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 Report #1>>

General Comments

The revised manuscript submitted by Wang et al is a substantial improvement. However, in a few cases I believe that additional clarification is needed in the author's responses. As both reviewers ask for justification of the applied methods it is a bit disappointing to see this comment being swept under the rug. My main concern is improper literature citations, which leads to a loose and quite regional referencing, which does not give credit to the original findings and developed methodologies. In many cases the this implies that the statement referenced is not actually addressed in the cited papers.

Original comment and response are given in italic below.

Line 32: “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.”

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-NH3 cluster system.This is not an isolated finding. For example, Ning et al. also found that the cluster formation rate of HIO3-DMA is higher than that of the HIO3-NH3 cluster system(Ning et al., 2022).

Citing Ning et al here, does not give credit to the original finding that DMA outcompetes

ammonia in acid-base nucleation and the general finding that base strength governs nucleation potential in acid-base clustering. This was originally shown by Kurtén et al (https://doi.org/10.5194/acp-8-4095-2008) in 2008. As this is a quite seminal paper that

essentially drove the entire community to investigate DMA in nucleation it should be acknowledged for this finding. Subsequently, for SA-base nucleation the fact that base strength dictate nucleation potential has been shown by Olenius (https://doi.org/10.1063/1.4819024), Ortega (https://doi.org/10.5194/acp-12-225 2012), Elm (https://doi.org/10.1021/acs.jpca.7b08962 and https://doi.org/10.1021/acs.jpca.7b05658) and Myllys (https://doi.org/10.1021/acs.jpca.8b02507 and https://doi.org/10.5194/acp-19-9753

2019). All this work outdates Ning et al. substantially. The finding that base strength governs nucleation potential in acid-base clustering has also been further extended to other acid systems in the Clusteromics series of papers.

Response: Thank you for your nice comment. The cluster formation rate of PA-DMA cluster formation is much higher than that of the PA-NH3 cluster system.This is not an isolated finding(Kurten et al., 2008; Olenius et al., 2013; Elm, 2017; Ortega et al., 2012; Elm et al., 2017; Myllys et al., 2018; Myllys et al., 2019).

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 yourstudy?

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.

The authors did not really address this comment. A similar comment was also raised by

the other reviewer. I am also not quite satisfied with the response that “Many previous

studies have adopted these methods and applied them to a wide range of acid-base cluster systems”, as this is not a justification. The applied computational methodology is based on substantial amount of research that has been carried out to identify the best methodology to sample atmospheric molecular clusters.

1) The applied computational workflow follows the funnelling approaches originally proposed 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. Also please state the ABCluster parameters used.

Response: Thank you for your nice comment. The applied computational workflow follows the funnelling approaches originally proposed by Temelso et al. (Temelso et al., 2018) and Kubecka et al.(Kubecka et al., 2019).

2) A large e ort has been carried out to identify that the ωB97X-D functional is the best choice for modelling atmospheric molecular clusters. This choice has been based on extensive benchmarks carried out for both the binding energies and geometries of atmospheric molecular clusters.

Binding energy benchmarks:

https://doi.org/10.1039/c3cp52616j

https://doi.org/10.1039/c6cp06851k

https://doi.org/10.1021/acs.jctc.2c00825

Geometry benchmarks:

https://doi.org/10.1021/acs.jctc.4c01046

https://doi.org/10.1021/acsomega.6c00573

The authors should justify their choice of functional based on such grounds.

Response: Thank you for your nice comment. A large effort has been carried out to identify that the ωB97X-D functional is the best choice for modelling atmospheric molecular clusters. This choice has been based on extensive benchmarks carried out for both the binding energies (Jensen and Elm, 2024; Elm et al., 2013; Elm and Kristensen, 2017) and geometries of atmospheric molecular clusters(Jensen et al., 2022; Knattrup et al., 2026).

3) The fact that the very small and quite old pople style basis set 6-31++G(d,p) is su icient for modelling atmospheric molecular clusters is also based on extensive benchmarks:

https://doi.org/10.1016/j.cplett.2014.09.060

https://doi.org/10.1016/j.comptc.2016.10.015

https://doi.org/10.1021/acsomega.6c00573

Response: Thank you for your nice comment. The fact that the very small and quite old pople style basis set 6-31++G(d,p) is sufficient for modelling atmospheric molecular clusters is also based on extensive benchmarks(Elm and Mikkelsen, 2014; Myllys et al., 2016a; Knattrup et al., 2026).

4) The application of DLPNO in molecular cluster studies was first advocated by Myllys et al (https://doi.org/10.1021/acs.jpca.5b09762) and subsequently benchmarked by Schmitz et al (https://doi.org/10.1021/acsomega.0c00436).

Also please state which PNO convergence criteria were used in the calculations and were (T) fully iteratively calculated?

The authors do not need to cite all these papers, but some of them can be used for justification of the methods. If the quantum chemical methods are not properly justified, how can we trust the results derived from them?

Response: Thank you for your nice comment. The application of DLPNO in molecular cluster studies was first advocated by Myllys et al (Myllys et al., 2016b)and subsequently benchmarked by Schmitz et al (Schmitz and Elm, 2020).

In our DLPNO-CCSD(T) calculations, we employed the NormalPNO convergence criteria as implemented in the ORCA program package. Specifically, the key truncation parameters are: TCutPairs = 1×10^{-4}, TCutPNO = 3.33×10^{-7}, TCutDO = 1×10^{-2}, and TCutMKN = 1×10^{-3}, which correspond to the default NormalPNO settings in ORCA. Regarding the treatment of the (T) correction, we used the default

non-iterative approach, i.e., DLPNO-CCSD(T0), in which the (T) contribution is evaluated non-iteratively and added to the CCSD energy.

Sincerely

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