

Author responses and changes to Manuscript: egusphere-2025-165

Dear reviewer Jonas Elm:

We are very grateful for the constructive comments from the editor and reviewers on our manuscript (ID: **egusphere-2026-1986**, original title: **Perchloric acid (HClO₄) Drives Atmospheric New Particle Formation Enhanced by Dimethylamine, ammonia and Sulfuric Acid: Mechanisms and Implications**). We have studied these comments carefully and have made corresponding revisions which marked in red in the revised manuscript. The all comments and our replies are listed as follows:

<<Comments from Reviewer Jonas Elm>>

Reviewer Comments

Wang et al studies the role of perchloric acid (PA) in atmospheric cluster formation involving sulfuric acid (SA), ammonia (NH₃) and dimethylamine (DMA). The cluster configurations are searched with the ABCcluster program and the applied computational methods are state-of-the-art for the problem at hand.

Overall, while the present study is interesting and the quantum chemical data is calculated at a decent level. However, I am missing some further interpretation of the results. I have three major critiques of the manuscript, that I would like the authors to address before I can recommend publication:

1) The introduction does not cover our knowledge on cluster formation from quantum

chemical studies. I.e. what have other people done and how does the current work fit in.

>>**Response:** Thank you for your nice comment. Engsvang et al. found PA has a high nucleation potential(Engsvang et al., 2024), but the specific nucleation mechanism remain unclear.

2) The methods (albeit state-of-the-art) are not justified. The authors should explain why certain functionals/methods are chosen based on benchmarks.

Response: Thank you for your nice comment. Many previous studies have adopted these methods and applied them to a wide range of acid-base cluster systems(Ning et al., 2026; Zhang et al., 2021; Liu et al., 2023). The initial structures will be modified and re-optimized until the optimization is successful in order to address convergence issues and failures, such as terminating with a false frequency in the optimization of the $(\text{PA})_{1-4}(\text{DMA})_{1-4}$, $(\text{PA})_{1-4}(\text{NH}_3)_{1-4}$ and $(\text{PA})_{1-4}(\text{SA})_{1-4}$ cluster geometries. In addition, these computational methods were also applied to CA-PA cluster systems (Figs. S13-S18).

3) The discussion is written in a very observant style and does not properly put in the literature into context.

Response: Thank you for your nice comment.

Each of these points are further elaborated in the comments below.

Comments

Line 30: “The results show that DMA and NH₃ can strongly interact with PA in both directions through hydrogen bonding and proton transfer.”

I do not understand the “both directions” part of the sentence here.

Response: Thank you for your nice comment. We have deleted “both directions” .

Line 32: “Even if the concentration of NH_3 exceeds that of DMA by 10-100 orders of magnitude, the cluster formation rate of PA-DMA cluster formation is much higher than that of the PA- NH_3 cluster system.”

This is a consistent finding with other acid-base clusters. Please elaborate on that this is not a unique finding and refer to the relevant literature.

Response: Thank you for your nice comment. The cluster formation rate of PA-DMA cluster formation is much higher than that of the PA- NH_3 cluster system. This is not an isolated finding. For example, Ning et al. also found that the cluster formation rate of HIO_3 -DMA is higher than that of the HIO_3 - NH_3 cluster system (Ning et al., 2022).

Line 35: “Clusters with the same number of PA molecules as DMA molecules play a key role in the growth of PA-DMA clusters.”

Similar to above, this is a usual property of acid-base clusters. Please elaborate on this aspect in the manuscript.

Response: Thank you for your nice comment. “Clusters with the same number of PA molecules as DMA molecules play a key role in the growth of PA-DMA clusters.”

This is a usual property of acid-base clusters (Lu et al., 2020).

Line 37: “The present results reveal the potential for new particle formation of PA in the Arctic boundary layer.”

I believe PA clusters were also studied in the recent work by Engsvang et al.

(<https://scholar.google.dk/citations?user=mVvvA3wAAAAJ&hl=da&oi=ao>). The

current work should be put into context with this study. See more below.

Response: Thank you for your nice comment. Engsvang et al. found PA has a high nucleation potential(Engsvang et al., 2024).

Line 46: “ At least 50% of the overall concentration of aerosol particles in the atmosphere is believed to be attributed to new particle formation (NPF) (Ehn et al., 2014).”

I do not believe this statement is a finding of Ehn et al 2014. Please find the original reference and give proper credit to the original work.

Response: Thank you for your nice comment. At least 50% of the overall concentration of aerosol particles in the atmosphere is believed to be attributed to new particle formation (NPF) (Gordon et al., 2017; Takegawa et al., 2020; Williamson et al., 2019; Zhang et al., 2012; Zhao et al., 2024).

Line 61: “ NPF can occur through a variety of nucleation pathways and involves important precursors like sulfuric acid (H_2SO_4), iodine oxoacids (HIO_x , HIO_2 , and HIO_3), low-volatility organic compounds, ammonia (NH_3), and amines, as shown by laboratory experiments and theoretical calculations (He et al., 2023; He et al., 2021;Kirkby et al., 2023).”

As this is a theoretical study there should be specific emphasis on what we know about cluster formation from calculations. What studies have there been on sulfuric acid-base cluster and clusters involving iodine oxides/oxoacids. You should put the current work into context of the existing literature.

Response: Thank you for your nice comment. Abundant atmospheric bases, such as

ammonia (NH_3) and alkylamines (methylamine (MA), dimethylamine (DMA), trimethylamine (TMA), and ethylenediamine (EDA) are recognized as important stabilizers for H_2SO_4 -driven nucleation(Almeida et al., 2013; Elm, 2017). A recent theoretical study found that mixed iodic acid-iodous acid (IA- HIO_2) clusters account for the rapid nucleation rate under neutral conditions due to the basicity of iodous acid (HIO_2) and the production of strong halogen bonds(Zhang et al., 2022).

Line 74: “ Previous studies have found that chloric acid makes a relatively small contribution to new particle formation (Wang et al., 2025).”

Quite a bit earlier than Wang et al. Engsvang (<https://scholar.google.dk/citations?user=mVvVA3wAAAAJ&hl=da&oi=ao>) studied both chloric/perchloric acid clusters with bases and other acids. This should be mentioned in the current work.

Response: Thank you for your nice comment. Engsvang et al. found PA has a high nucleation potential(Engsvang et al., 2024).

Line 75: “Perchloric acid is a major component of chloric acid, ...”

I do not understand this sentence. Do you meant that chloric acid is a precursor to perchloric acid?

Response: Thank you for your nice comment. Perchloric acid is a major component of chlorine oxyacids.

Line 79: “ The concentration of DMA surpasses 3 parts per trillion by volume, according to experiments, and the nucleation rates of DMA are significantly higher than those of ambient ammonia (Almeida et al., 2013).”

From the abstract and introduction, I get the impression that the authors are targeting the Arctic. The work by Almeida et al. is from CLOUD chamber experiments. Is the concentration of DMA in the Arctic also reaching 3 ppt? The authors should clearly convey what region they are interested in modelling.

Response: Thank you for your nice comment. During the Arctic summer, alkylamines have been detected at ppt levels (Ferrero et al., 2019). The concentration of dimethylamine (DMA) is estimated to be between 0.1 and 10 ppt.

Computational methods:

Funelling approach: The applied computational workflow follows a standard routine, which is inspired by the funnelling approaches by Temelso et al. (<https://doi.org/10.1021/acs.jpca.7b11236>) and Kubecka et al. (<https://doi.org/10.1021/acs.jpca.9b03853>). It would be worth mentioning these works in the paper for justifying the workflow. What parameters were used in the ABCluster calculations.

Choice of DFT functional: Why did you choose the ω B97X-D functional for your study? Please justify your choice by referring to potential benchmarks that demonstrate that this functional performs well for atmospheric molecular clusters.

Choice of basis set: Please justify the choice of the 6-31++G(d,p) basis set for the final geometry optimization and vibrational frequency calculations.

DLPNO-CCSD(T)/aug-cc-pVTZ: Please justify that DLPNO-CCSD(T)/aug-cc-pVTZ yield sufficiently accurate binding energies of the clusters. Which PNO convergence criteria were used in the calculations and were (T) fully iteratively calculated?

Response: Thank you for your nice comment. Many previous studies have adopted these methods and applied them to a wide range of acid-base cluster systems(Ning et al., 2026; Zhang et al., 2021; Liu et al., 2023). normal PNO was used in the calculations.

Line 120: “The results of the experiments employing the birth and death equations and the conclusions of the ACDC simulations correspond well(Mcgrath et al., 2012b).”

I do not understand this sentence. Which experiments are you referring to here? Also, the references Mcgrath et al., 2012a and Mcgrath et al., 2012b appears to be the same.

Response: Thank you for your nice comment. We have deleted Mcgrath et al., 2012a.

Line 126: “According to the ACDC manual (Mcgrath et al., 2012b), a system size of 6 molecules is large enough.”

To the best of my knowledge there is no manual in that paper. However, there is a manual at Tinja Olenius’ GitHub page. However, I cannot find the mentioning of 6 molecule clusters being “large enough” . Consider deleting this sentence.

Response: Thank you for your nice comment. We have deleted this sentence.

Line 127: “The resulting PA-DMA systems (PA)₅(DMA)₅ cluster is set as boundary clusters.”

This seems like an odd choice for the boundary clusters and will have an impact on the dynamics. If only the 5-5 cluster is allowed to grow out and contribute to the nucleation rate, the simulations will artificially not allow monomer collisions to contribute to the rate. Perhaps the (PA)₅(DMA)₄ cluster should also be added to the

boundary clusters.

Response: Thank you for your nice comment. The resulting PA-DMA systems $(\text{PA})_5(\text{DMA})_5$ and $(\text{PA})_5(\text{DMA})_4$ clusters are set as boundary clusters.

Line 128: “The concentration ranges of [PA], [SA], [DMA] and [NH₃] were defined at $10^6 - 10^8 \text{ cm}^{-3}$, $10^6 - 10^8 \text{ cm}^{-3}$, 0.1–100 ppt and 1–100 ppt, respectively”

Could the authors elaborate on why these concentration ranges were chosen and what region it may correspond to? For instance, as written in line 72 the PA concentration has been detected in an upper limit of $10^6 \text{ molecules cm}^{-3}$, so why is this the lower limit investigated?

Response: Thank you for your nice comment. We have revised Figure 5. The PA concentration of 10^6 to 10^8 cm^{-3} is indeed on the high side; it is used for computational simulations, not as an actual atmospheric value. Therefore, the PA range 10^4 to 10^8 cm^{-3} in our ACDC simulations was chosen to span the threshold over which PA-DMA nucleation becomes kinetically viable.

Line 133: Section 3 is very descriptive in nature, without many explanations about the implications of the findings. In each subsection, when describing your findings, please put it into context in the broader field of atmospheric chemistry.

Response: Thank you for your nice comment. We have made several amendments to Section 3.

Line 136-156: In Figure 1 and the surrounding text, how does these trends compare to the $(\text{PA})_{1-2}(\text{DMA})_{1-2}$ cluster structures obtained by Engsvang et al? Do you see large differences in the obtained cluster structures and stabilities?

Response: Thank you for your nice comment. Upon comparison, no significant differences were found in terms of the clustering structure and its stability(Engsvang et al., 2024).

Line 142 and 153: “N-H...Cl-O”

I guess this should be “N-H...O-Cl”

Response: Thank you for your nice comment. We have changed to “N-H...O-Cl” .

Line 160: “ ... indicating that pure PA molecules are thermodynamically less susceptible to forming clusters.”

Less susceptible compared to what in this context? Do you mean not susceptible?

Response: Thank you for your nice comment. We have changed to “...indicating that pure PA molecules are thermodynamically susceptible to forming clusters.

Line 164: “Furthermore, the negative correlation between temperature and the ΔG values of PA-DMA clusters is discovered (Figure S7, S8 and S9), suggesting that the stability of PA-DMA clusters diminishes as the temperature rises.”

This is a natural consequence of the clustering process. Upon clustering the enthalpy and entropy change is negative. Hence, the free energy will always be lower at lower temperature. I suggest you remove this sentence.

Response: Thank you for your nice comment. We have remove this sentence.

Line 168: “ ,... which suggests the possibility of collisional growth of DMA with (PA)₁₋₄ clusters.”

Did you not just establish in line 160 that the (PA)₁₋₄ clusters will not form?

Response: Thank you for your nice comment. We have remove this sentence “which

suggests the possibility of collisional growth of DMA with (PA)₁₋₄ clusters.”

Line 172: “The PA–SA cluster system exhibits the greatest ΔG values among the PA – DMA, PA – NH₃, and PA – SA cluster systems, suggesting that it is a thermodynamically challenging system.”

“ Thermodynamically challenging “ sounds a bit odd. Perhaps say “thermodynamically least stable” instead?

Response: Thank you for your nice comment. We have changed to “thermodynamically least stable” .

Line 180: “The evaporation rate of DMA-rich clusters is higher than that of PA-rich clusters, as illustrated in Fig. 3, suggesting that clusters with a high percentage of PA molecules are more stable.”

I would perhaps not say “a high percentage of PA molecules are more stable” . Consider saying “with more PA molecules are more stable” instead.

Response: Thank you for your nice comment. We have changed to “with more PA molecules are more stable” .

Line 197: “ At 278 K, for the PA – DMA cluster system, (PA)₁(DMA)₁, (PA)₂(DMA)₂, (PA)₃(DMA)₃, and (PA)₄(DMA)₄ clusters are the primary pathways and the growth process is unimpeded.”

The fact that the clusters on diagonal has the lowest actual free energy has also been seen in other acid-base systems (Olenius et al (<https://doi.org/10.1063/1.4819024>) and Elm et al (<https://doi.org/10.1021/acs.jpca.7b08962>)). It would be good to discuss that this phenomenon is consistent with the literature.

Response: Thank you for your nice comment. The fact that the clusters on diagonal has the lowest actual free energy has also been seen in other acid-base systems (Olenius et al., 2013; Elm, 2017).

Line 223: “As the temperature decreases (from 298 K to 258 K), the J value of the PA-DMA cluster system increases.”

As also discussed above, this is a direct consequence of lower T leading to a lower free energy and in turn leading to a lower evaporation rate. Please elaborate on this aspect.

Response: Thank you for your nice comment. As also discussed above, this is a direct consequence of lower T leading to a lower free energy and in turn leading to a lower evaporation rate.

Line 226: “The J value of the PA-DMA system is $1.65 \text{ cm}^{-3} \text{ s}^{-1}$ at 258 K, $[\text{DMA}] = 1 \text{ ppt}$ and $[\text{PA}] = 106 \text{ cm}^{-3}$.”

Please elaborate on what this finding tells us about the role of PA nucleation in the Arctic atmosphere. Is this competitive with other nucleation schemes such as iodine/sulfuric acid nucleation?

Response: Thank you for your nice comment. J values for the SA-DMA cluster system were about $10^{-5} - 10^0 \text{ cm}^{-3} \text{ s}^{-1}$ at 278 K, $[\text{DMA}] = 1 \text{ ppt}$ and $[\text{SA}] = 10^6 - 10^7 \text{ cm}^{-3}$ (Xie et al., 2017). J values for the PA-DMA system were about 10^{-1} to $10^3 \text{ cm}^{-3} \text{ s}^{-1}$ at 278 K, $[\text{DMA}] = 1 \text{ ppt}$ and $[\text{PA}] = 10^6 - 10^7 \text{ cm}^{-3}$. Therefore, the cluster formation rate in the PA-DMA cluster system is 3 to 4 times higher than that in the SA-DMA cluster system.

Line 244: “Eventually (PA)₅(DMA)₄ and (PA)₅(DMA)₅ clusters are stable enough to grow from the PA-DMA system.”

I do not understand how the (PA)₅(DMA)₄ cluster can grow out of the system. In the method section it was stated that only (PA)₅(DMA)₅ clusters were allowed to grow out.

Response: Thank you for your nice comment. We have changed to “Eventually (PA)₅(DMA)₅ clusters is stable enough to grow from the PA-DMA system.”

Line 264: “, ... thus promoting the rapid formation of ...”

Technically, the free energies do not tell us anything about the formation rate. Perhaps remove the word “rapid” here.

Response: Thank you for your nice comment. We have removed the word “rapid” here.

Line 284: “This study extends this paradigm to a overlooked ocean-derived chlorinated precursor: perchloric acid.”

And line 300: “... previously unrecognized atmospheric “sink” for HClO₄.”

This gives the impression that the authors are the first to state that perchloric acid could be important for nucleation in the marine atmosphere. This was also stated in the work by Engsvang et al. Please tone down such statements.

Response: Thank you for your nice comment. We have deleted “This study extends this paradigm to a overlooked ocean-derived chlorinated precursor: perchloric acid.”

“... previously unrecognized atmospheric “sink” for HClO₄.” In a region where conventional sulfuric acid-amine/ammonia nucleation is often limited by low

precursor concentrations, this PA-DMA pathway offers an additional source of ultrafine particles that can grow into cloud condensation nuclei. This has direct consequences for CCN budgets and, consequently, for cloud microphysical properties and shortwave radiative forcing over the Arctic and other remote marine environments.

This additional sink may influence the atmospheric residence time and vertical profile of HClO_4 , with potential ramifications for oxidative capacity and halogen-mediated chemistry in the polar troposphere. These findings underscore the need to revisit how chlorine-containing species are represented in global and regional climate models. Current Earth system models typically neglect HClO_4 and its interaction with amines in aerosol nucleation schemes. Incorporating the PA-DMA nucleation mechanism, especially in high-latitude and marine domains, could improve simulations of aerosol-cloud-climate interactions.

Sincerely

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