Dear Editor,

Thank you very much for your handling our manuscript "**Molecular-level evidence for marine aerosol nucleation of iodic acid and methanesulfonic acid**" (MS No.: acp-2021-595) and giving us the opportunity to refine manuscript. According to reviewer's valuable comments, we have revised the manuscript carefully and listed the point-to-point responses to the reviewers' comments as below:

Responses to Referee #3's comments:

The authors have satisfactorily addressed my comments regarding the inconsistencies between their earlier study and the present study. I applaud the authors for deciding to prepare a corrigendum for Rong et al. 2020 paper and the corrections made to this paper concerning IA cluster structures.

Unfortunately, the author failed to address several key concerns which I had in the preface of my last review. After addressing the first-round reviews, the data quality of this manuscript is better. The revised data, to my opinion, clearly suggest that the IA-MSA particle formation mechanism quantitatively fails to explain both the field observations and laboratory investigations. This conflicts with the theme of this manuscript.

However, I think the data presented in this manuscript are still valuable if interpreted correctly. The authors should quantitatively compare their results with laboratory formation rates and conclude based on the comparison. They will find that their IA-MSA formation rates are too low (6 orders of magnitude lower) compared to the laboratory results and other species must be needed.

I understand that scholars tend to be reluctant to report negative results these days but I personally think a correctly interpreted negative result is certainly more valuable than misunderstood positive results. Thus, I urge the authors to make the suggested modifications.

Response: Thanks sincerely to the reviewer's helpful and professional comments. We have revised the manuscript accordingly. The detailed point-to-point responses are listed as follows.

Major comments:

Comment 1. In my previous review, I suggested that additional cluster geometries and free energies were needed to complete this study which was not adopted by the authors. The authors cited the statements from the ACDC manual and I attach the original whole paragraph below:

The criteria for clusters to grow out of the simulation, also known as boundary conditions, are essential parameters in an ACDC simulation. When a collision results in a cluster not included in the simulation set, it must be decided what to do with this product: is it reasonable to let it leave the simulation, or is it more likely that the cluster evaporates back to a smaller size? If the cluster composition can be assumed to be stable, i.e. molecular collisions are likely to dominate over evaporation, the cluster can be let out. As by default there is no information on the stabilities of clusters outside the system, the outgrowth criteria must be decided based on the existing data (molecular composition of the clusters along the main growth pathways, trends in the collision and evaporation rates inside the system...) and the best understanding (general chemistry of the clusters). An unreasonable choice of outgrowth criteria, on the other hand, may distort the simulation results.

The manual suggests that molecular collision should "dominate" evaporation. "Dominate" does not mean collision/evaporation equals one. So, lines starting line162 and SI are clearly misinterpretations. The authors can check e.g., Fig. 5.1 in the ACDC manual and relevant figures in e.g., Myllys et al. 2018, Elm et al. 2017 which all have much larger out-of-box collision to evaporation ratios.

The authors argue that their consideration of acid = 1e6 cm-3 is stringent and so the ratio equal to 0.2 is fine. This is not true. The authors should ensure that the out-of-box cluster has dominant collision over evaporation under all considered conditions (acid concentration, temperature etc.). A ratio of 10 is more adequate compared to 1. Thus, additional calculations are needed.

Additionally, I have a further question on the newly added equation SI. Can the authors specify where did they cite the equation from? The denominator is the sum of evaporation pathways which could be evaporating IA, MSA, IAMSA, IA2 etc but the numerator is the collision between IA and IA4MSA2? How about MSA and IA4MSA2? Please reconsider this.

Response: Thanks for the review's valuable suggestions. These suggestions are important for the rigor of the data presented.

Item 1) from the reviewer: The manual suggests that molecular collision should "dominate" evaporation. "Dominate" does not mean collision/evaporation equals one. So, lines starting line162 and SI are clearly misinterpretations. The authors can check e.g., Fig. 5.1 in the ACDC manual and relevant figures in e.g., Myllys et al. 2018, Elm et al. 2017 which all have much larger out-of-box collision to evaporation ratios.

Response: Indeed, the "dominate" in the ACDC manual does not correspond to a quantitative criterion. In our manuscript, the criterion of whether the collision/evaporation ratio exceeds 1 is based on the following statement in ACDC manual (section 5.1):

"If the relative evaporation rate decreases along the likely cluster growth pathway so that it is exceeded by the collision rate for the largest clusters, the system size can be considered sufficient."

Accordingly, the defined $\beta C / \sum\gamma > 1$ corresponds to the cluster evaporation rate being exceeded by the collision rate.

Furthermore, according to the reviewer's helpful suggestion, we have checked the mentioned Fig. 5.1 of the ACDC manual and relevant figures in e.g., Myllys et al. 2018, Elm et al. 2017. The larger out-of-box collision to evaporation ratios are presented in these studies. For example, in Fig. 5.1 of the ACDC manual, the value of $\beta_{(H2SO4)}C_{(H2SO4)} / \sum\gamma$ ($5H_2SO_4{\cdot}5NH_3$ cluster) is **2×10^1** in the H_2SO_4-NH_3 system at $T = 280$ K and $[H_2SO_4] = 5.0\times10^6$ molecules cm^{-3} (a median value of the range of $[H_2SO_4]$, $10^6 \sim 10^7$ molecules cm^{-3}). Under similar conditions ($T = 278$ K and $[HIO_3] = 1.0\times10^7$ (a median value of $[HIO_3]$, $10^6 \sim 10^8$ molecules cm^{-3}), for the IA-MSA system, the $\beta_{(HIO3)}C_{(HIO3)} / \sum\gamma$ for $(IA)_4{\cdot}(MSA)_2$ and $(IA)_6$ cluster is **2×10^1** and **7×10^1**, respectively. The values of $\beta C / \sum\gamma$ presented are closely related to the employed temperature and nucleation monomer concentrations. Although our results are significantly lower than those for colliding with NH_3, namely $\beta_{(NH3)}C_{(NH3)} / \sum\gamma$ ($5H_2SO_4{\cdot}5NH_3$ cluster) in Fig. 5.1, colliding with acids ($\beta_{(H2SO4)}C_{(H2SO4)} / \sum\gamma$) would be a better boundary setting because of the instability of cluster with more base and less acid (Myllys et al., 2019).

To make the presented results more reliable, we performed additional cluster calculations and recalculated the relevant data according to the reviewer's professional suggestion, see the details in response for Item 2).

Item 2) from the reviewer: The authors argue that their consideration of acid = 1e6 cm-3 is stringent and so the ratio equal to 0.2 is fine. This is not true. The authors should ensure that the out-of-box cluster has dominant collision over evaporation under all considered conditions (acid concentration, temperature etc.). A ratio of 10 is more adequate compared to 1. Thus, additional calculations are needed.

Response: Thanks for the reviewer's careful review. As the reviewer expertly suggested, the ratio of cluster collision to evaporation is influenced by the considered conditions (temperature, acid concentration etc.). Generally, the lower temperatures and the higher acid concentrations employed, the larger ratio ($\beta C / \sum \gamma$) obtained.

The ratio of 0.2 presented in Figure S2 is the minimum value for $(IA)_6$ cluster under conditions of the highest studied temperature (T = 298 K) and lowest acid concentration ([IA] = 1.0×10^6 molecules cm^{-3}). But it is not fine to perform simulations under such conditions ($\beta_{IA} C_{IA} / \sum \gamma < 1$). Hence, as shown in Figure 6 (d) of previous manuscript, we in fact simulated the case at 298 K with [IA] higher than 5.0×10^6 molecules cm^{-3}, at which the collision dominates over evaporation ($\beta_{IA} C_{IA} / \sum \gamma > 1$). And at $T \leq$ 278 K, the ACDC simulations were performed under condition of [IA] = $10^6 \sim 10^8$ molecules cm^{-3}, when $\beta_{IA} C_{IA} / \sum \gamma > 1$. In all the ACDC simulations that have been performed, the out-of-box cluster has dominant collision over evaporation under the conditions employed.

Although, according to the ACDC manual, the system size is sufficient when the collision rate of the largest cluster exceeds its evaporation rate ($\beta C / \sum \gamma > 1$), we agree with the reviewer that larger ratio than 1 is more adequate. Hence, according to the reviewer's helpful suggestion, we performed the additional cluster conformation calculations to find more stable $(IA)_6$ and $(IA)_4(MSA)_2$ clusters requested in the last Comment 3 from the reviewer. Here, we have doubled the conformational search range (5000 → 10,000), retaining 1000 structures from these initial 10,000 generations by ABCluster (Zhang and Dolg, 2015), on the basis of which a multi-step conformational search is further performed. The details of additional calculation as well as the resulting atomic coordinates for the new low-energy cluster are summarized in the appendix of this response.

Finally, inspired by the valuable suggestions of the reviewer, we find a $(IA)_6$ cluster with lower free energy. As show in Figure A1, the ΔG_{298K} of the new $(IA)_6$ cluster (-72.22 kcal mol^{-1}) is 2.10 kcal mol^{-1} lower than the previous one (-70.12 kcal mol^{-1}).

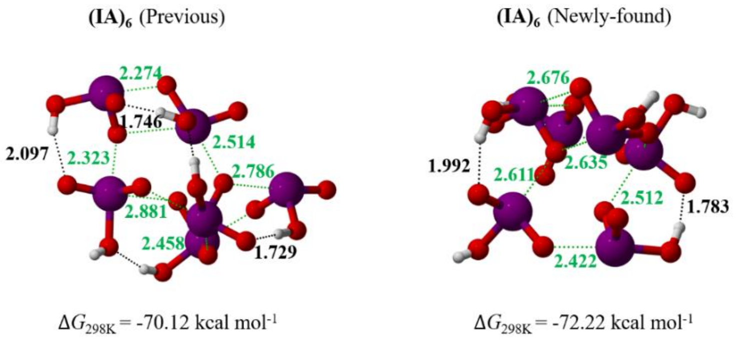

Figure A1. The $(IA)_6$ cluster structure in the previous manuscript and the new $(IA)_6$ structure found after extended calculations. The black and green dashed lines indicate hydrogen and halogen bonds, respectively. The lengths of hydrogen and halogen bonds are given in Å.

Accordingly, we modified the structures of the $(IA)_6$ clusters in Figure S1 and updated the corresponding atomic coordinates in Table S7 in the revised Supporting Information (SI). And the newly-found $(IA)_6$ cluster is also mentioned in the method section. Further we recalculated the collision to evaporation ratio at 278 K and 298 K after changing the $(IA)_6$ clusters. The values of $\beta_{\mathrm{IA}}C_{\mathrm{IA}} / \sum\gamma$ increased from 0.2 to 5 at 298 K and from 7 to 3×10^2 at 278 K. The corrected data plots are presented in Figure 2 of the revised manuscript and Figure S2 and Figure S3 in SI. In addition, all data affected by changing $(IA)_6$ cluster were recalculated, and the corrected graphs and tables are highlighted in main text and SI.

Item 3) from the reviewer: Additionally, I have a further question on the newly added equation SI. Can the authors specify where did they cite the equation from? The denominator is the sum of evaporation pathways which could be evaporating IA, MSA, IAMSA, IA2 etc but the numerator is the collision between IA and IA4MSA2? How about MSA and IA4MSA2? Please reconsider this.

Response: We thank the reviewer's professional suggestions, which can make the data clearer for the readers. The newly added equation in SI was derived from the ratio of the collision rate to the evaporation rate, namely $\beta_{\mathrm{IA}}C_{\mathrm{IA}}\cdot C_{\mathrm{cluster}} / \sum\gamma\cdot C_{\mathrm{cluster}} = \beta_{\mathrm{IA}}C_{\mathrm{IA}} / \sum\gamma$. In fact, both cluster-monomer collisions and cluster-cluster collisions are considered in the performed ACDC simulations. Only collisions with IA monomers are presented here because the equilibrium concentration of clusters (e.g., $(IA)_1(MSA)_1$, $(IA)_2$) is significantly lower than that of IA monomers, and therefore collision of IA monomers is more possible than that of colliding clusters.

In addition, for the collision between MSA and $(IA)_4(MSA)_2$, it is considered and noted in the previously revised manuscript (Line 167), Section S1 (SI), and the previous response to the Comment 3 (item 1). For example, in Line 167 of previously revised manuscript, the statement is: “Among these clusters, the largest $(IA)_4{\cdot}(MSA)_2$ and $(IA)_6$ clusters ($\beta_{IA}C_{IA}/\sum\gamma > 1$) incline to collide with IA monomer (or MSA monomer) to grow out of the simulated system”. Moreover, the boundary clusters in the performed simulations at 278 K contain $(IA)_7$, $(IA)_6{\cdot}(MSA)_1$, $(IA)_4{\cdot}(MSA)_3$, and $(IA)_5{\cdot}(MSA)_2$ clusters, which were obtained by considering the collisions with IA or MSA monomer (Figure A2).

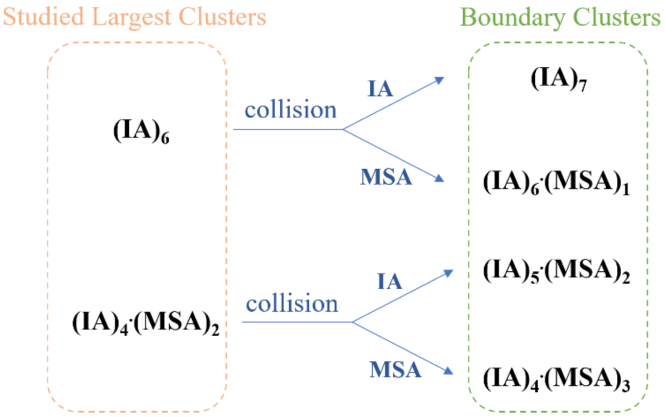

Figure A2. The baseline for setting the boundary clusters in ACDC simulations at 278K.

We thank the reviewer’s valuable suggestion. Presenting the collision with MSA in a similar figure for IA is necessary for the clarity of the reader, as the statement alone is not clear. Hence, we have added the data of the colliding MSA monomers to Figure 2 of the revised manuscript, Figure S2 and Figure S3 in SI.

----

2. The authors need to include the formation rates from He et al. 2021 in their figures (e.g., Figure 3, 6). This way it will be apparent that there are 6 orders of magnitude differences between the CLOUD results and the present manuscript. While my suggestions concerning adding clusters will likely reduce the discrepancy, it will not resolve such a 6 orders of magnitude difference.

The author argued that both experiments and QC calculations have errors. However, such a huge error cannot be explained by systematic errors. QC+ACDC is a developed toolset and has been verified in multiple studies concerning e.g., SA + NH3 + DMA. Previous studies has reported reasonably well comparison with the CLOUD rates (e.g, Myllys et al. 2019; Myllys et al. 2016; Almeida et al. 2013; Olenius et al 2013). The 6 orders of magnitude discrepancy in this study mush be due to other reasons.

The authors made a good point in their response that He et al. 2021 concluded that other iodine species (such as HIO2) are also critical in iodine particle formation processes. Therefore, the calculation of the pure-IA system in this manuscript is distinct from that of He et al. 2021. My revisit to the mentioned papers confirms their statement. Nevertheless, this affirms the fact that additional species are required to explain iodine + sulfur induced nucleation in marine and polar environments. I took a closer look at He et al 2021, particularly the part on how these HIO3 and HIO2 are formed. They seem to conclude that these species are simultaneously produced from iodine oxidation processes with relatively simple conditions analogous to the atmosphere. This would suggest that, besides HIO3, other iodine species are also present. Have the authors considered this possibility (e.g. is HIO2 important in the iodine nucleation?)?

Response: Thanks for the reviewer's valuable comments. These suggestions are helpful for refining the conclusions. The responses to each item are listed below.

Item 1) from the reviewer: The authors need to include the formation rates from He et al. 2021 in their figures (e.g., Figure 3, 6). This way it will be apparent that there are 6 orders of magnitude differences between the CLOUD results and the present manuscript. While my suggestions concerning adding clusters will likely reduce the discrepancy, it will not resolve such a 6 orders of magnitude difference.

Response: According to the reviewer's suggestion, the formation rates from He et al., 2021 has been included in Figure 3 of the revised manuscript. And we also discussed the differences between the simulated cluster formation rates and CLOUD results (Lines 191 – 197 of the revised manuscripts). For review convenience, we have copied the details as below:

"As shown in Fig. 3, the simulated *J* of pure-IA nucleation (purple line) is much lower than the rate obtained from the CLOUD experiment (He et al. 2021). … Briefly, MSA can promote *J* of IA clusters to a higher level, which is a reflection of the stabilizing effect of MSA on IA clusters. However, the *J* of IA-MSA nucleation was still much less than the experimental results (He et al. 2021), even at a high [MSA] (10^8 molecules cm^{-3}). The large rate difference suggests that MSA stabilizes IA less efficiently than the potential iodine-containing components."

In addition, the additional clusters have been calculated and considered in the simulation of formation rate according to the reviewer's suggestion. As the reviewer expertly deduced, adding clusters does not significantly reduce the discrepancy, which means that this is not the main reason and other iodine-containing acids potentially play a key role in nucleation.

Item 2) from the reviewer: The author argued that both experiments and QC calculations have errors. However, such a huge error cannot be explained by systematic errors. QC+ACDC is a developed toolset and has been verified in multiple studies concerning e.g., SA + NH3 + DMA. Previous studies has reported reasonably well comparison with the CLOUD rates (e.g, Myllys et al. 2019; Myllys et al. 2016; Almeida et al. 2013; Olenius et al 2013). The 6 orders of magnitude discrepancy in this study mush be due to other reasons.

Response: Indeed, in the mentioned studies, the QC+ACDC simulations shows a better fit with the CLOUD results. This is likely attributed to the fact that the employed nucleation precursors in the ACDC simulation are similar to those in the CLOUD chamber.

In contrast, our work aimed to study the stabilizing effect of MSA on IA, so iodine components other than IA were not considered. However, the iodine oxides and iodous acid are presented in the CLOUD experiment (He et al. 2021). We agree with the reviewer that the 5 ~ 6 orders of magnitude discrepancy should come from other causes, most likely the impact of iodine oxides and iodous acid.

Item 3) from the reviewer: The authors made a good point in their response that He et al. 2021 concluded that other iodine species (such as HIO2) are also critical in iodine particle formation processes. Therefore, the calculation of the pure-IA system in this manuscript is distinct from that of He et al. 2021. My revisit to the mentioned papers confirms their statement. Nevertheless, this affirms the fact that additional species are required to explain iodine + sulfur induced nucleation in marine and polar environments. I took a closer look at He et al 2021, particularly the part on how these HIO3 and HIO2 are formed. They seem to conclude that these species are simultaneously produced from iodine oxidation processes with relatively simple conditions analogous to the atmosphere. This would suggest that, besides HIO3, other iodine species are also present. Have the authors considered this possibility (e.g. is HIO2 important in the iodine nucleation?)?

Response: The reviewer's suggestions are far-sighted. Iodine species other than iodic acid (e.g., I_2O_4, I_2O_5, and HIO_2) were unfortunately not considered in the manuscript because the original purpose of this study was to explore the stabilizing effect of MSA on IA. Considering other iodine species would make it difficult to identify the role of MSA in IA nucleation, and would result in a triple or even larger calculation efforts. Through this revised manuscript, especially inspired by the reviewers, we realized that other iodine species may play a more important role than MSA in IA cluster formation. Therefore, in order to simulate the real atmospheric environment and clarify the role of other iodine-containing components in IA nucleation, nucleation models including more iodine species, especially HIO_2, will be built in the future study.

----

3. In fact, the authors agree with my comments above by stating additional species, such as HIO2, iodine oxides, SA, NH3, amines can be important in marine and coastal particle formation processes too (lines 268 - 273). While I agree with the authors that marine environments are vast and different mechanisms can take place in different regions, the mechanism proposed in this study explains none of the mentioned field observations (Beck et al. 2021; Baccarini et al. 2020; Sipila et al. 2016).

The authors argue that their results do not conflict with Sipila et al. 2016 since they also suggest IA is important at Mace Head. However, at IA = 1E8, the authors calculated a formation rate of around 1e-2 cm-3 and even with additional MSA = 1E8, they get a formation rate of around 1 cm-3. However, the particle formation events at Mace Head are significantly stronger at the same acid concentration (Figure 1 in Sipila et al 2016 at IA = 1E8), sometimes reaching 1e7 cm-3 (O'dowd et al. 1999).

The same applies to Baccarini et al. 2020. Figure 1 in Baccarini et al. 2020 is at around 268 K which is not present in this manuscript. However, we can generously take the value from the results at 258K in this study (Figure 6c). With HIO3 at around 5e6, the formation rate is below 1e-5 cm-3 in this manuscript which indicates there should be no particle formation. This conflicts with Baccarini et al. 2020 since they observe strong particle formation events there.

The authors have removed the controversial Fig. 6 in the original manuscript which is good. In that figure, Beck et al 2021 also does not support the IA-MSA mechanism.

Considering these field observations and results from this manuscript, the correct derivation is that IA-MSA explains none of the mentioned field observations and additional species must be needed. The authors are also encouraged to discuss the potential contributing species.

Response: This is a very helpful point – thanks for bringing it up. The correct presentation of negative results would be more valuable for future studies. We agree with the reviewer that this data discrepancy needs to be reduced by considering additional components. Hence, we discussed the potential species contributing to particle formation in section of Abstract, Results and Conclusion, respectively. The details are as follows:

a) **Abstract.**

Lines 14 - 16: "… in the nucleation process. However, the nucleation rate of the IA-MSA mechanism is much lower than that of field observation, indicating that the role of additional nucleation precursors needs to be considered (e.g., H_2SO_4, HIO_2, NH_3 and amines)."

b) **Results.**

Lines 196 - 199: "Briefly, MSA can promote *J* of IA clusters to a higher level, which is a reflection of the stabilizing effect of MSA on IA clusters. However, the *J* of IA-MSA nucleation was still much less than the experimental results (He et al. 2021), even at a high [MSA] (10^8 molecules cm^{-3}). The large rate difference suggests that MSA stabilizes IA less efficiently than the potential iodine-containing components."

Lines 274 – 280: "Compared to the field observations at Mace Head (Sipila et al. 2016) and Arctic Sites (Beck et al. 2021), the rate of the IA-MSA mechanism is also significantly lower. This indicates that the contribution of MSA to IA particle formation under atmospheric conditions is relatively limited, and more efficient stabilizer for IA should be involved in the nucleating process, such as other iodine-containing components such as HIO_2 and iodine oxides (I_2O_4 and I_2O_5). Moreover, considering the complexity of the marine atmosphere, other non-iodine nucleation precursors (SA, NH_3, amines, etc.) may also affect the nucleation process, particularly with SA, because MSA and SA are both formed during the oxidation of DMS and coexist in the marine atmosphere. Therefore, in future studies, the influence of the above factors on the nucleation mechanism of marine aerosols will also be considered."

c) **Conclusion.**

Line 289 – 293: "However, IA-MSA nucleation rates are far from sufficient to explain the field observations, indicating that additional essential precursors need to be considered (e.g.,

H_2SO_4, HIO_2, NH_3 and amines). Nucleation among these components is likely to be synergistic, with only varying magnitudes of contribution. For example, both SA and MSA originate from the oxidation of DMS, so their coexistence in the atmosphere may synergistically promote the formation of IA clusters, which is worthy of future studies."

----

4. L13: Before getting into the IA-MSA nucleation. 1) compare Pure IA results with experimental results and point out the difference. 2) explain the enhancement of Pure IA nucleation by MSA. 3) the combined effect is still too small compared to field observations. 4) additional species need to be considered (reasonably specify a few). The same applies to the conclusion part.

Response: Thanks for the reviewer's valuable suggestions, which are essential to refine the theme of this manuscript. Details of the revision for the Abstract and Conclusion sections are as follows.

a) Abstract.

Line 12 - 16: "The findings show that the pure-IA nucleation rate was much lower than the results of CLOUD experiments. MSA can promote IA cluster formation through stabilizing IA via both hydrogen and halogen bonds, especially under conditions with lower temperatures, sparse IA and rich MSA. However, the nucleation rate of the IA-MSA mechanism is much lower than that of field observation, indicating that the effect of additional nucleation precursors needs to be considered (e.g., H_2SO_4, HIO_2, NH_3 and amines)."

b) Conclusion

Line 284 - 293: "…Atmospheric Cluster Dynamics Code (ACDC). The results suggest that the self-nucleation rate of IA is much lower than that of CLOUD experiment, indicating stabilizers are essential for IA nucleation process. We find that MSA can stabilize IA cluster via both hydrogen and halogen bonds, and thus promote IA cluster formation rate, especially in low-temperature environments with sparse IA and rich MSA. The corresponding IA-MSA nucleating mechanism can be described by two distinct pathways: i) pure-IA cluster formation and ii) IA-MSA cluster formation, indicating that IA and MSA can jointly nucleate. The IA-MSA nucleation is highly dependent on the distribution of MSA and IA in the marine atmosphere. However, IA-MSA nucleation rates are far from sufficient to explain the field observations, indicating that additional essential precursors need to be considered (e.g., H_2SO_4, HIO_2, NH_3 and amines). Nucleation among these components is likely to be synergistic, with only varying magnitudes of contribution. For example, both SA and MSA originate from the oxidation of DMS, so their coexistence in the atmosphere may synergistically promote the formation of IA clusters, which is worthy of future studies."

Minor comments:

L40: My read does not find that He et al. 2021 suggests the involvement of I2O5 and I2O4 in the nucleation? It looks to me that they cannot conclude the role of I2O4/I2O5. But maybe the authors can refer me to the relevant sentences.

Response: The statement in the work of He et al. 2021 regarding the involvement of I_2O_5 and I_2O_4 in nucleation is in the section of "Particle Composition". Additionally, the role of I_2O_4 and I_2O_5 in nucleation is presented in the Figure 3 (He et al. 2021). For the convenience of the reviewer, the relevant sentences were copied as below.

"The measurements presented in Fig. 1B provide strong evidence that HIO_3 drives the growth of iodic particles above 1.8 nm. However, we have seen that additional iodine compounds play important roles during nucleation: HIO_2 for neutral nucleation, and the formation of iodine oxides—I_2O_5 and I_2O_4 —in the charged and neutral clusters, respectively (Fig. 2)."

L67: Aside from the difference in calculation methods, the authors should also write clearly that the geometries of IA2 and IA3 are different from what they have presented in their response.

Response: Thanks for the reviewer's helpful suggestion. The differences in the IA2 and IA3 cluster have been corrected. The differences of employed cluster structures are also described in the Methods section of the revised manuscript.

In addition, to further weaken the impact of IA-MSA mechanism, the additional changes were made as following:

Thanks to the reviewer's very important suggestion, we accordingly refine the theme of this manuscript and change the title as following.

Original Title: Molecular-level evidence for marine aerosol nucleation of iodic acid and methanesulfonic acid.

Corrected: Molecular-level nucleation mechanism of iodic acid and methanesulfonic acid.

Lines 16 – 17: “The IA-MSA nucleation mechanism revealed in this study may help to elucidate some missing sources of marine NPF.”
Corrected: “The IA-MSA nucleation mechanism revealed in this study may help to gain insight into the joint effect of marine sulfur- and iodine-containing components on marine NPF.”

Line 196: Briefly, MSA can promote *J* of IA clusters to a higher level, which may help explain the rapid formation of IA-involved particles in some marine NPF.
Corrected: “Briefly, MSA can promote *J* of IA clusters to a higher level, which is a reflection of the stabilizing effect of MSA on IA clusters.”

Thanks again for the reviewer’s professional and carefulness review. Accordingly, we have tried our best to improve the manuscript.

Sincerely Yours,
Prof. Xiuhui Zhang

Appendix.

Additional calculation details.

First, the artificial bee algorithm combining the UFF force field (Rappe et al., 1992) was adopted to yield 1000 initial-guess structures from 10,000 generations by ABCluster software (Zhang and Dolg, 2015). After pre-optimization by the PM7 method (Stewart, 2013) with MOPAC2016 (James J. P. Stewart, 2016), the 100 lower-energy structures were left for further optimization at ωB97X-D/6-31+G* + Lanl2DZ (for iodine) level of theory. The final cluster structure were optimized at ωB97X-D/6-311++G(3df,3pd) (H, C, O and S) (Francl et al., 1982) + aug-cc-pVTZ-PP with ECP28MDF (for I) (Peterson et al., 2003).

All the additional calculation result files for each step are available at the following URL: https://www.icloud.com/iclouddrive/011Z9EW6_j0-XVvsJ0AzSWvZQ#IA-MSA_.Additional_Calculation)

Table A1. Atomic coordinates of the $(IA)_6$ cluster in the previous manuscript and in this revised manuscript.

$(IA)_6$ (Previous):

Atoms	X	Y	Z
I	2.0142330	-1.9502430	0.1062340
O	3.5813460	-2.3077960	-0.6609640
O	1.2147740	-0.8403890	-1.0583760
O	1.0568390	-3.5830250	-0.4682790
H	1.3933920	-3.8971680	-1.3144030
I	4.0616510	1.1772010	0.5078450
O	3.6480600	1.4144440	-1.2121400
O	2.9102220	-0.0865740	1.1649480
O	5.4562590	-0.1115870	0.2184390
H	5.0709030	-0.9080240	-0.1938550
I	-1.9509040	-2.0075870	1.2785530
O	-0.3728890	-1.2094910	1.5384160
O	-2.2436270	-1.9045460	-0.4983290
O	-1.2923970	-3.8204880	1.2425070
H	-0.5887520	-3.9170540	0.5764410
I	-3.5541860	1.5105690	0.6518740
O	-4.9348430	2.0979990	1.5719390
O	-3.0518940	0.0320430	1.5940770
O	-4.5205320	0.6939320	-0.7634460
H	-3.9463030	0.3947540	-1.5156220

I	0.6743480	1.8105790	0.3807700
O	2.2811220	2.5127150	0.9739480
O	-0.4695840	3.0879240	0.7922740
O	1.0853560	2.2419120	-1.4546750
H	2.0513300	2.0382580	-1.5418810
I	-1.2858540	-0.3923390	-2.1824110
O	-1.2960600	0.8181160	-0.8255000
O	-2.9363330	-0.1593290	-2.8052690
O	-0.3635120	0.7547110	-3.4115000
H	0.1587040	1.3911450	-2.8870510

(IA)$_6$ (New):

Atoms	X	Y	Z
I	2.2808360	-0.2753710	-2.1881650
O	2.9719550	-0.8720370	-0.6598240
O	0.7608060	0.5949180	-1.7316370
O	3.3326370	1.3014170	-2.4413400
H	2.9510610	2.0411620	-1.9103970
I	0.6413140	2.4184810	-0.0083520
O	-0.8608180	3.0004440	-0.8644300
O	1.9683430	3.1662190	-0.9376500
O	0.6243090	3.7769460	1.3626620
H	1.1942090	4.4944990	1.0581850
I	-2.7890380	1.8068790	-0.2953190
O	-1.7709380	1.3170510	1.1505700
O	-2.4200660	0.6546250	-1.5917610
O	-4.3947320	0.9695600	0.3615050
H	-4.1653500	0.0378670	0.5465660
I	-1.4589660	-1.0321300	1.8638060
O	-0.1031870	-0.9421340	0.6382260
O	-2.8761320	-1.3267160	0.8107060
O	-1.1795240	-2.8714060	2.2946450
H	-1.2063490	-3.3478930	1.4394730
I	-0.9196570	-2.0764910	-1.5666630
O	-1.0281490	-3.5252090	-0.5362830
O	0.7784970	-2.1746890	-2.1884340
O	-1.7723570	-2.8490540	-3.1160810
H	-1.6671070	-3.8081140	-3.0746010
I	2.1173610	-0.7524830	2.0447950
O	0.8024440	-0.7625620	3.2681640
O	2.3028120	0.9848650	1.6935780
O	3.6177060	-0.9370970	3.2444890
H	3.6566860	-0.1695010	3.8285950

References:

Myllys, N., Elm, J., Halonen, R., Kurtén, T., and Vehkamäki, H.: Coupled Cluster Evaluation of the Stability of Atmospheric Acid–Base Clusters with up to 10 Molecules, J. Phys. Chem. A, 120, 621–630, https://doi.org/10.1021/acs.jpca.5b09762, 2016.

Myllys, N., Ponkkonen, T., Passananti, M., Elm, J., Vehkamäki, H., and Olenius, T.: Guanidine: A Highly Efficient Stabilizer in Atmospheric New-Particle Formation, 122, 4717–4729, https://doi.org/10.1021/acs.jpca.8b02507, 2018.

Myllys, N., Chee, S., Olenius, T., Lawler, M., and Smith, J.: Molecular-Level Understanding of Synergistic Effects in Sulfuric Acid–Amine–Ammonia Mixed Clusters, J. Phys. Chem. A, 123, 2420–2425, https://doi.org/10.1021/acs.jpca.9b00909, 2019.

Rong, H., Liu, J., Zhang, Y., Du, L., Zhang, X., and Li, Z.: Nucleation mechanisms of iodic acid in clean and polluted coastal regions, Chemosphere, 253, 126743, https://doi.org/10.1016/j.chemosphere.2020.126743, 2020.

Beck, L. J., Sarnela, N., Junninen, H., Hoppe, C. J. M., Garmash, O., Bianchi, F., Riva, M., Rose, C., Peräkylä, O., Wimmer, D., Kausiala, O., Jokinen, T., Ahonen, L., Mikkilä, J., Hakala, J., He, X., Kontkanen, J., Wolf, K. K. E., Cappelletti, D., Mazzola, M., Traversi, R., Petroselli, C., Viola, A. P., Vitale, V., Lange, R., Massling, A., Nøjgaard, J. K., Krejci, R., Karlsson, L., Zieger, P., Jang, S., Lee, K., Vakkari, V., Lampilahti, J., Thakur, R. C., Leino, K., Kangasluoma, J., Duplissy, E., Siivola, E., Marbouti, M., Tham, Y. J., Saiz-Lopez, A., Petäjä, T., Ehn, M., Worsnop, D. R., Skov, H., Kulmala, M., Kerminen, V., and Sipilä, M.: Differing Mechanisms of New Particle Formation at Two Arctic Sites, Geophys Res Lett, 48, https://doi.org/10.1029/2020GL091334, 2021.

Sipilä, M., Sarnela, N., Jokinen, T., Henschel, H., Junninen, H., Kontkanen, J., Richters, S., Kangasluoma, J., Franchin, A., Peräkylä, O., Rissanen, M. P., Ehn, M., Vehkamäki, H., Kurten, T., Berndt, T., Petäjä, T., Worsnop, D., Ceburnis, D., Kerminen, V.-M., Kulmala, M., and O'Dowd, C.: Molecular-scale evidence of aerosol particle formation via sequential addition of HIO3, Nature, 537, 532–534, https://doi.org/10.1038/nature19314, 2016.

Baccarini, A., Karlsson, L., Dommen, J., Duplessis, P., Vüllers, J., Brooks, I. M., Saiz-Lopez, A., Salter, M., Tjernström, M., Baltensperger, U., Zieger, P., and Schmale, J.: Frequent new particle formation over the high Arctic pack ice by enhanced iodine emissions, Nature Communications, 11, 4924, https://doi.org/10.1038/s41467-020-18551-0, 2020.

He, X.-C., Tham, Y. J., Dada, L., Wang, M., Finkenzeller, H., Stolzenburg, D., Iyer, S., Simon, M., Kürten, A., Shen, J., Rörup, B., Rissanen, M., Schobesberger, S., Baalbaki, R., Wang, D. S., Koenig, T. K., Jokinen, T., Sarnela, N., Beck, L. J., Almeida, J., Amanatidis, S., Amorim, A., Ataei, F., Baccarini, A., Bertozzi, B., Bianchi, F., Brilke, S., Caudillo, L., Chen, D., Chiu, R., Chu, B., Dias, A., Ding, A., Dommen, J., Duplissy, J., El Haddad, I., Gonzalez Carracedo, L., Granzin, M., Hansel, A., Heinritzi, M., Hofbauer, V., Junninen, H., Kangasluoma, J., Kemppainen, D., Kim, C., Kong, W., Krechmer, J. E., Kvashin, A., Laitinen, T., Lamkaddam, H., Lee, C. P., Lehtipalo, K., Leiminger, M., Li, Z., Makhmutov, V., Manninen, H. E., Marie, G., Marten, R., Mathot, S., Mauldin, R. L., Mentler, B., Möhler, O., Müller, T., Nie, W., Onnela, A., Petäjä, T., Pfeifer, J., Philippov, M., Ranjithkumar, A., Saiz-Lopez, A., Salma, I., Scholz, W., Schuchmann, S., Schulze, B., Steiner, G., Stozhkov, Y., Tauber, C., Tomé, A., Thakur, R. C., Väisänen, O., Vazquez-Pufleau, M., Wagner, A. C., Wang, Y., Weber, S. K., Winkler, P. M., Wu, Y., Xiao, M., Yan, C., Ye, Q., Ylisirniö, A., Zauner-Wieczorek, M., Zha, Q., Zhou, P., Flagan, R. C., Curtius, J., Baltensperger, U., Kulmala, M., Kerminen, V.-M., Kurtén, T., et al.: Role of iodine oxoacids in atmospheric aerosol nucleation, 371, 589–595, https://doi.org/10.1126/science.abe0298, 2021.

Elm, J., Passananti, M., Kurtén, T., and Vehkamäki, H.: Diamines Can Initiate New Particle Formation in the Atmosphere, J. Phys. Chem. A, 121, 6155–6164, https://doi.org/10.1021/acs.jpca.7b05658, 2017.

McGrath, M. J., Olenius, T., Ortega, I. K., Loukonen, V., Paasonen, P., Kurtén, T., Kulmala, M., and Vehkamäki, H.: Atmospheric Cluster Dynamics Code: a flexible method for solution of the birth-death equations, Atmos. Chem. Phys., 12, 2345–2355, https://doi.org/10.5194/acp-12-2345-2012, 2012.

Olenius, T., Kupiainen-Määttä, O., Ortega, I. K., Kurtén, T., and Vehkamäki, H.: Free energy barrier in the growth of sulfuric acid–ammonia and sulfuric acid–dimethylamine clusters, 13, 2013.

Almeida, J., Schobesberger, S., Kürten, A., Ortega, I. K., Kupiainen-Määttä, O., Praplan, A. P., Adamov, A., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Donahue, N. M., Downard, A., Dunne, E., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Guida, R., Hakala, J., Hansel, A., Heinritzi, M., Henschel, H., Jokinen, T., Junninen, H., Kajos, M., Kangasluoma, J., Keskinen, H., Kupc, A., Kurtén, T., Kvashin, A. N., Laaksonen, A., Lehtipalo, K., Leiminger, M., Leppä, J., Loukonen, V., Makhmutov, V., Mathot, S., McGrath, M. J., Nieminen, T., Olenius, T., Onnela, A., Petäjä, T., Riccobono, F., Riipinen, I., Rissanen, M., Rondo, L., Ruuskanen, T., Santos, F. D., Sarnela, N., Schallhart, S., Schnitzhofer, R., Seinfeld, J. H., Simon, M., Sipilä, M., Stozhkov, Y., Stratmann, F., Tomé, A., Tröstl, J., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Virtanen, A., Vrtala, A., Wagner, P. E., Weingartner, E., Wex, H., Williamson, C., Wimmer, D., Ye, P., Yli-Juuti, T., Carslaw, K. S., Kulmala, M., Curtius, J., Baltensperger, U., Worsnop, D. R., Vehkamäki, H., and Kirkby, J.: Molecular understanding of sulphuric acid–amine particle nucleation in the atmosphere, Nature, 502, 359–363, https://doi.org/10.1038/nature12663, 2013.

O'Dowd, C., McFiggans, G., Creasey, D. J., Pirjola, L., Hoell, C., Smith, M. H., Allan, B. J., Plane, J. M. C., Heard, D. E., Lee, J. D., Pilling, M. J., and Kulmala, M.: On the photochemical production of new particles in the coastal boundary layer, Geophysical Research Letters, 26, 1707–1710, https://doi.org/10.1029/1999GL900335, 1999.

Francl, M. M., Pietro, W. J., Hehre, W. J., Binkley, J. S., Gordon, M. S., DeFrees, D. J., and Pople, J. A.: Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements, J. Chem. Phys., 77, 3654–3665, https://doi.org/10.1063/1.444267, 1982.

James J. P. Stewart: MOPAC2016, Colo. SpringsCOUSA, 2016.

Myllys, N., Kubečka, J., Besel, V., Alfaouri, D., Olenius, T., Smith, J. N., and Passananti, M.: Role of base strength, cluster structure and charge in sulfuric-acid-driven particle formation, Atmospheric Chem. Phys., 19, 9753–9768, https://doi.org/10.5194/acp-19-9753-2019, 2019.

Peterson, K. A., Figgen, D., Goll, E., Stoll, H., and Dolg, M.: Systematically convergent basis sets with relativistic pseudopotentials. II. Small-core pseudopotentials and correlation consistent basis sets for the post- *d* group 16–18 elements, J. Chem. Phys., 119, 11113–11123, https://doi.org/10.1063/1.1622924, 2003.

Rappe, A. K., Casewit, C. J., Colwell, K. S., Goddard, W. A., and Skiff, W. M.: UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations, J. Am. Chem. Soc., 114, 10024–10035, https://doi.org/10.1021/ja00051a040, 1992.

Stewart, J. J. P.: Optimization of parameters for semiempirical methods VI: more modifications to the NDDO approximations and re-optimization of parameters, J. Mol. Model., 19, 1–32, https://doi.org/10.1007/s00894-012-1667-x, 2013.

Zhang, J. and Dolg, M.: ABCluster: the artificial bee colony algorithm for cluster global optimization, Phys. Chem. Chem. Phys., 17, 24173–24181, https://doi.org/10.1039/C5CP04060D, 2015.