Jing Li and coworkers have responded to our concerns and significant improvements have been made to the revised manuscript. A lot of the discussion in the response letter is very valuable to the present study, so we would like the authors to add more of the comments in the response letter explicitly to the manuscript. Hence, we believe that a minor further revision is needed before publication. Our remaining concerns are outlined below:

SOC: The authors did not entirely address our concern regarding this point. Spin-orbit TD-DFT is, as far as we are aware, not implemented in Gaussian16. There are some third-party programs that can take the output of a Gaussian TD-DFT calculation and calculate the spin-orbit coupling. Furthermore, the dhf-TZVP-2c is a basis set only implemented in ORCA. Thus, we are in doubt about how you have performed these calculations. Please elaborate how exactly these calculations were carried out and do this explicitly in the manuscript. And a further correction on your statement on the results in Engsvang et al., it stabilizes at a maximum of 0.3 kcal/mol for the pure HIO3—HIO3 interaction.

Electronic Energies: Errors below 1 kcal/mol are usually said to be within chemical accuracy. If you have an error larger than this in the binding energy, you expect an error in the formation rate of at least an order of magnitude. This is based on the calculation of the evaporation rate (Ortega et al. 2012), where the binding free energy of the cluster is used in the exponential. How is this congruent with an error of 1.68 kcal/mol on for example the IA—DMA. Would that not indicate a significant overestimation of the formation rate? Could this not explain why it is only the lower bounds of your later results that overlap with the actual observations? Would it not also "leave room" for all the other nucleation pathways / stabilizing effects (ionization, hydration) that would be present in reality? Furthermore, the findings in Table R1 should be added to the manuscript or supplementary information.

Furthermore, we suggest that you tone down the argument about good agreement with observations. The agreement is because you are looking at a limited model system. Refining that system to the highest degree of accuracy will obviously result in predictions that are equal to or below the actual measurements. This is due to all the other factors that could also contribute, because very rarely experiments are set up to isolate a single nucleation mechanism (even if they try to interpret it as such). Thus, if you are overestimating the formation rate with a subset of the nucleation, you would greatly overestimate it with the whole.

The Cluster Formation Rate:

> **Limited cluster size:** We do acknowledge that your largest clusters could be past the critical cluster size. But the exact location of the critical point will depend on the binding strength of the gasses involved. Furthermore, you set out to predict the formation rate (usually reported at 1.5 nm), during the process of growing from the 1.2 nm cluster up to the 1.5 nm, clusters may be lost due to for example coagulation processes. Thus, the number, you report will still be an overestimation due to the losses incurred before they are measured.
>
> You cite a passage from Kubečka et al., however, we believe that you might have miscited the text. The context of the passage is valid in the low temperature, high

concentration regime, where SA—EDA exhibits strong, stable nucleation. The full citation is *"Nevertheless, even for the SA—EDA system, a small drop in particle formation rate is observed when increasing simulation scheme size from 3x3 to 4x4. Hence, an even larger simulation scheme with more postcritical clusters might be required to calculate the true J. This clearly indicates that, for most of the computational two-component NPF studies, the particle formation rate is overestimated at the given cluster stabilities."*

The effect of increasing the size is larger if you are not in the high concentration regime, which is most likely not the case with trace gases in the Arctic. Generally, you could expect an order of magnitude drop, all depending on how the lower temperature of your site cancels out with the lower availability of gases.

We suggest that you revise the passage you added to more adequately reflect the findings. Furthermore, we believe you should also add a section discussing the difference in your simulated formation rate and the nucleation rate reported due to the loss processes from 1.2 to 1.5 nm as pointed out above.

SA vs. MSA: The results and the discussion in your response letter is very relevant, and we strongly recommend that you include this discussion in the revised manuscript as well.

Cluster Formation Pathway Section:

Line 234: We believe that we might have misunderstood each other here. As far as we understand the IA—DMA structures and energies are obtained from Ning et al. However, the point is that at [IA] above 10^7 cm^-3, you see a reduction of the ternary nucleation to the binary IA—DMA nucleation. Thus, at these concentrations the primary nucleation pathway follows the structures calculated in Ning et al. Therefore, your simulation reduces to that of Ning et al. above this threshold, revealing further complexity below this threshold. It would be good to explicitly state that this is an original finding in Ning et al and not in the present manuscript.

Comparison with Field Observations:

For Marambio: We believe that the expanded figure is a very good addition. However, in relation to the discussion added to this we have a few minor points:

1: HIO_3 varies over this expanded interval over the time periods considered in the Quéléver et al paper which is why we believe that the expanded figure is better. However, in their discussion of the relative contributions of the two mechanisms the authors do not consider concentration when nucleation events are observed. The lower bound of 10^4 molecules cm^{-3} is during the middle of the night. For the events shown in figure 4 of that paper, it varies from a maximum of around 10^6 molecules cm^{-3} down to around 2-3×10^5 molecules cm^{-3}, with a median of 3×10^5 molecules cm^{-3} during event days. Thus, from your figure 6, IA—DMA shouldn't, on its own, account for most of the nucleation?

2: Do not set "exceed or match" as the ultimate goal. You are looking at a simulated subsystem of the atmosphere, where you are only considering the contribution of IA, MSA, and DMA. What about the potential contribution from SA, which, as shown in fig. 4 and 5 of Quéléver et al. is also present? Could other bases such as AM not also add to this? We urge the authors to discuss this in the article (see for example the previous comment on the SA vs. MSA for parts of this). Likewise, we believe that you should discuss the effects of all the contributions that you have left out of your simulated system such as ions and water. Currently you match or exceed with a relatively limited subset of the whole, which implies that you would wildly overestimate the nucleation rate if you also added SA, AM, or some of the many other things that could improve the chemical picture.

For Aboa: All experimental values reported in Xavier et al. are from Jokinen et al., figure 1c of Jokinen et al also only shows a single event day. In the supplement of Jokinen et al., fig S1A-F, they report the time-resolved simultaneous measurement of IA, MSA, and SA. The events marked in black are the events on which you base the experimental range. Based on some rough reading of the figures, we get that during events:

1: MSA is often around the lower end of your range: around 2-3×10^6 molecules cm^{-3} but did not observe any events with MSA below 2×10^6 molecules cm^{-3}, with a few events at 3-4×10^6 molecules cm^{-3} and another at 8-9×10^6 molecules cm^{-3}. Would this not indicate that we are more likely to be closer to the middle of your band, and thus more likely to exceed the observed nucleation?

2: IA is split between some events in the 3-5×10^5 molecules cm^{-3} range and some in the 7-9×10^5 molecules cm^{-3} range. With this, would we not have that it is split between the case where IA—DMA is irrelevant, and the case where it starts to account for a significant part of the nucleation?

3: SA does not dip below 10^7 molecules cm^{-3} during events, and it is thus always more prevalent than MSA. How does this fit with the figure in your response showing the relative strength of IA-SA-DMA and IA-MSA-DMA?

Generally: Overall, we would like more discussion in the manuscript of how your mechanisms fit into a broader context of the other research that has taken place. This is still excellent work. If it turns out that the MSA-assisted nucleation is maybe only a minor part of the total nucleation, that is also very much a result worthy of publication.

Furthermore: In lines 328-334 in the revised manuscript, you still cite Xavier et al. for the Aboa measurements. All the experimental/field measurements are from Jokinen et al.. The work by Xavier et al. attempts to simulate these measurements.