 – 10^8 molec. cm^{-3}.

[MSA]	$J_{\Delta G}$	$J_{\Delta G-1}$	$J_{\Delta G+1}$
1.00×10^{6}	5.13×10^{0}	4.31×10^{0}	5.29×10^{0}
1.27×10^{6}	5.35×10^{0}	4.46×10^{0}	5.53×10^{0}
1.62×10^{6}	5.64×10^{0}	4.65×10^{0}	5.84×10^{0}
2.07×10^{6}	6.01×10^{0}	4.90×10^{0}	6.25×10^{0}
2.64×10^{6}	6.50×10^{0}	5.22×10^{0}	6.78×10^{0}
3.36×10^{6}	7.14×10^{0}	5.63×10^{0}	7.47×10^{0}
4.28×10^{6}	7.99×10^{0}	6.17×10^{0}	8.40×10^{0}
5.46×10^{6}	9.12×10^{0}	6.87×10^{0}	9.64×10^{0}
6.95×10^{6}	1.06×10^{1}	7.80×10^{0}	1.13×10^{1}
8.86×10^{6}	1.27×10^{1}	9.04×10^{0}	1.36×10^{1}
1.13×10^{7}	1.56×10^{1}	1.07×10^{1}	1.68×10^{1}
1.44×10^{7}	1.96×10^{1}	1.30×10^{1}	2.14×10^{1}
1.83×10^{7}	2.53×10^{1}	1.61×10^{1}	2.78×10^{1}
2.34×10^{7}	3.35×10^{1}	2.05×10^{1}	3.71×10^{1}
2.98×10^{7}	4.55×10^{1}	2.68×10^{1}	5.07×10^{1}
3.79×10^{7}	6.31×10^{1}	3.60×10^{1}	7.08×10^{1}
4.83×10^{7}	8.93×10^{1}	4.95×10^{1}	1.01×10^{2}
6.16×10^{7}	1.29×10^{2}	6.98×10^{1}	1.46×10^{2}
7.85×10^{7}	1.88×10^{2}	1.01×10^{2}	2.13×10^{2}
1.00×10^{8}	2.78×10^{2}	1.49×10^{2}	3.15×10^{2}

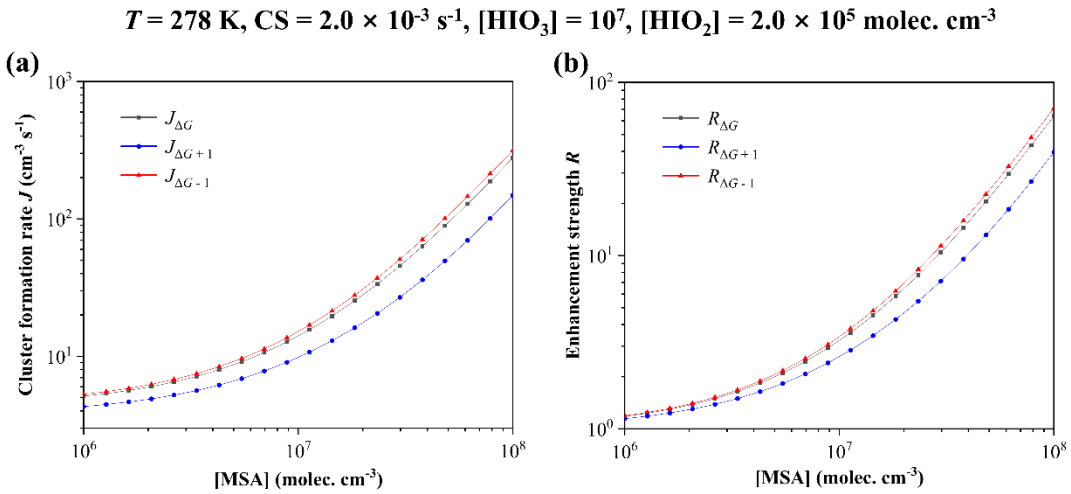

Figure S16. Cluster formation rate J **(a)** and enhancement strength R of MSA **(b)** as a function of [MSA] = 10^6 – 10^8 molec. cm^{-3}, with different energy of ΔG_{278K} (black line), ΔG_{278K} + 1 (blue line), ΔG_{278K} – 1 (red line), at T = 278 K, CS = 2.0 × 10^{-3} s^{-1}, [HIO_3] = 10^7, [HIO_2] = 2.0 × 10^5 molec. cm^{-3}.

For the convenience of the review, we have copied Table S8 and Figure S16 and the corresponding analysis (in the revised supporting file) as following: "As reported by Kupiainen[9] et al. (2012), the differences between the computational (DFT//RI-CC2 method) and experimental ΔG values are about 1 kcal mol^{-1} or less[10]. Accordingly, Almeida[11] et al. (2013) calculated the uncertainty range of ACDC simulated cluster formation resulting from QC calculations by adjusting the binding energy (±1 kcal mol^{-1}). Further given the consistency of our research framework (DFT//RI-CC2 + ACDC) with Almeida et al. (2013), herein we have performed the uncertainty analysis of R_{MSA} caused by QC calculations through adding or subtracting 1 kcal mol^{-1} from the ΔG (using ΔG_{278K} as a reference). As shown in Table S8 and Fig. S16, adjusting the ΔG_{278K} of clusters by ±1 kcal mol^{-1} resulted in a minor variation in J and R of MSA, with the overall trend remaining consistent."

Technical comments:

Comment 5: Line 24: nucleating -> nucleation. This replacement should be done in several places in the text.

Response: Thanks for this helpful comment., the "nucleating" has been changed to "nucleation" in the revised manuscript.

Comment 6: Line 27: remove the second comma.

Response: The second comma has been removed in the revised manuscript.

Comment 7: Line 35: might be rewritten as: Although the efficient nucleation of HIO_3 and HIO_2 is overall consistent with the CLOUD measurements, this mechanism does not account for all HIO_3-induced nucleation in the real atmosphere.

Response: Thanks, the wording suggested by the reviewer is more appropriate. Accordingly, the sentence has been rewritten as "Although the efficient nucleation of HIO_3 and HIO_2 is overall consistent with the CLOUD measurements, this mechanism does not account for all HIO_3-induced nucleation in the real atmosphere." in Lines 34-36 of the revised manuscript.

Comment 8: Line 48: might be rewritten as: the importance of the HIO_3-HIO_2-MSA nucleating mechanism may differ under distinct ambient conditions.

Response: According to this helpful suggestion, the sentence has been rewritten as "the importance of the HIO_3-HIO_2-MSA nucleation mechanism may differ under distinct ambient conditions" in Lines 47-48 of the revised manuscript.

Comment 9: Line 72: remove 'and'

Response: According to the reviewer's suggestion, the "and" has been removed in the Line 71 of revised manuscript.

Comment 10: Line 116: present -> presented

Response: The "present" has been corrected as "presented" in the Line 122 of revised manuscript.

Comment 11: Line 144: observed -> shown

Response: The "observed" has been corrected as "shown" in the Line 153 of revised manuscript.

Comment 12: Line 160: across-> through

Response: The “across” has been corrected as “through” in the Line 162 of revised manuscript.

Comment 13: Line 169: contribute to 74% of cluster formation

Response: Accordingly, the sentence has been corrected as “contribute to 74% of cluster formation” in the Line 171 of revised manuscript.

Comment 14: Line 214: access-> assess

Response: Thanks for the reviewer’s careful reading, the “access” has been corrected as “assess” in the Line 240 of revised manuscript.

Reference:

[1] M.J. McGrath, T. Olenius, I.K. Ortega, V. Loukonen, P. Paasonen, T. Kurtén, M. Kulmala, H. Vehkamäki, Atmospheric Cluster Dynamics Code: a flexible method for solution of the birth-death equations, Atmos. Chem. Phys. 12 (2012) 2345–2355.

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[6] D. Xia, J. Chen, H. Yu, H.B. Xie, Y. Wang, Z. Wang, T. Xu, D.T. Allen, Formation Mechanisms of Iodine-Ammonia Clusters in Polluted Coastal Areas Unveiled by Thermodynamics and Kinetic Simulations, Environ. Sci. Technol. 54 (2020) 9235-9242.

[7] H. Yu, L. Ren, X. Huang, M. Xie, J. He, H. Xiao, Iodine speciation and size distribution in ambient aerosols at a coastal new particle formation hotspot in China, Atmos. Chem. Phys. 19 (2019) 4025–4039.

[8] M. Sipilä, N. Sarnela, T. Jokinen, H. Henschel, H. Junninen, J. Kontkanen, S. Richters, J. Kangasluoma, A. Franchin, O. peräkylä, M.P. Rissanen, M. Ehn, H. Vehkamäki, T. Kurten, T. Berndt, T. Petäjä, D. Worsnop, D. Ceburnis, V.M. Kerminen, M. Kulmala, C. O'Dowd, Molecular-scale evidence of aerosol particle formation via sequential addition of HIO_3, Nature 537 (2016) 532–534.

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