Response to Reviews

We highly appreciate the comments from the reviewers and all the points have been addressed in the revised paper. We hope that the following responses are satisfying and that the paper can be accepted for publication. The reviewers' comments have been reproduced in blue text below, followed by our point-by-point replies. The page numbering refers to the marked manuscript.

Reviewer #1

The authors have addressed the most essential suggestions, primarily by revising the figures and removing some disputable text. While these changes represent a necessary first step, the manuscript would benefit significantly from a more rigorous and comprehensive investigation of the observed trends. The current analysis leaves the impression that the authors have not yet fully explored the depth and context of their data. Two key observations motivate this recommendation: 1) The authors' analysis focuses on a limited set of selectively chosen comparisons, despite the availability of a rich dataset that could be analyzed more broadly. (Unfortunately, the thermochemical differences in the selected comparisons are often so subtle that they approach the accuracy limit of the employed quantum-chemistry methodology. Ultimately, it remains at the authors' discretion to determine how far they are willing to push the interpretation of their data.)

Again we have addressed some of the points directly in the PDF, and picked out a few comments related the comment above to directly address here:

"Although CCSD(T) is commonly considered to reach chemical accuracy (1kcal/mol), it remains a bold statement to say something is "1 kcal/mol less stable" based on calculations only. From my perspective, the only safe statements here are:
1) All three clusters including 1SA,1DMA are of similar stability. All three clusters including 2SA,2DMA are of similar stability.
2) 2SA,2DMA,OOM clusters are more stable than 1SA,1DMA,OOM clusters. "

Author reply:

We agree with the reviewer that these are only minor nuances, and it might be worth to be more transparent in the fact that the clusters are very similar in free energies. However, we still believe it is worth to point out the trends, despite these being minor differences. We have added the following sentence to the manuscript to clarify.

Page 8 added

It is seen that all the $(SA)_{1-2}(Base)_{1-2}(OOM)_1$ clusters have very similar free energies for all three OOMs within each cluster type. Not surprisingly, ...

"Again, you compare calculations in the sub 1 kcal/mol region. You say that SA1,MA2,PDPE2 is 0.6 kcal/mol more stable thant SA1,DMA2,PDPE2, which in relative terms is 1.2% more stable. You are not honestly believing that DLPNO-CCSD(T) calculations are that accurate, right?"

Author reply:
We agree with the reviewer that a 0.6 kcal/mol difference is indeed within the uncertainty of the applied method. We still believe it is worth to explicitly state these minor differences but acknowledge that it should be more transparent that is within the uncertainty. We have added the following sentence to clarify.

Added page 10:
However, it should be noted that the 0.6 kcal mol^{-1} difference is within the uncertainty of the DLPNO-CCSD(T_0) energies.

"In line 175, you write that PDPE less likely to grow beyond two units, because all carboxyl groups form bonds. In contrast, for CHA and MBTCA you predict that there are possibilities for growth due to the free carboxyl groups. Here it reads like all OOMs will behave the same upon growth beyond two units.

Author reply:
We agree with the reviewer that we are not very specific here. We have modified the sentence to clarify that we are referring to PDPE in line 175.

Page 7 from
This does mean that there is no obvious places for growth, and expanding the cluster would therefore involve some restructuring.

to:
This does mean that there is no obvious places for growth for the PDPE cluster, and expanding the cluster would therefore involve some restructuring.

Also, while for the pure organic clusters, PDPE is expected to cluster worse than MBTCA and CHA, for the mixed clusters you have shown that MBCTA clusters worse than PDPE and CHA. Could you comment on that? "

Author reply:
Indeed, it is worth to comment on that just because the $(OOM)_2$ dimer cluster leads to "closed" structures, it does not mean that this is the same case once sulfuric acid and bases are thrown in the mix. We agree that this point is worth further stressing in the manuscript.

Page 7 from:
However, introducing other nucleation precursors into the clusters might change their structure.

to:
However, introducing other nucleation precursors such as sulfuric acid and bases into the clusters might change their structure and lead to additional hydrogen bond moieties that support further growth.

2) Although the full dataset reveals distinct differences among PDPE, CHA, and MBTCA,

the authors conclude that their behavior is effectively the same. Their data, however, tells a clear story: CHA and PDPE behave differently from MBTCA.

Author reply:
Indeed, there is a noticeable change between the three tricarboxylic acids in the cluster thermochemistry data, as described in section 3.1. However, the cluster formation potentials, which is essentially the atmospherically relevant parameter, illustrates that the three compounds behave similarly once the kinetics are taken into account. We acknowledge that this might seem like a contradiction and has clarified this aspect in the conclusions.

Page 15 from
Using quantum chemical calculations, we studied the intermolecular interactions between the OOMs and SA–base clusters, and used the thermochemical data to study the cluster formation potentials of SA–base–OOM clusters. We find that all three OOMs are present in the most important outgrowing clusters, and that the trends across all three OOMs are similar, especially in the SA–DMA–OOM systems, which also had the highest cluster formation potentials. The insentivity to the specific OOM suggests that the functional groups, rather than the organic molecule itself, is most important for cluster formation and growth

to:
Using quantum chemical calculations, we studied the intermolecular interactions between the OOMs and SA–base clusters, and used the thermochemical data to study the cluster formation potentials of SA–base–OOM clusters. While the thermochemistry reveals distinct differences among PDPE, CHA, and MBTCA, the cluster formation potentials show similar trends cross all three OOMs, especially in the SA–DMA–OOM systems. We find that all three OOMs are present in the most important outgrowing clusters. The insentivity to the specific OOM suggests that the functional groups, rather than the organic molecule itself, is most important for cluster formation and growth.

Reviewer #3

In this study, Pedersen et al. study potential new particle formation of clusters with various tricarboxylic acids, sulfuric acid, and various bases (amines and ammonia). The selection of these molecules is certainly relevant. First, it follows the clusters-of-functional groups approach. Second, there is an increasing amount of literature indicating that organic molecules, and specifically carboxylic acids, promote aerosol formation. The authors find that these organic acids promote cluster formation of SA and the bases. I especially appreciate how their manuscript highlights the interplay between binding free energy strength and the geometric arguments of growth. This is a well-thought-out study, and I recommend it for publication once the following comments are addressed.
1. The methodology in Section 2.2 describing configurational sampling is somewhat unclear. It appears that ABCluster is used for initial sampling, after which only the lowest energy GFN1-xTB structure is passed to CREST. The wording suggests that CREST may only explore internal rotations of this single configuration. If so, how do the authors ensure that the relative arrangement of molecules identified at the GFN1-xTB level is representative of the global minimum, given known inaccuracies in the GFN1-xTB potential energy surface? If the 100 cluster structures selected were chosen from a combined set of both ABCluster and

CREST structures, that should be clarified.

Author reply:
It is correct that all the 100 clusters passed on to DFT optimization originates from the CREST calculations. The wording in the methodology section may be unclear, as CREST uses metadynamics to search the potential energy surface and escape local minima. ABCluster is an algorithmic tool, also designed to search the entire potential energy surface, however, with the settings used, it does not allow bond rotation, which is why CREST has also been used. We have updated the manuscript to make this more clear.

Page 4 from:
The initial cluster structures were generated using ABCluster. These were optimized using GFN1-xTB. The structure with the lowest electronic energy at this level was used as input for additional configuration sampling using CREST, which accommodated internal rotations of bonds for flexible molecules when searching the PES.

To:
The initial cluster structures were generated using ABCluster. These were optimized using GFN1-xTB. The structure with the lowest electronic energy at this level was used as input for additional configuration sampling using CREST. The molecular and metadynamics within CREST allows for thorough exploration of the PES, including the internal rotations of bonds for flexible molecules, which was not accomodated for in ABCluster.

2. Section 2.2 notes that DLPNO energies were calculated for the five clusters with the lowest electronic energy at the DFT-level. What energetic range did this cover? Please compare this to average errors of the electronic energies of the functional.

Author reply:
The energetic range varies. This cutoff is not defined by a specific energy threshold; rather, it is motivated by the findings of Jensen et al. who demonstrated that across 117 cluster systems studied at the ωB97X-D/6-31++G(d,p) level of theory, the true minimum-energy structure fell outside the five lowest-energy candidates in only 4 cases. This reasoning has been added to the manuscript.

Page 4 from:
Single point energies using DLPNO-CCSD(T_0)/aug-cc-pVTZ were calculated for the five clusters with the lowest electronic energy at the DFT-level.

To:
Single point energies using DLPNO-CCSD(T_0)/aug-cc-pVTZ were calculated for the five clusters with the lowest electronic energy at the DFT-level, as recommended by Jensen et al.

3. Please add a discussion of how Gibbs free energies were computed. Were anharmonic effects considered in the thermochemistry? If so, please clarify how they were treated. The quasi-harmonic threshold is mentioned in the Figure 3 caption but not in the main text.

Author reply:

The anharmonic effects are not considered in the thermochemistry. Low-lying rotational degrees of freedom are treated with the quasi-harmonic approximation, and we agree that proper discussion of this was wrongly omitted from the manuscript. This has been added to the manuscript for clarity.

Added page 4-5:
The binding Gibbs free energy $\Delta G_{\text{binding}}$ is calculated as

$$\Delta G_{\text{binding}} = G_{\text{cluster}} - \sum_i G_{\text{monomer},i}. \quad (1)$$

The quasi-harmonic approximation is implemented, with a threshold value of 100 cm^{-1}, to mitigate unphysical stabilizing effects from low-lying vibrational frequencies.

4. Is there a reason that clusters containing two different OOM species were not considered? Including mixed OOM systems could introduce additional geometric flexibility and potentially expose functional groups (e.g., COOH) that facilitate further growth. A brief justification of this choice would strengthen the study.

Author reply:
We agree with the reviewer that it would be interesting to explore the effect of different OOMs. The data presented in the current manuscript represents many months of run-time on our local computing cluster, and is thereby not feasible for this study. However, we agree that this aspect should be mentioned in the manuscript. We have added an elaborating sentence to the conclusions. *Added page 15:*
It would also be interesting to further study mixed OOM systems, as these could introduce additional geometric flexibility and potentially expose additional COOH functional groups that facilitate the further growth.

Small edits: 1. Many instances of "figure" and "table" are not capitalized in the text. This will need correcting. 2. Abstract: "MTBCHA AND CHA" should be "MTBCHA and CHA"

Author reply:
We appreciate these corrections, and the manuscript has been updated accordingly.