

Responses to Referee #3's comments

Thanks for the reviewer's professional and helpful comments on our manuscript "**Molecular-level evidence for marine aerosol nucleation of iodic acid and methanesulfonic acid**" (MS No.: acp-2021-595). We have revised the manuscript carefully according to reviewer's comments. The point-to-point responses to the Referee #3's comments are summarized below:

Major comments:

Comment 1: The authors deployed identical QC methods in this work and their earlier work (Rong et al. 2020; Xiuhui Zhang is the corresponding author for both studies). The authors calculated formation rates for pure IA nucleation in both studies, but a 1000 to 10,000 times difference can be found by comparing Fig. 3 of this study and Fig. 2 in Rong et al. 2020. A further check on Table S12 in Rong et al. 2020 and Table S2 in this study shows substantially different Gibbs free energy values for the same IA clusters at the same temperature. E.g., at 278 K, Rong et al. 2020 gives a ΔG of $-5.92 \text{ kcal mol}^{-1}$ while this study gives $-9.51 \text{ kcal mol}^{-1}$. The difference seems small but as it goes in the exponential part of the evaporation rate equation, the resulted evaporation rates can be significantly different. My simplified calculation suggests that a $-9.51 \text{ kcal mol}^{-1}$ value easily results in a 500 times lower evaporation rate of iodic acid dimer compared to a value of -5.92 .

A further investigation on this matter comparing these two papers suggest at least two major differences. Rong et al. 2020 uses a double zeta basis set (aug-cc-pVDZ-PP) while this study uses a triple-zeta basis set (aug-cc-pVTZ-PP). However, I highly doubt that this is the primary reason for such a significant difference. I further tried to compare the geometries of the IA dimer in these two papers. As the authors provided wrong coordinates for IA dimer in Supp-Section 6 in Rong et al. 2020, I have to infer from their Fig. S3 (cited here as Figure R1). The IA dimer is connected by two halogen bonds. However, in this study, the IA dimer is connected by two hydrogen bonds from my reproduced results based on coordinates in Table S7 of this manuscript. Additionally, the geometries of larger IA clusters in this study are also significantly different from Rong et al. 2020. The authors should visualize the IA clusters and any other clusters which are not yet visualized besides IA-MSA clusters in Fig S1.

Because of these significant differences in these two papers, the authors are urged to do at least as follows: 1) they should calculate all the commonly used clusters (at least all of the IA clusters) in Rong et al. 2020 and this study by both the double zeta and triple zeta basis sets for two sets of geometries provided in both papers (so 2x2 matrix for every cluster). 2) the authors should discuss the results coming from item 1) in the Main Text and give reasons for their updated

results and potential errors associated with the Rong et al. 2020 or this study. 3) The authors are encouraged also to discuss in the main text why the geometries provided in their current study should represent global minima and why the geometries are significantly different in Rong et al. 2020 and this study.

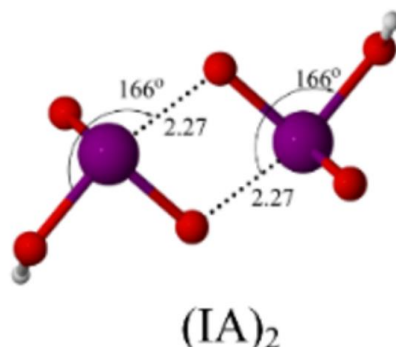


Figure R1. Screenshot of Figure S3 in Rong et al. 2020.

Response: Thanks for the reviewer’s professional and valuable comments. The responses to each of the reviewer’s comments are presented below.

Item 1) from the reviewer: “they should calculate all the commonly used clusters (at least all of the IA clusters) in Rong et al. 2020 and this study by both the double zeta and triple zeta basis sets for two sets of geometries provided in both papers (so 2x2 matrix for every cluster).”

Response: As suggested by the reviewer, all of the studied IA clusters in Rong et al. 2020 and this study have been calculated at both double zeta and triple zeta basis sets. The resulting ΔG_s at 278K of IA clusters are collected in the following Table A1, which has also been added in the revised supporting file (Table S2).

Table A1. The Gibbs formation free energies ΔG_{278K} (kcal mol⁻¹) of the studied IA clusters in Rong et al. 2020 and this study calculated at the RI-CC2/aug-cc-pVTZ(-PP)// ω B97X-D/6-311++G(3df,3pd) + aug-cc-pVDZ-PP (for I) (DZ) and RI-CC2/aug-cc-pV(T+d)Z(-PP)// ω B97X-D/6-311++G(3df,3pd) + aug-cc-pVTZ-PP (for I) (TZ), respectively.

Cluster	ΔG_{278K} -Rong (DZ)	ΔG_{278K} -Rong (TZ)	ΔG_{278K} -this study (DZ)	ΔG_{278K} -this study (TZ)
(IA) ₂	-5.92	-8.07	-7.96	-9.51
(IA) ₃	-15.73	-18.47	-16.05	-18.79
(IA) ₄	-34.41	-38.48	-34.41	-38.48
(IA) ₅	-52.37	-56.28	-52.37	-56.28
(IA) ₆	-70.67	-74.41	-70.67	-74.41

It is worth noting that the (IA)₂ and (IA)₃ clusters in Rong et al. 2020 and this study are different. Specifically, the (IA)₂ in Rong is halogen-bonded, while in this study it is hydrogen-bonded. And this issue will be further discussed in the response to item 2) below.

Item 2) from the reviewer: “the authors should discuss the results coming from item 1) in the Main Text and give reasons for their updated results and potential errors associated with the Rong et al. 2020 or this study.”

Response: Thanks for the reviewer’s valuable suggestion. The following are **A)** the causes of the differences in values, **B)** the reasons for updating the data, and **C)** the potential errors in the Rong et al. 2020 or this study.

A) In the Rong et al. 2020 and this study, the levels of theory employed in cluster structure optimization and frequency calculations are different. The larger triple- ζ basis set (aug-cc-pVTZ-PP (for iodine)) was used in this study compared to the double- ζ basis set (aug-cc-pVDZ-PP (for iodine)) of Rong et al., (2020). As shown in the above Table A1 (second and third columns), the different basis sets lead to differences in the calculated ΔG s of IA clusters ((IA)₂₋₆) in the range of 2.15 ~ 4.06 kcal mol⁻¹. This is one reason for the difference in the calculated ΔG s values.

In addition, as mentioned above and shown in Fig. A1, the geometries of IA clusters (IA dimer and IA trimer) employed in the Rong et al. 2020 and the present manuscript are different. This is another reason. It further leads to a difference of 0.32 ~ 1.44 kcal mol⁻¹ of ΔG s values, at the same level of theory (third and fifth columns in Table A1).

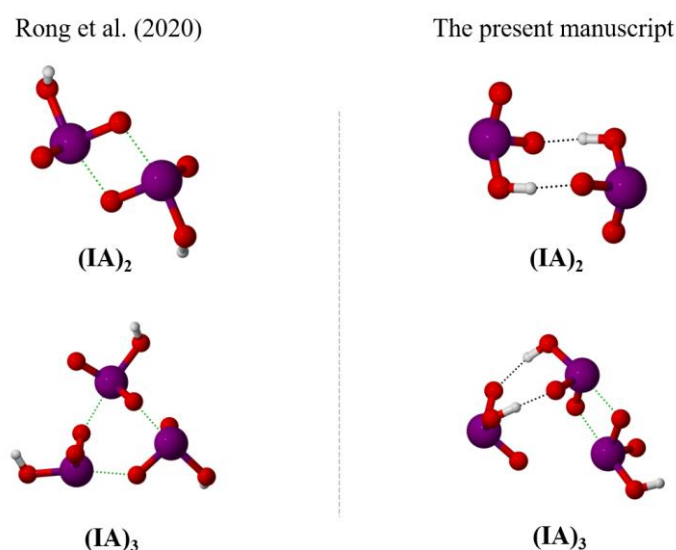


Figure A1. The different IA cluster structures employed in Rong et al. (2020) and the present manuscript (including IA dimer and trimer).

B) The following are the reasons for the choice of the double- ζ basis set in the Rong et al. 2020, and the subsequent update of the results in the present paper:

Due to large number of electrons in iodine atom, the QC calculations of clusters involving IA are expensive. Considering the variety of clusters calculated in the Rong et al. 2020, coupled with the limited computational resources available at that time, the double- ζ basis set was chosen as a compromise between computational accuracy (Benchmark, Table S1-S6 in Rong et al. 2020) and resource consumption to present the reasonable trends and corresponding mechanisms of sulfuric acid and NH_3 promoting IA cluster formation. After updating the computational resources, in the present manuscript, the larger triple- ζ basis set was herein used to reduce errors in the subsequent dynamic simulations because higher level of theory usually implies a better calculation accuracy.

As suggested by the reviewer, we have declared the reason for updating the results in the lines 66-69 of the revised manuscript.

C) The potential errors in the Rong et al. 2020 or this study are as follows:

Thanks for the reviewer's professional comments. After careful comparison (Table A1) we found that with the same structure, the ΔG calculated in Rong et al. 2020 at the double- ζ basis set (aug-cc-pVDZ-PP for iodine) is higher than those under triple- ζ basis set (aug-cc-pVTZ-PP for iodine), which will lead to a lower cluster formation rate.

Item 3) from the reviewer: "The authors are encouraged also to discuss in the main text why the geometries provided in their current study should represent global minima and why the geometries are significantly different in Rong et al. 2020 and this study."

Response: Thanks for the reviewer's helpful suggestion. The reasons for the selection of the different IA cluster conformations (IA dimer and trimer) in the Rong et al. 2020 and this work are summarized below:

The sampling process of cluster isomers is computationally demanding and subject to uncertainties (Elm et al., 2020). The employed IA dimer and trimer in this manuscript are not the lowest-energy isomers due to our incomplete consideration. Thanks for the reviewer's careful review. The IA dimer and trimer with lowest energy obtained after recalculation are consistent with those of Rong et al. 2020. In addition, we have also checked the other employed IA clusters and confirmed that these clusters were selected with the lowest energies.

Thanks again for the reviewer's professional comment. We have corrected the structure of IA dimer and trimer to be consistent with that of Rong et al. 2020. Accordingly, we have also

recalculated all relevant data and updated graphs and tables in the revised manuscript and revised supporting file.

Item 4) from the reviewer: “The authors should visualize the IA clusters and any other clusters which are not yet visualized besides IA-MSA clusters in Fig. S1.”

As suggested by the reviewer, all the clusters studied in the present manuscript, containing IA clusters as well as other previously unrepresented clusters, have been visualized in the revised Fig. S1 of the supplement. In addition, by a comparison of with the original data, we find that the mentioned Cartesian coordinates of IA dimer and trimer provided in SI of Rong et al. (2020) lost the corresponding negative sign due to typos. And the corrected coordinates are added in the Appendix in this response. Further, we are contacting the corresponding publisher to correct this issue in these days.

Comment 2: Another fundamental problem is that neither this study nor Rong et al. 2020 seem to even remotely repeat CLOUD measurements on pure iodic acid nucleation (He et al. 2021). For example, this study calculates 6 orders of magnitude lower cluster formation rates compared to He et al. 2021 and the difference goes to 9 orders when comparing Rong et al. 2020 with He et al. 2021. While it is understandable that the large number of electrons in iodine atom cause substantial challenges in QC calculations, such a substantial difference must be explained, as it could potentially suggest that either there are some fundamental errors in the QC + ACDC calculations related to coding, methods and basis sets employed or because the authors are calculating based on wrong assumptions.

Response: Thanks for the reviewer’s constructive suggestions. We realized that there is a significant discrepancy between the simulated rates in the present manuscript and the CLOUD measurements (He et al. 2021). The reasons for this phenomenon are as follows (A and B):

A) The nucleation components involved in the ACDC simulation (only IA) of the present manuscript and CLOUD experiment (He et al., 2021) are different. If we understand correctly, He et al., (2021) presented a high dependence of the nucleation rate on the concentration of IA (Fig. 1, He et al., 2021), but in fact, not only IA is involved in nucleation, but also other iodine components, such as I_2O_4 , I_2O_5 , and HIO_2 , play a non-negligible role in forming IA particles (Fig. 2 and Fig. 3, He et al., 2021). Therefore, using the simulated rate containing only IA to compare the experimental nucleation rates of multiple iodine components such as I_2O_4 , I_2O_5 , and HIO_2 , will inevitably lead to large differences.

B) In addition to the differences in the components mentioned in item 1), as the reviewer

mentioned, there are uncertainties in both experiments and simulations. The superposition of errors may further amplify the difference between experiments and simulations. In addition, there are also differences in the way nucleation rates are calculated between the experiments and simulations. All of these would lead to the fact that we cannot simply assess the cause of the discrepancy and attribute it to one point.

Therefore, there is uncertainty in comparing the specific results of experiments and simulations in this case. In fact, theoretical calculations prefer to show that the IA-MSA system have higher cluster formation rates than the pure-IA system, indicating the enhancement of MSA on IA cluster formation, which is particularly evident in marine regions with rich MSA and sparse IA.

Comment 3: I'm not convinced that there are sufficient IA-MSA clusters calculated in this study which would allow the authors to consider larger clusters than IA4MSA2 and IA6 as nucleated clusters. The largest ratios of growth to evaporation in Fig. 2c are 2 (IA4MSA2) and 7 (IA6) which barely provide growth potential for these clusters. How can these clusters be considered stable enough? This even more true when looking at the Fig. S2C in which the largest value is 0.2. This is an essential assumption for this study and all other QC + ACDC studies and many of the numbers in this study will make no sense if this is not varied. The author should extend their calculations until finding stable clusters.

Additionally, the authors mistakenly conclude in lines 171-172 that “condensation sink” has a minor impact on the cluster formation rate. First, likely the authors are not talking about condensation sink but coagulation loss or a combination of other losses. This should be clarified, and they should describe clearly that whether they applied the “CS” uniformly for all clusters. Typical in ACDC models one would set monomer species as constants and therefore condensation sink does not affect the monomer condensation. If their calculations correctly find stable clusters with low enough evaporation rates (and thus high growth potential from condensation), they will likely find the “CS” as an important factor influencing their calculated cluster formation rates. It's possible that they find such odd results because they have not found the clusters with low enough evaporation rates as mentioned above. This is evident from the fact that if stable clusters are found, condensational growth is likely dominating the growth and its value is comparable to their “CS” values of $1e-4$ to $2.6e-3$ s^{-1} when acid is ranging from $1e6$ to $1e8$ cm^{-3} . The lowest evaporations rates given in this study (Fig. 2B) are not far from the “CS”.

Response: Thanks for the reviewer's professional comment. The specific response to each item

of the reviewer are as follows:

Item 1) from the reviewer: “The largest ratios of growth to evaporation in Fig. 2c are 2 (IA4MSA2) and 7 (IA6) which barely provide growth potential for these clusters. How can these clusters be considered stable enough?”

Response: In ACDC simulations (McGrath et al., 2012), relatively stable clusters are those in which collisions with molecules can be assumed to dominate over cluster evaporation (Oona and Tinja, 2020). Specifically, it is to calculate the ratio of the rate at which the studied cluster collides with the IA or MSA monomer to its total evaporation rate. The following is an example of the IA4MSA2 cluster.

$$\frac{\beta_1 C_1}{\sum \gamma} = \frac{\beta_1 C_1 \cdot C_{IA4MSA2}}{\sum \gamma_{IA4MSA2} \cdot C_{IA4MSA2}} = 2 > 1$$

where β_1 is the rate coefficient of cluster collision with IA monomer, C_1 is the concentration of IA monomer, and $\sum \gamma$ is the total evaporation rate coefficient of the studied cluster.

If $\beta_1 C_1 / \sum \gamma > 1$, the corresponding cluster would be considered to be relatively stable against evaporation, and has the “growth potential”. Once these stable clusters on the boundary form and grow further out of the simulated system, these formed clusters out of system are unlikely evaporate back into the system (Oona and Tinja, 2020; McGrath et al., 2012). Thus, as suggested by the reviewer, the controversial statement “stable enough” has been changed to “relatively stable” in the revised manuscript. In addition, the above explanation has been added in lines 162 – 167 (main text) and Section S1 (supplement) for the clarity of the reader.

Item 2) from the reviewer: This even more true when looking at the Fig. S2C in which the largest value is 0.2. This is an essential assumption for this study and all other QC + ACDC studies and many of the numbers in this study will make no sense if this is not varied.

Response: This is a very helpful point – thank you for bringing it up. In fact, the present ratios of growth to evaporation ($\beta_1 C_1 / \sum \gamma$) in Fig. 2C, Fig. S2C and Fig. S3C are the lowest values, since the chosen C_1 at this point is the lowest concentration of IA monomer (1.0×10^6 molecules cm^{-3}). The $\beta_1 C_1 / \sum \gamma$ of the mentioned cluster is in the range of 0.2 - 20 under the studied range of IA concentration ($10^6 - 10^8$ molecules cm^{-3}). In this case, the clusters (value of 0.2 at $[IA] = 1.0 \times 10^6$ molecules cm^{-3}) can grow out of the system at most of studied $[IA]$ ($5 \times 10^6 \sim 10^8$ molecules cm^{-3}).

Thanks to the professional advice of the reviewer. In order to let the reader know that the presented $\beta_1 C_1 / \sum \gamma$ is the minimum value, we have added notes in lines 163 – 165 (main text) and Section S1 (supplement) to remind the reader.

Item 3) from the reviewer: “First, likely the authors are not talking about condensation sink but coagulation loss or a combination of other losses. This should be clarified, and they should describe clearly that whether they applied the “CS” uniformly for all clusters.”

Response: As pertinently suggested by the reviewer, the statement about “CS” uniformly for all clusters has been added in line 184 of the revised manuscript. This treatment is also commonly used in other theoretical simulation studies (Bork et al., 2014; Shen et al., 2019; Xu et al., 2020).

Item 4) from the reviewer: “Additionally, the authors mistakenly conclude in lines 171-172 that “condensation sink” has a minor impact on the cluster formation rate... .

Response: In this study, before getting the corresponding conclusions (“the different CS ($1.0 \times 10^{-4} \sim 2.6 \times 10^{-3} \text{ s}^{-1}$) have a minor impact on the cluster formation rate”), we have tested the effect of different CS values on cluster formation rate J ($\text{cm}^{-3} \text{ s}^{-1}$) in Fig. S4 of supporting file. For the reviewer’s convenience, we have copied and presented it as follows.

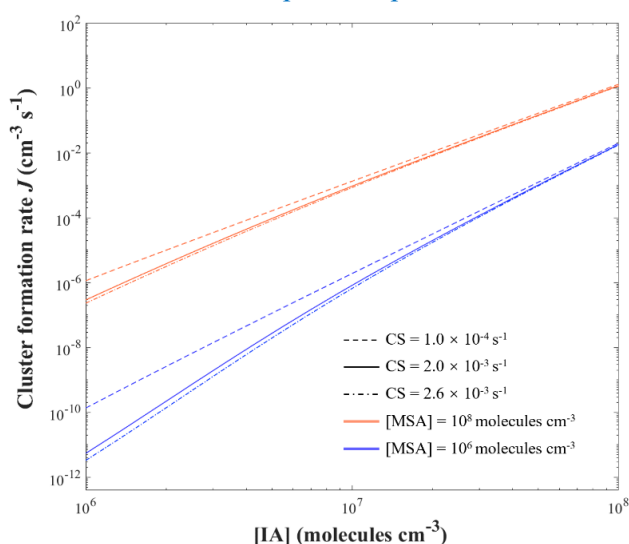


Figure S4. The simulated cluster formation rate J ($\text{cm}^{-3} \text{ s}^{-1}$) of the IA-MSA system at different condensation sink (CS) coefficients ($\text{CS} = 1.0 \times 10^{-4} \sim 2.6 \times 10^{-3} \text{ s}^{-1}$), $T = 278 \text{ K}$, $[\text{IA}] = 10^6 \sim 10^8 \text{ molecules cm}^{-3}$, and $[\text{MSA}] = 10^6$ (blue lines), 10^8 (orange lines) molecules cm^{-3} .

As the reviewer expertly suggested, as shown in Fig. 4, different CS values indeed have an impact on J . In the case of higher $[\text{IA}]$ and $[\text{MSA}]$, the J is relatively high and the effect of CS is relatively little. However, the effects of different CS values are more pronounced in the case of low J because the order of magnitude of J at this moment is comparable to or lower than the employed CS values. To ensure the rigor of the statement, we have changed the “the different CS have a minor impact on the cluster formation rate” to the “the different CS have an impact on the simulated J , especially in the case of low J (Fig. S4), but less on presenting the promotion of MSA on IA cluster formation and the main conclusions of this study.” in lines 182-184 of

the revised manuscript. Thanks again for the reviewer's kind reminder.

Specific comments:

Comment 4. The authors mention three important studies (Sipilä et al. 2016, Baccarini et al. 2020 and Beck et al. 2020) as the backbone of this study. However, none of these studies support their calculations. Sipilä et al. 2016 and Baccarini et al. 2020 indicate that IA NPF dominate the NPF events they observed at Mace Head and the central Arctic, respectively, while Beck et al. 2020 suggests SA-NH₃ is the dominating nucleation mechanism in Ny Alesund by comparing SA with nucleation rates. They do, however, suggest MSA contributes to particle growth. These studies go against what the authors suggest.

Lines 273-274: this is not enough to respond my comments in the initial screening. Agreeing with the importance of other molecules goes against their title, and thus the main theme of this manuscript. If I understand correctly from the literature, other iodine species can be formed at the same time as iodic acid. Similarly, both MSA and SA are formed from DMS in marine environments. These species are very likely to co-exist in marine environments at different levels. Picking up two species from the list and claim it to be a marine aerosol nucleation mechanism is not acceptable unless it is either supported by their calculations or by field observations. However, the mentioned three studies clearly disagree with the IA-MSA nucleation mechanisms. Additionally, the cluster formation rates derived in this study are too low to explain field observations (details below).

Response: Thanks for your pertinent feedback and suggestions. The reviewer's comments and corresponding responses are summarized below.

Item 1) from the reviewer: "The authors mention three important studies (Sipilä et al. 2016, Baccarini et al. 2020 and Beck et al. 2020) as the backbone of this study. However, none of these studies support their calculations."

Response: We agree with you that the three mentioned references (Sipilä et al., 2016; Baccarini et al., 2020; Beck et al., 2021) do not support the importance of the IA-MSA mechanism. However, the findings of these studies were based on observations obtained in specific areas and do not inherently conflict with the results presented in this manuscript. The reasons are as follows (A, B, and C):

- A) For Mace Head (Sipilä et al., 2016), the simulations were only compared with the observations at this site in Fig. 5b of original manuscript. The simulation results show that the IA-MSA mechanism plays a much smaller role of 1% in Mace Head where IA

concentrations can be as high as 10^8 molecules cm^{-3} . In the lines 238 - 239 of preprint manuscript, we have also emphasized that for regions with high IA concentrations like Mace Head, the contribution of the IA-MSA mechanism is minor and the NPF process remains dominated by IA. This conclusion does not seem to conflict with Sipilä et al. (2016).

- B) During the Arctic Ocean 2018 expedition (Baccarini et al., 2020), the simulation results based on the field conditions ($T = 268$ K, $\text{CS} = 1 \times 10^{-4} \text{ s}^{-1}$, $[\text{IA}] = 10^5 \sim 10^6$ and $[\text{MSA}] = 10^5$ molecules cm^{-3}) in the present manuscript shows a contribution of 1% - 16% to cluster formation from the IA-MSA mechanism. Most of the contribution is attributed to nucleation of IA (declared in lines 250 - 254 of the preprint manuscript). This seems not to be in conflict with the conclusion that the NPF observed by Baccarini et al. (2020) is mainly driven by IA.
- C) As to Ny-Ålesund (Beck et al., 2020), the present results in Fig. 6 suggest that the simulated rate of IA-MSA mechanism only partially matches a small fraction of the observed rates, and most of the unmatched rate might come from the contribution of SA-NH₃ ion-induced nucleation (declared in lines 270 - 272 of the preprint manuscript). This result seems also not conflicting.

In addition to the mentioned specific regions with higher $[\text{IA}]$ and relatively lower $[\text{MSA}]$, considering the vastness of the ocean, the simulations presented in this manuscript suggest that the IA-MSA mechanism could potentially play an important role in regions with sparse IA and rich MSA.

Thanks again for the reviewer's careful review and valuable comment. To add, the original intention of citing the work of Sipilä et al. (2016) and Baccarini et al. (2020) in the background was only to show that IA is a key NPF driver in coastal and polar regions, not to support the importance of IA-MSA mechanisms in these regions. And in the section of rate analysis, the citation of Sipilä et al. (2016) aims to support the reasonableness of the IA atmospheric concentration range employed in the simulations, rather than compare with the corresponding field observation.

Item 2) from the reviewer: "Similarly, both MSA and SA are formed from DMS in marine environments. These species are very likely to co-exist in marine environments at different levels. Picking up two species from the list and claim it to be a marine aerosol nucleation mechanism is not acceptable unless it is either supported by their calculations or by field observations. However, the mentioned three studies clearly disagree with the IA-MSA

nucleation mechanisms. Additionally, the cluster formation rates derived in this study are too low to explain field observations (details below)”.

Response: Indeed, as the reviewer expertly suggested, there are many components in the real atmosphere besides IA and MSA, such as SA or other iodine components that may participate in the nucleation process together. However, this study focuses more on the impact of MSA, a representative oceanic sulfur-containing acid. And other components will be taken into account in future research.

Comment 5. Fig 6: this figure is misleading. The authors overlooked the conclusions from Beck et al. 2020 which suggested SA-NH₃ to be the nucleating mechanism in Ny-Alesund, supported by measurement data. The authors adopted the cluster formation rates from Beck et al. 2020 and presented it as a rectangle in the plot which falsely overlaps with their data. If iodic acid is nucleating with MSA in Ny Alesund, one would expect that the cluster formation rates go up with increasing iodic acid. If the data are correctly presented, the authors will find that their data are very far away from the field observation they presented. All the discussions following this figure are therefore problematic. If I have to assume that the authors do calculate the IA-MSA cluster formation rates correctly (which I doubt as presented below), the results suggest that the IA-MSA mechanism does not play a role in Ny Alesund thus agreeing with Beck et al. 2020.

Response: Thanks for the helpful comments. As professionally suggested by the reviewer, we realized that the cluster formation rate of the IA-MSA mechanism simulated in Fig. 6 is at variance with the reported rate (Beck et al. 2020). Thus, the controversial Fig. 6 has been removed from the revised manuscript.

In addition, we have rewritten the corresponding results section (lines 240 – 273 in the revised manuscript) to focus more on the simulation results rather than any comparison with the field observation.

Comment 6. 5B: the authors cited iodic acid data from another study and assumed an MSA value of $1e7 \text{ cm}^{-3}$. While I agree with the authors that there are not enough MSA measurements around the world, the authors should not overclaim their quantitative results because of their huge uncertainties. Additionally, many other species are not considered in the current mechanism which further deepens their discrepancy. The numbers in this plot are repeated in the Discussions and are presented as the key results in the Results part. This will be very misleading for future readers and should be all removed since there is no way for this study to

get any remotely correct estimations.

Response: As professionally suggested by the reviewer, the simulations in Fig. 5B would indeed overestimate the impact of the IA-MSA mechanism on regions with MSA concentrations below 10^7 molecules cm^{-3} . We agree with you and have therefore removed Fig. 5B from the revised manuscript. Moreover, to present the results that the contribution of the IA-MSA mechanism is highly dependent on the MSA and IA concentration, the contribution of the different growth pathway varying with $[\text{MSA}]$ (10^6 – 10^7 molecules cm^{-3}) and $[\text{IA}]$ (10^6 – 10^8 molecules cm^{-3}) has been presented in the redrawn Fig. 5b, as follows:

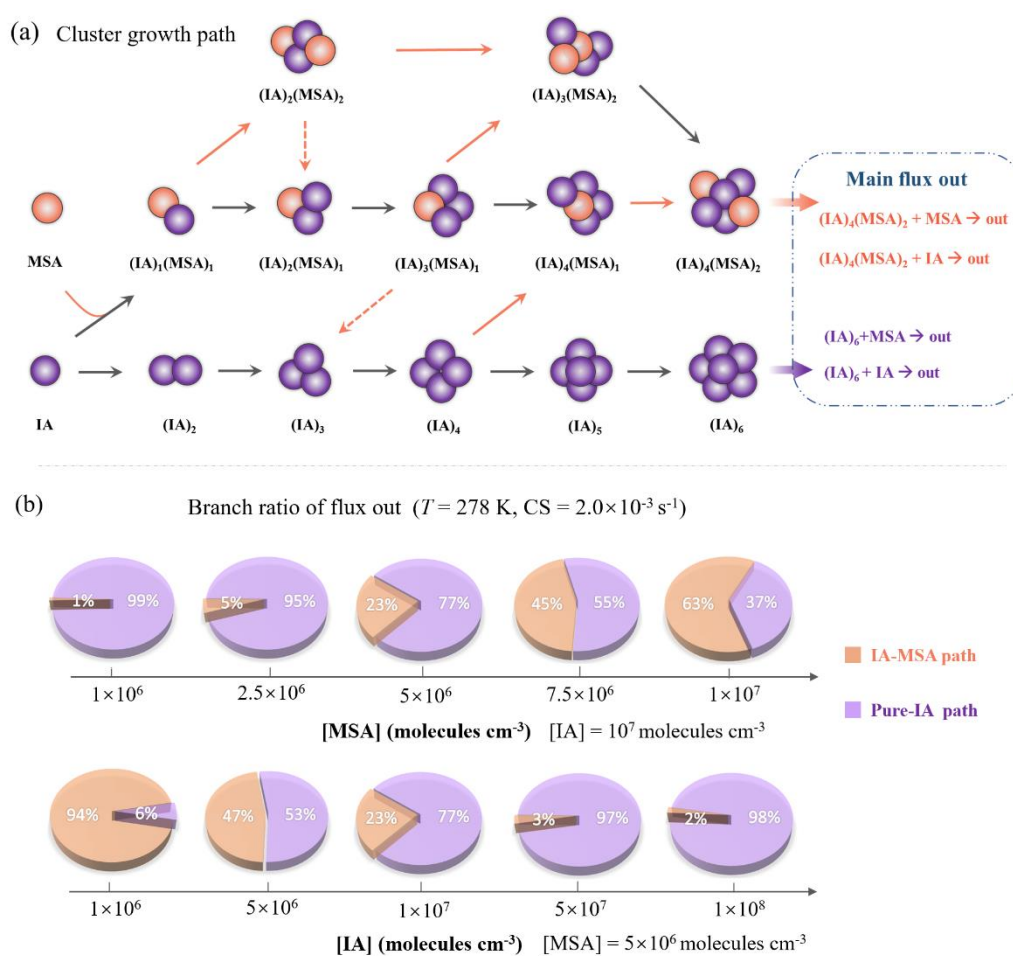


Figure 5. (a) Main cluster growth pathway of IA-MSA nucleating system at $T = 278$ K, $\text{CS} = 2.0 \times 10^{-3} \text{ s}^{-1}$, $[\text{IA}] = 10^7$ and $[\text{MSA}] = 5 \times 10^6$ molecules cm^{-3} . The black and orange arrows refer to the pathways of colliding with IA and MSA, respectively, where the dashed arrows indicate the evaporation of MSA. (b) Branch ratio of IA-MSA (orange pie) and pure-IA (purple pie) growth pathway under varying $[\text{MSA}]$ (10^6 – 10^7 molecules cm^{-3}) and $[\text{IA}]$ (10^6 – 10^8 molecules cm^{-3}).

In addition, given that the results at $[\text{MSA}] = 10^7$ molecules cm^{-3} would overestimate the impact of the IA-MSA mechanism on some sites, the relevant statement has been removed from the revised manuscript.

Minor comments:

Line13-16: repeating message.

Response: Thanks for the reviewer’s carefulness reading. The repeating message has been removed and integrated in lines 13 – 15 of revised manuscript as follows: “Moreover, MSA can promote IA clusters formation, particularly in cold marine regions with sparse IA and rich MSA. For the IA-MSA nucleation mechanism, in addition to self-nucleation of IA, the IA-MSA-involved clusters can also directly participate in the nucleation process.”

Line24: ground based open ocean nucleation was not frequently measured but relatively rarely

Response: Thanks for the reviewer’s suggestion, the “frequent” has been removed in the revised manuscript.

Line29: Marine NPF, particularly in remote areas, is more ...

Response: Accordingly, the corresponding sentence has been changed to “Marine NPF, particularly in remote marine areas, is more affected by biological emissions compared to ...” in line 26 of the revised manuscript.

Line40: The coastal NPF and low tide correlation was already established back to the early 2000s, e.g., O’Dowd, 2002.

Response: According to the reviewer’s professional suggestion, the corresponding reference for O’Dowd, 2002 has been added in line 38 of the revised manuscript.

Line45: I do not find particle composition measurements of MSA and IA in Beck et al. 2020?

Response: In fact, in the study of Beck et al. 2020, the original statement is “At Ny-Ålesund, MSA, IA and nitrate/nitric acid are detected in some of the smallest clusters...” in the caption of Fig. 3 (Beck et al., 2020). Herein, according to the study (Beck et al., 2020), the “MSA and IA found in particles” has been corrected to “MSA and IA were detected in the smallest clusters” in line 45 of the revised manuscript.

Line47: mechanism should either be singular to plural.

Response: Thanks for the reviewer’s suggestion. For consistency, the “mechanisms” has been changed to “mechanism”.

Line53: in marine environments / in marine regions

Response: According to the reviewer's suggestion, the "at marine regions" has been changed to "in marine environments".

Line92: "t" to "the"

Response: "t" has been corrected to "the".

Line143: boundary layer to troposphere? Tropopause? Stratosphere? Clarify.

Fig. 2 and throughout this manuscript. Either use molecules cm⁻³ or pptv throughout this manuscript. Don't mix these two units.

Response: Thanks for the reviewer's professional comment. According to the previous study (Williamson et al., 2019), it is "boundary layer to free troposphere". As suggested by the reviewer, the unit (pptv) used in Fig. 2 has been changed to "molecules cm⁻³" throughout this manuscript to ensure uniformity of units.

Line 152: explain beta and C. What are the subscriptions for beta and C in Fig 2C?

Fig.4: write the exact conditions (fixed values) for the three sets of simulations explicitly in the caption.

Response: Thanks for the reviewer's helpful suggestion. In Fig. 2C, the β and C represent the collision rate coefficient and monomer concentration, respectively. The subscription 'I' for $\beta_I C_I$ represents IA. Specially, β_I is the rate coefficient of cluster collision with IA monomer, and C_I is the concentration of IA monomer. These explanations have been added in the caption of Fig. 2 (lines 173 – 175 of the revised manuscript).

In addition, according to the reviewer's suggestion, the exact conditions (fixed values) for the three sets of simulations in Fig. 4 has been added in the corresponding caption (lines 204 - 205).

Line 204: it is not clear to me why reduced collision rates result in reduced R since all collision rates are reduced not just collisions between MSA and IA.

Response: Thanks! This is a valuable suggestion from the reader's perspective. I am sorry for our unclear presentation. Indeed, as the reviewer expertly analyzed, the decrease in temperature would reduce the intermolecular collision between IA and MSA, as well as IA and IA. The cause of R decay needs to be analyzed in terms of its definition as follows:

$$R = \frac{J_{\text{IA-MSA}}}{J_{\text{pure-IA}}} = \frac{J(\text{IA-MSA cluster} + \text{pure-IA cluster})}{J(\text{pure-IA cluster})}$$

The numerator term $J_{\text{IA-MSA}}$ is affected by the formation of both pure-IA clusters and IA-MSA clusters. While the denominator term $J_{\text{pure-IA}}$ is only affected by the formation of pure-IA clusters. Therefore, when the overall collision rate between IA and IA, as well as IA and MSA, is reduced due to the decrease in temperature, the numerator would be affected more than the denominator, which in turn leads to a reduced R . For the avoidance of confusion, the corresponding explanation has been added in lines 218 - 221 of the revised manuscript.

Line 221: these findings. I don't find MSA and IA detected in the particle phase in Beck et al. 2020. Could the authors specify where I can find the information there?

Response: Thanks for the reviewer's helpful suggestion. The restatement in the present manuscript is not accurate and should be "smallest clusters" rather than "particles". The corresponding statement in the work of Beck et al. 2020 is in the caption of Fig. 3 of "At Ny-Ålesund, MSA, IA and nitrate/nitric acid are detected in some of the smallest clusters...".

Line 233: the MSA concentrations are likely not always this high in these sites. Could the authors give a bit more reasoning in their choice of $1\text{e}7 \text{ cm}^{-3}$?

Response: Thanks for your valuable comment. The reason is that according to the global distribution of MSA simulated by GEOS-Chem model (Chen et al., 2018), MSA concentrations can reach ppt level in most marine areas (Fig. 2(d) in Chen et al. 2018) including our studied regions. Hence, the MSA concentration employed in the simulations was chosen at the order of 10^7 cm^{-3} .

As professionally suggested by the reviewer, the simulations in Fig. 5b ($[\text{MSA}] = 10^7 \text{ molecules cm}^{-3}$) would overestimate the impact of the IA-MSA mechanism on regions with concentrations below $10^7 \text{ molecules cm}^{-3}$. Considering the fact that the MSA concentration of $10^7 \text{ molecules cm}^{-3}$ is not applicable for some marine regions, Fig. 5b has been removed from the main text.

 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

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Appendix

Table 1. Cartesian coordinates of the IA dimer and trimer in the study of Rong et al., (2020) at the ω B97X-D/6-311++G(3df,3pd) + aug-cc-pVDZ-PP with ECP28MDF (for I) level of theory.

(IA)₂

Atoms	X	Y	Z
I	1.605061	-0.109352	-0.267819
O	2.025006	-1.477616	0.807848
O	0.441189	0.976342	0.730524
O	3.150010	1.046146	0.139201
H	3.315691	1.034733	1.088579
I	-1.605061	0.109352	0.267819
O	-0.441189	-0.976343	-0.730522
O	-2.025004	1.477616	-0.807848
O	-3.150011	-1.046145	-0.139204
H	-3.315691	-1.034732	-1.088582

(IA)₃

Atoms	X	Y	Z
I	1.545974	-1.434287	0.250626
O	2.033030	-0.476331	-1.207134
O	-0.211853	-1.929524	-0.055720
O	2.265224	-3.140916	-0.427111
H	2.210512	-3.143192	-1.389052
I	0.660386	1.874886	-0.216130
O	0.871637	0.519496	1.066009
O	-0.317464	3.088235	0.662250
O	2.415626	2.687111	0.162019
H	2.319948	3.214632	0.964029
I	-2.180521	-0.650525	-0.103596
O	-1.227504	0.715410	-0.917840
O	-2.135176	-0.387443	1.665104
O	-3.929096	0.185073	-0.450347
H	-4.015338	0.965703	0.109455