Responses to Referee #1's comments

Thanks very much for taking your time to review this manuscript. We really appreciate all your valuable 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 #1's comments are summarized below:

General Comments:

Particle nucleation events have been repeatedly observed in marine environments and are associated with large increases in the concentration of particles smaller than 20 nm. While atmospheric observations provide the definitive evidence on which compounds are essential for this process, computational methods have the advantage of studying simple binary or ternary systems and revealing important interactions. Ning et al. investigated the nucleation mechanisms of iodic acid (IA) and methane sulfonic acid (MSA) using high level quantum chemical calculations combined with the Atmospheric Clusters Dynamic Code (ACDC). They proved that MSA can participate in the early nucleation steps with HIO_3 molecules, at least from a molecular dynamic point of view. They further show that the MSA enhancement over the HIO_3 system is dependent on the HIO_3 concentration and the temperature. The paper is well written and presents new insights into the marine nucleation mechanism. Therefore, I recommend the publication of this study in ACP after considering the comments listed below.

Response: We would like to thank the reviewer for the positive and valuable comments, and we have revised our manuscript accordingly.

Comment 1: The authors have put a big emphasis on comparing their results to atmospheric observations, which is invalid in some cases and has weakened this study. For example, Figure 5b assumes that MSA concentration is equal to 1×10^7 molecules/cm^3 in all presented sites, clearly overestimating the MSA concentration in many locations. Additionally, the comparison to Beck (Beck et al., 2021)et al. (2020) shown in Figure 6 does not give additional merit to the proposed MSA-IA mechanism, especially that the authors are aware that sulfuric acid (SA) and ammonia seem to play a significant role at this site and that IA and SA could have a synergetic

role (Rong et al., 2020). It is recommended to put less emphasis on this comparison and instead focus on the results of the simulations, for example, moving figure S5 or S6 from the supplementary to the main text.

Response: We appreciate this constructive suggestion. As suggested by the reviewer (comment 1 and comment 19), the original Figure 5b has been moved to the supplement in order to weaken the comparison with the field observation. In its place, the redrawn Figure 5b in the revised manuscript presents the contribution of the IA-MSA clustering pathway at different [MSA] (10^6 – 10^7 molecules cm^{-3}) and [IA] (10^6 – 10^8 molecules cm^{-3}) in a similar form to Rong et al. (2020)'s Figure 3b. To further put less emphasis on comparison to Beck et al. (2020), Figure 6 has been replaced with Figure S5 in the main text according to the reviewer's suggestion.

Comment 2: The authors are encouraged to discuss the reasons behind the discrepancy in the formation rates presented here and in a previous study. The same group have reported that the formation rates of the pure IA system at [IA] of 1×10^8 cm^{-3} with a temperature of 278K and 2×10^{-3} s^{-1} CS is below 1×10^{-5} cm^{-3} s^{-1} (Rong et al., 2020), while the formation rates presented in Figure 3 of this study at similar conditions is higher than 1×10^{-2} cm^{-3} s^{-1}.

Response: Thanks for your suggestions. The discrepancy in the formation rates is attributed to the fact that the cluster structure and thermodynamic properties were calculated at a different level of theory in the present work. In the previous study (Rong et al., 2020), the double-ζ basis set (aug-cc-pVDZ-PP) was employed for iodine atom. To get more accurate results, the larger triple-ζ basis set (aug-cc-pVTZ-PP) was used for iodine in the quantum chemical calculations of the present manuscript. In that case, the simulated J by ACDC based on the different ΔGs of the clusters obtained by quantum chemical calculations will differ because of the sensitivity of cluster evaporation to ΔG.

Comment 3: The authors should also further discuss the limits of this study, causing 'discrepancies' with results reported in the literature. A very brief explanation is currently given in lines 273-274, but it is not sufficient. Optimally, the reader would understand the limits of this study compared to chamber or atmospheric measurements at an early stage of the manuscript. For example, the authors should discuss the difference between this study and that of He et al. (2021), resulting in different formation rates for the pure IA system, or that MSA is

never present in the atmosphere without SA or that the MSA clusters are expected to be stabilized by water in the atmosphere (Chen et al., 2020).

Response: This is a very pertinent point – thank you for bringing it up. According to the reviewer's suggestion, we have added a description of the limitations of the IA-MSA nucleation mechanism in lines 106-111 of the revised manuscript as follows:

"In addition, for nucleation processes driven by iodine-containing components, the significant impact of HIO_2 and iodine oxides (I_2O_4 and I_2O_5) needs to be considered (He et al., 2021). The present study focuses more on the nucleation mechanism of MSA and the essential driver IA. In the real marine atmosphere, other nucleation precursors, such as SA, NH_3, amine, etc., may also affect the nucleation process. Particularly with SA, because MSA and SA coexist in the air and both are formed during the oxidation of DMS in the marine atmosphere. The settings of the boundary conditions of the ACDC simulations are summarized in Table S5."

Specific comments:

Comment 4.

Line 42: Please add here the corrections He et al. (2021) made on the Sipila et al. (2016) proposed IA self-nucleation mechanism.

Response: According to the reviewer's helpful suggestion, the corrections He et al. (2021) made on the Sipila et al. (2016) was added in lines 42-44 of the revised manuscript as follows:

"…the coastal NPF is primarily driven by subsequential addition of IA and involves the participation of I_2O_5. More recently, He et al. (2021) demonstrated experimentally that, in addition to IA and I_2O_5, iodous acid (HIO_2) and I_2O_4 are also involved in the cluster formation process, with HIO_2 playing a key role in the stabilization of neutral IA clusters."

Comment 5.

Line 45: Beck et al. (2020) did not measure MSA and IA in the particle phase but in clusters using a CI-API-TOF (which could be gaseous). Thus, the sentence in its current form is misleading.

Response: Thanks for the reviewer's reminding. "…in the particle phase" has been corrected as "…in the clusters" according to the study of Beck et al. (2020).

Comment 6.

Line 83: There is no footnote for the electronic supplementary information (ESI). Please remove the symbol after 'ESI'. (Also in lines 127 and 133).

Response: According to the reviewer's suggestion, all the symbols after 'ESI' have been removed from the revised manuscript.

Comment 7.

Line 84: Please add more information on the ACDC simulations. For example, that the simulations do not include the effect of water or charge.

Response: As suggested by the reviewer, more information on ACDC simulations has been added in lines 103–106 of the revised manuscript as follows:

"In the present study, the ACDC simulations only modelled the neutral cluster formation process and did not consider the charge, nor the effect of water. Since IA is weakly bound to water, it is less inclined to exist as hydration of IA in tropospheric conditions (Khanniche et al., 2016). Meanwhile, the nucleation efficiency of MSA and water is very low (Arquero et al., 2017). Thus, the effect of water on the conclusion is limited."

Comment 8.

Line 88: What does the *J* in equation (2) stand for? It is misleading to have *J* here because the reader would think that it refers to formation rate, and the formation rate is not equal to dc/dt.

Response: Thanks for the reviewer's professional suggestion. *J* does cause some misleading in equation (2) and has been removed from that equation.

Comment 9.

Line 99: Please refer to the ACDC boundary conditions presented in Table S5 in this section or somewhere else in the text.

Response: According to the reviewer's suggestion, the ACDC boundary condition has been referred to the Table S5 in line 111 of the revised manuscript. The added content is: "The

settings of the boundary conditions of the ACDC simulations are summarized in Table S5."

Comment 10.

Line 113: Please replace 'the' by 'a' in the sentence: The similar situation...

Response: As suggested by the reviewer, 'the' has been replaced with 'a' in the similar situation of the manuscript.

Comment 11.

Line 144: Table S2 contains information about the Gibbs formation free energy only and does not include evaporation rates. Evaporation rates are presented in Table S4 and only at one temperature. This should be clarified.

Response: Thanks for the reviewer's suggestion. The contents in Table 2 and Table 4 were clarified in lines 156 and 161 of the revised manuscript separately.

Comment 12.

Line 149: Refer to Table S4 after referring to Fig. 2b.

Response: According to the reviewer's suggestion, Table S4 has been referred after referring to Fig. 2b in the revised manuscript.

Comment 13.

Line 155: The supplement also shows similar figures to Fig. 2 but at 298 K (Fig. S2) and 258 K (Fig. S3). Please refer to these figures in the main text or delete them.

Response: According to the reviewer's suggestion, Fig. S2 and Fig. S3 have been referred in the main text.

Comment 14.

Line 171: Should this be referring to the coagulation sink instead?

Response: Thanks for the reviewer's valuable suggestion. Coagulation sink is indeed an important treatment. Considering that a cluster size dependent coagulation sink coefficient has

no important effect on steady-state cluster concentrations (McGrath et al., 2012), the constant condensation sink coefficients were chosen in the ACDC simulations of the present study.

Comment 15.

Line 191: Please adjust the caption of Fig. 4 to include the MSA concentration in the purple cones, the IA concentration in the red cones and the IA and MSA concentration in the blue cones.

Response: According to the reviewer's suggestion, the description of the color of cones in the caption of Figure 4 has been added to the revised manuscript.

Comment 16.

Line 193: Also refer to Table S6 here.

Response: Table 6 has been referred in line 205 of the revised manuscript as follows: "The specific *R* values were summarized in Table S6."

Comment 17.

Line 193: Please refer to and discuss Figure S5 while presenting the temperature effect.

Response: According to the reviewer's suggestion, Figure S5 has been referred and the corresponding discussion to were added in the lines 243-245 of revised manuscript.

Comment 18.

Line 224: Beck et al. (2020) did not show MSA-IA clusters and did not measure these exclusively in the particle phase (see comment on Line 45), so this reference cannot be used here to support your conclusion here.

Response: According to the reviewer's suggestion, the citation of Beck et al. (2020) has been removed from the revised manuscript.

Comment 19.

Lines 225-255: As the authors mention, the analysis shown in this section is highly dependent

on the chosen MSA concentration for the simulations. An average MSA concentration of 1×10^7 molecules cm^{-3} is an overestimate for MSA measured in most of the cites sites. Thus, I suggest that the analysis is repeated with a more reasonable concentration or the reference to locations is omitted, and a figure similar to Rong et al. (2020)'s Figure 3b is presented instead (it could also be presented as a stacked bar graph with different temperatures listed next to each other). Otherwise, Figure 5b can be moved to the supplement, and less emphasis on it is given in the main text.

Response: According to the reviewer's valuable suggestion, the mentioned analysis has been repeated at a more reasonable concentration of MSA (2.5×10^6 molecules cm^{-3}) (Bork et al., 2014) and the resulting Figure 5b has been moved to the supplement (Fig. S5). In the revised manuscript, the modified Figure 5 presents the contribution of the IA-MSA clustering pathway at varying [MSA] (10^6 – 10^7 molecules cm^{-3}) and [IA] (10^6 – 10^8 molecules cm^{-3}), which is like Rong et al. (2020)'s Figure 3b. For your convenience, the modified Figure 5 in the revised manuscript is presented as following:

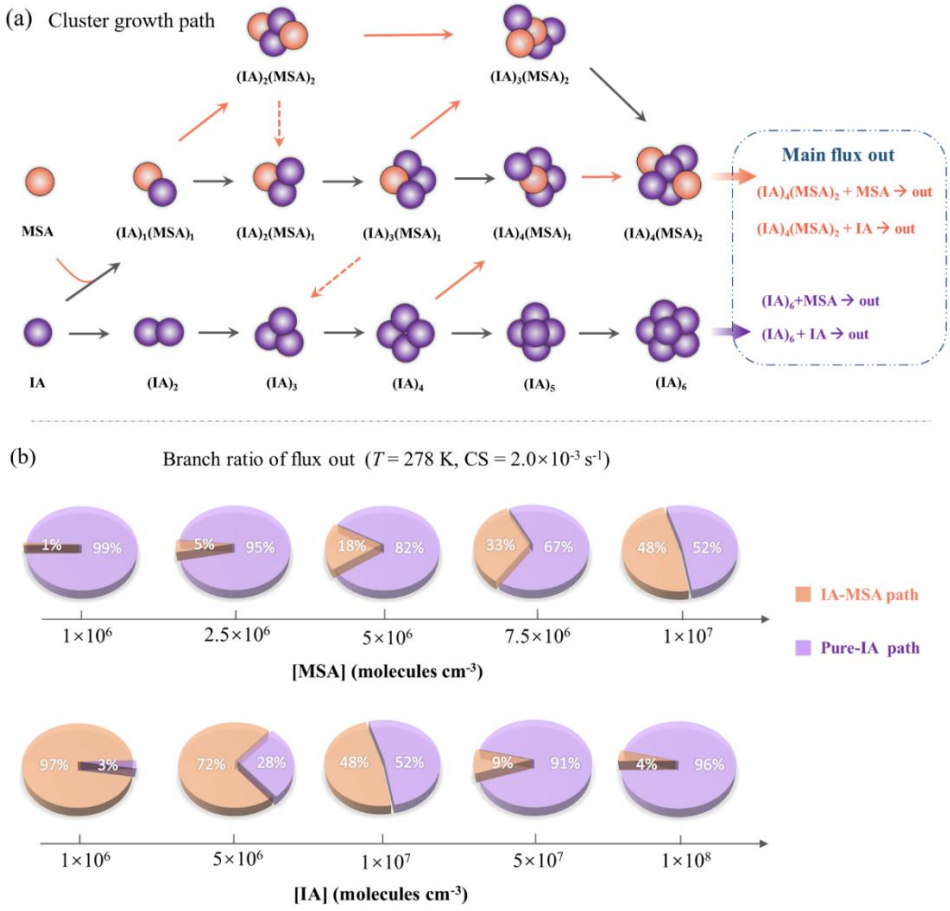

Figure 5. (a) Main cluster growth pathway of IA-MSA nucleating system at T = 278 K, CS = 2.0×10^{-3} s^{-1}, [IA] = 10^7 and [MSA] = 10^7 molecules cm^{-3}. The black and orange arrows refer to the

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 [MSA] = 10^6 – 10^7 molecules cm^{-3} and [IA] = 10^6 – 10^8 molecules cm^{-3}.

The corresponding statements of Figure 5b were added as follows:

"In the atmosphere, the distribution of IA and MSA varies by region, affecting the contribution of IA-MSA clustering pathways accordingly. Hence, the branch ratios of flux out through the IA-MSA path (orange pie) and pure-IA path (purple pie) at varying [MSA] (10^6 – 10^7 molecules cm^{-3}) and [IA] ([IA] = 10^6 – 10^8 molecules cm^{-3}) are presented in Fig. 5b to access the IA-MSA mechanism. As shown in Fig. 5b, the branch ratio of IA-MSA path and pure-IA is highly dependent on [MSA] and [IA]. At the condition of T = 278 K, CS = 2.0×10^{-3} s^{-1} and [IA] = 10^7 molecules cm^{-3}, the contribution of IA-MSA path increases from 1% to 48% with the increasing of [MSA]. Additionally, given the uneven distribution of IA, the analysis was further carried out within the atmospherically relevant range of [IA] (10^6 – 10^8 molecules cm^{-3}). The results show that the contribution of IA-MSA path decreases from 97% to 4% with the increasing of [IA] (10^6 →10^8 molecules cm^{-3}). These findings indicate that the IA-MSA mechanism contributes more in colder regions with higher [MSA] and lower [IA]. Furthermore, the branch ratio was calculated based on field conditions (temperatures and [IA]) reported by He et al. (2021) and presented in Fig. S5. The results indicate that the IA-MSA mechanism does have stronger effects in polar regions than in mid-latitude coastal regions due to lower temperatures, which is also consistent with the above findings."

To further put less emphasis on comparison to Beck et al. (2020), Figure 6 in the revised manuscript has been replaced with Figure S5 according to the reviewer's suggestion.

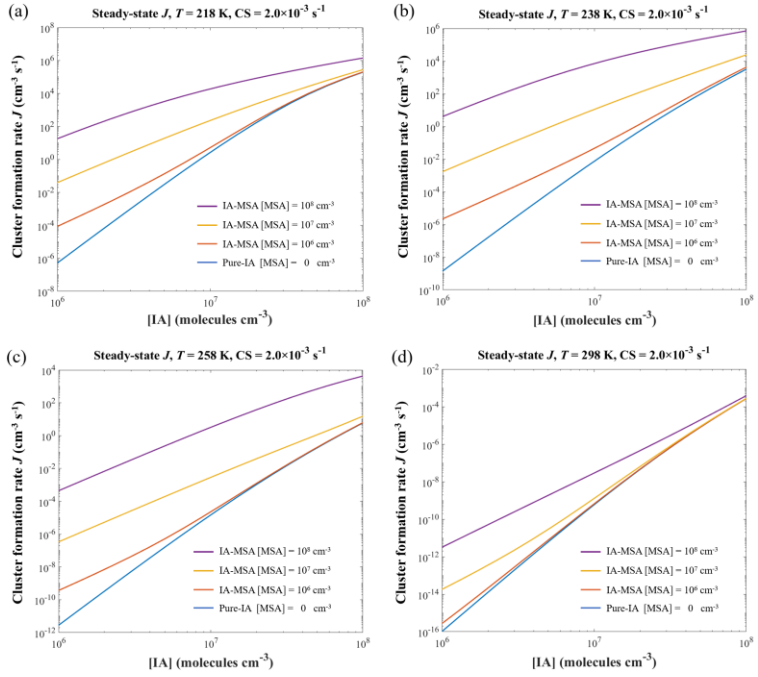

Figure 6. The simulated cluster formation rate J (cm^{-3} s^{-1}) of the IA-MSA system at different temperatures (a) 218, (b) 238, (c) 258, (d) 298 K, [IA] = 10^6–10^8 molecules cm^{-3}, [MSA] = 0, 10^6, 10^7, 10^8 molecules cm^{-3}, and CS = 2.0×10^{-3} s^{-1}.

The corresponding statements of Figure 6 were added in the revised manuscript as follows:

"Most of the analysis above in the text was performed at 278 K. In fact, temperature has a strong influence on cluster formation, so it is necessary to further probe the impact of temperature on *J* systematically. Figure. 6 presents the simulated *J* at additional temperatures (218, 238, 258 and 298 K), [IA] = 10^6 – 10^8 molecules cm^{-3}, [MSA] = 10^6 (red line), 10^7 (yellow line), 10^8 (purple line) molecules cm^{-3}. At a relatively high *T* = 298 K (Fig. 6d), the improvement by the addition of MSA was not significant compared to the pure-IA system, except at higher [MSA] = 10^8 molecules cm^{-3} and relatively lower [IA]. At lower *T* = 258 K (Fig. 6c), the enhancement on *J* by MSA is stronger in all cases except at lowest [MSA] = 10^6 molecules cm^{-3}. Moreover, such boost on *J* was further enhanced at 238 K (Fig. 6b). Lower concentrations of MSA (10^6 molecules cm^{-3}) also significantly promote the formation of IA clusters, mainly because the low temperature weakens the cluster evaporation."

Comment 20.

Lines 256-276: This section is dedicated for ACDC simulations at conditions of MSA, IA, temperature, and CS identical to those reported in Beck et al. (2020). However, the comparison to the measurements at Ny- Ålesund is not straightforward, as mentioned in the 1st general comment. Please discuss more the limitations or give less emphasis on this comparison.

Response: According to the reviewer's value suggestion, the comparison to the measurements at Ny- Ålesund (the original Figure 6) and the corresponding statement have been removed from the revised manuscript.

Comment 21.

Lines 284-286: This sentence must be rephrased to have a less strong statement because the analysis performed depends highly on the chosen MSA concentration.

Response: Thanks for the reviewer's constructive suggestion. The statement about the contribution of IA-MSA clustering pathways has been rephrased to a less strong form in lines

277-280 of the revised manuscript as follows:

"Moreover, the IA-MSA clustering pathway potentially contributes more in the colder polar regions, especially with higher [MSA] and lower [IA], than that of the mid-latitude coastal regions. The impact of the IA-MSA mechanism is highly dependent on the distribution of MSA and IA in the marine atmosphere."

Comment 22.

Line 293: It is essential to mention here the other important players. For example, MSA is never present in the atmosphere without SA as both are important DMS oxidation products.

Response: According to the reviewer's pertinent suggestion, the statement about other important players for marine NPF was added in lines 280-283 of the revised manuscript as follows:

"… multi-component nucleation model. 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."

Comment 23.

Line 307: Please review the reference list:

- There are references with missing journal names or abbreviated journal names in the author list. For example, Bates et al. (2020), Elm and Kristensen et al. (2017), Hatakeyama et al. (1982), Takegawa et al. (2020).
- There are some references that do not have the complete author list. For example, Beck et al. (2020) and He et al (2021).
- The Seinfeld and Pandis citation is incorrect and refers to Jeffrey Steinfeld's review of the book.
- Provide a URL for Stewart (2016).

Response: Thanks for the reviewer's carefulness review. The above references have been completed and all references have been double-checked.

Comment 24.

Figure S1: The caption of this figure could be misleading because the word 'stable' could be

interpreted from the view of having a ratio of collision frequency to total evaporation that is higher than 1 (Fig. 2c). So please replace the word ‘stable’ with the ‘lowest free energy’. Please also include the temperature in the caption.

Response: Thanks for the reviewer’s valuable suggestion. “…identified stable configurations” has been corrected to “…identified configurations with lowest free energy” in the revised supplement. The temperature has been added in the caption of Figure S1.

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

Reference

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