

Atmos. Chem. Phys. Discuss., referee comment RC1
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Comment on acp-2021-595

Anonymous Referee #1

Referee comment on "Molecular-level nucleation mechanism of iodic acid and methanesulfonic acid" by An Ning et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-595-RC1>, 2021

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.

General comments

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/cm³ in all presented sites, clearly overestimating the MSA concentration in many locations. Additionally, the comparison to Beck 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.

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 $1 \times 10^8 \text{ cm}^{-3}$ with a temperature of 278K and $2 \times 10^{-3} \text{ s}^{-1}$ CS is below $1 \times 10^{-5} \text{ cm}^{-3} \text{ s}^{-1}$ (Rong et al., 2020), while the formation rates presented in Figure 3 of this study at similar conditions is higher than $1 \times 10^{-2} \text{ cm}^{-3} \text{ s}^{-1}$.

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).

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.

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.

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).

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.

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 .

Comment 9, Line 99: Please refer to the ACDC boundary conditions presented in Table S5 in this section or somewhere else in the text.

Comment 10, Line 113: Please replace 'the' by 'a' in the sentence: *The similar situation...*

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.

Comment 12, Line 149: Refer to Table S4 after referring to Fig. 2b.

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.

Comment 14, Line 171: Should this be referring to the coagulation sink instead?

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.

Comment 16, Line 193: Also refer to Table S6 here.

Comment 17, Line 199: Please refer to and discuss Figure S5 while presenting the temperature effect.

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.

Comment 19, Line 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 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.

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.

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.

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.

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 Seinfeld's review of the book.
- Provide a URL for Stewart (2016).

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.

References:

Chen, Dongping, et al. "Atmospheric implications of hydration on the formation of methanesulfonic acid and methylamine clusters: A theoretical study." *Chemosphere* 244 (2020): 125538.

He, Xu-Cheng, et al. "Role of iodine oxoacids in atmospheric aerosol nucleation." *Science* 371.6529 (2021): 589-595.

Rong, Hui, et al. "Nucleation mechanisms of iodic acid in clean and polluted coastal regions." *Chemosphere* 253 (2020): 126743.