

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2021-595

Anonymous Referee #3

Referee comment on "Molecular-level nucleation mechanism of iodic acid and methanesulfonic acid" by An Ning et al., Atmos. Chem. Phys. Discuss.,
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This manuscript investigates the nucleation mechanism of iodic acid and methanesulfonic acid, two important species for marine particle formation and growth processes. While the topic is interesting and the presentation of this work (text, figure) is good, there are substantial flaws associated with the content.

The conclusion of this manuscript is in clear conflict with several important field observations cited here (Sipilä et al. 2016, Baccharini et al. 2020 and Beck et al. 2020). Despite the authors tried very hard to somehow use these studies to validate this manuscript, the presented results in this manuscript really show the opposite – IA-MSA nucleating is probably not very important in these regions, as shown by not matching results compared to field observations (if we have to assume that they are calculating the right cluster formation rates).

I'm surprised by comparing an earlier but recent work from the same group (Rong et al. 2020; Xiuhui Zhang is the corresponding author for both studies) and found that there are substantial differences (3 to 4 orders of difference) in the calculated cluster formation rates for the same system (pure IA nucleation) using similar methods. My investigation on this suggests that the authors are using slightly different methods (double zeta basis set in Rong et al. 2020 and triple zeta basis set in this manuscript) in these two manuscripts. However, this is unlikely the primary reason for such a substantial difference. Additionally, the authors used different geometries for the iodine clusters presented in these two studies. E.g., in Rong et al. 2020 the iodic acid dimer is connected by two halogen bonds while in this study they are connected by two hydrogen bonds. I'm astonished by the fact that there is not a single word mentioning this in this manuscript.

Additionally, a fundamental criterion in all QC+ACDC studies is that the cluster formation of the larger clusters (out of box clusters) needs to be at the kinetic rate (McGrath et al. 2012), so the accommodation coefficient can be assumed unity. This is not the case as shown by Fig.2C and Fig. S2C. The largest calculated growth to evaporation ratio (thus somehow a growth potential) is around 7 at 278 K and is around 0.2 at 298 K. In my

opinion, these are too small numbers to be considered stable and the authors need to continue their calculations to find the stable clusters. As this is a fundamental problem, the whole manuscript would need to be substantially modified to accommodate this change.

Finally, the clusters formation rates for pure iodic acid provided in this study are roughly 6 orders of magnitude lower than recent results published by the CLOUD experiments (He et al. 2021). While I understand that quantum chemical calculations can have uncertainties and experiments also have errors, such a substantial difference is not acceptable since this potentially points out substantial problems in the calculations. Note, addressing my last point will increase the discrepancy, not reducing it.

Given the significant problems noted above, I would recommend rejecting this manuscript from ACP. However, if the authors are given chance to respond, the authors are urged to address all the raised points and to interpret their results properly even if they get negative results which are still much better than overstatements, especially considering most ACP audiences do not have strong backgrounds in quantum calculations and will adopt wrong numbers from this study.

Major comments:

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 ΔG of -5.92 kcal mol⁻¹ while this study gives -9.51 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 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.

2. Another fundamental problem is that neither this study nor Rong et al. 2020 seem to even remotely repeat CLOUD measurements on pure iodine 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.

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".

4. The authors mention three important studies (Sipilä et al. 2016, Baccharini 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 Baccharini 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).

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 iodine acid is nucleating with MSA in Ny Alesund, one would expect that the cluster formation rates go up with increasing iodine 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.

6. 5B: the authors cited iodine 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.

Minor comments:

Line13-16: repeating message

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

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

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

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

Line47: mechanism should either be singular to plural.

Line53: in marine environments / in marine regions

Line92: "t" 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.

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.

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.

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?

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 $1\text{e}7 \text{ cm}^{-3}$?

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