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

Dear editor and reviewers:

We are very grateful for the constructive comments from the editor and reviewers on our manuscript (ID: **egusphere-2026-1986**, original title: **Perchloric acid ($HClO_4$) 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 Anonymous Reviewer #1>>

General Comments

Utilizing a combination of quantum chemical calculations and cluster dynamics simulations (ACDC), Wang et al. investigated the clustering mechanisms of perchloric acid (HClO4, PA) with sulfuric acid (SA), dimethylamine (DMA), or ammonia (NH3). The cluster configurational space is explored using standard methodologies, relying on the global search algorithm of the ABCluster program and narrowing down the generated configurations using a funneling approach. Single-point energy calculations were then performed at the DLPNO-CCSD(T)/aug-cc-pVTZ// ω B97X-D/6-31++G(d,p) level of theory, followed by the simulation of cluster formation rates and growth pathways using ACDC.

To further strengthen the work, I suggest expanding additional discussion to better emphasize the atmospheric implications of the findings. Additionally, some improvements to the formatting and language are needed. Overall, the study presents valuable computational results and provides useful insights into the chemical mechanisms of PA cluster formation and will be suitable for publication after minor revision. Therefore, I recommend a Minor Revision. Detailed comments are provided below.

Major Comments

Lines 30 – 34: "Halogen bonding is not found in PA-DMA and PA-NH3 Even if the concentration of NH3 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-NH3 cluster system. Clusters with the same number of PA molecules as DMA molecules play a key role in the growth of PA-DMA clusters. Compared with the nucleation of PA with SA, PA nucleates more easily with alkaline gas."

Since halogen bonding is absent in all studied PA-containing clusters, repeatedly emphasizing this finding across multiple sections of the manuscript is unnecessary. Additionally, the observation that PA nucleates more easily with alkaline gases than with SA is an important and distinctive finding; this conclusion would be more impactful if introduced earlier in the abstract (e.g., at line 31).

>>**Response:** Thank you for your nice comment. PA nucleates more easily with alkaline gases than with SA. We have deleted "Halogen bonding is not found in

PA-DMA and PA-NH_3 clusters".

Lines 74 – 77: "Previous studies have found that chloric acid makes a relatively small contribution to new particle formation (Wang et al., 2025). Perchloric acid is a major component of chloric acid, and its contribution to new particle formation requires further investigation."

The research rationale requires further elaboration: the introduction does not provide a sufficiently discussion of the potential atmospheric significance of PA in new particle formation (NPF). The authors should clarify why, given that chloric acid shows limited contributions to NPF, the individual component PA is worth investigating separately.

>>**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. Perchloric acid is a major component of chlorine oxyacids, and its contribution to new particle formation requires further investigation(Engsvang et al., 2024).

Lines 101 – 106: "1000 structures with comparatively low energy were selected. In the multistep sampling scheme, the geometry optimization is carried out at the PM7, ω B97X-D/6-31+G(d,p) and ω B97X-D/6-31++G(d,p) levels of theory, and the single-point energy calculations are executed at the DLPNO-CCSD(T)/aug-cc-pVTZ level of theory based on the ω B97X-D/6-31++G(d,p) theory level."

The manuscript describes the global minimum structure search and thermodynamic calculations but does not explain why specific methods, such as PM7 for

pre-optimization, ω B97X-D for geometry optimization, and DLPNO-CCSD(T) for single-point energies, were selected. The authors should briefly justify the choice of each method and address their suitability for acid–base cluster systems. The authors are also encouraged to reference the supplementary information more systematically in the main text; while the supplementary material appears to include additional figures and computational details, these are not yet described or formally cited in the Methods section.

>>**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 $(PA)_{1-4}(DMA)_{1-4}$, $(PA)_{1-4}(NH_3)_{1-4}$ and $(PA)_{1-4}(SA)_{1-4}$ cluster geometries. In addition, these computational methods were also applied to CA-PA cluster systems (Figs. S13-S18).

Lines 112–113: "PA-DMA clusters' free energy of formation (ΔG) is computed at various temperatures (238, 258, and 278 K)."

The study calculates ΔG values at 238 K, 258 K, and 278 K. However, the rationale for selecting these specific temperatures is not adequately explained in the context of the Arctic or mid-latitude marine boundary layer. Additionally, the figure caption for Figure 4 does not specify the concentrations of PA or DMA used when computing the actual Gibbs free energies.

>>**Response:** Thank you for your nice comment. Previous study (Liu et al., 2023) show detailed atmospheric conditions are 253 K at April-2015 in Greenland, 268 K at May-2013 in Ny-Ålesund and 290 K at Aug-2019 in Helsinki. The temperatures of 238 K, 258 K, and 278 K encompass both mid-latitude coastal regions (e.g., Mace Head) and high-latitude regions (e.g., Greenland). Actual Gibbs free energy of the PA-DMA clusters at 278, 258 and 238K of [PA] = 10^6 cm^{-3}; [DMA] = 3 ppt.

Sections 3.3 and 3.4 – Atmospheric representativeness of simulated conditions:

One important issue in this study concerns the atmospheric representativeness of the simulated conditions. The PA concentration range used in the ACDC simulations (106 to 108 cm-3) is significantly higher than the concentrations recently observed in the Arctic atmosphere by Tham et al. (2023, Nature Communications, https://doi.org/10.1038/s41467-023-37387-y). As a result, the calculated nucleation rates likely overestimate what would occur under realistic atmospheric conditions. Furthermore, the concentration ranges assumed for SA and DMA are also not supported by observational references in the main text.

>>**Response:** Thank you for your nice comment. The concentration ranges of [PA], [SA], [DMA] and [NH_3] were defined at 10^6 −10^8 cm^{-3}, 10^6 −10^8 cm^{-3}, 0.1−100 ppt and 1−100 ppt, respectively(Xie et al., 2017; Ge et al., 2011; Jen et al., 2014; Almeida et al., 2013). 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). 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.

Lack of quantitative comparison with known nucleation systems:

The paper notes that the PA-DMA cluster system exhibits the fastest nucleation rate among the three systems studied, but it does not provide an in-depth quantitative comparison with other atmospherically important nucleation mechanisms. To demonstrate the significance of PA as a nucleation precursor, the authors should compare the PA-DMA system ' s nucleation rates with those of well-established systems such as SA-DMA, SA-NH3, and iodine oxoacid-driven nucleation (e.g., HIO3-DMA), as reported in recent literature.

>>**Response:** Thank you for your nice comment. *J* values for the SA-DMA cluster system were about 10^{-5} - 10^{0} cm^{-3} s^{-1} at 278 K, [DMA] = 1 ppt and [SA] = 10^6- 10^7 cm^{-3} (Xie et al., 2017). *J* values for the PA-DMA system were about 10^{-1} to 10^3 cm^{-3} s^{-1} at 278 K, [DMA] = 1 ppt and [PA] = 10^6 - 10^7 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.

Minor Comments

Title (line 3): The word "ammonia" is lowercase while all other compound names in the title ("Perchloric acid," "Dimethylamine," "Sulfuric Acid") are capitalized.

>>**Response:** Thank you for your nice comment. We have change "ammonia" to "Ammonia".

Line 72 – 73: The observed atmospheric concentration of PA is given as “3 × 104 – 1 × 106 cm-1.” The unit cm-1 is incorrect for a number concentration.

>>**Response:** Thank you for your nice comment. We have change “cm^{-1}” to “cm^{-3}”.

Line 70 – 71: “Tham et al. shown the presence of PA in the Arctic region”, should be “Tham et al. showed the presence” or “Tham et al. have shown the presence.”

>>**Response:** Thank you for your nice comment. We have change “Tham et al. shown the presence of PA in the Arctic region” to “Tham et al. have shown the presence.”

Line 95: “…we used a multi-step global minimum sampling approach. the ABCluster software was employed…”, the word “the” begins a new sentence but is not capitalized.

>>**Response:** Thank you for your nice comment. We have change “the” to “The”.

Figure 6 (page 25): The three panels of Figure 6 are labelled “(A) Steady-state J, T = 238 K,” “(B) Steady-state J, T = 258 K,” and “(A) Steady-state J, T = 298 K.”

References (lines 377 – 382): The two references cited as “McGrath et al., 2012a” and “McGrath et al., 2012b” appear to be identical.

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

Line 107 vs. Reference (line 350 – 351): The main text states that “The PM7 and ω B97X-D computations were carried out utilizing the GAUSSIAN 09 program package,” yet the corresponding reference (Frisch et al., 2016) is for Gaussian 16, Revision A.03.

The unit “molec. cm-3” is used inconsistently throughout the manuscript. It appears in the caption of Figure 6 but is omitted in Figure 5 and in the body text of Section 3.3 (e.g., lines 213 – 216), where concentration values are given in cm-3 without the “molec.” qualifier.

>>**Response:** Thank you for your nice comment. We have change the corresponding reference.

Furthermore, the conclusion section does not follow the published author guide (https://www.atmospheric-chemistry-and-physics.net/policies/guidelines_for_authors.html).

To be published as a preprint, please address all of the referee's comments, revise the conclusion section, and place more focus on the atmospheric implications.

Also, the presentation quality requires significant improvement. I recommend that the authors seek out a professional language editing service.

If these points can be addressed the paper can advance to the preprint stage.

>>**Response:** Thank you for your nice comment. 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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