Responses to Referee #3's comments

We are grateful to the reviewers for their valuable and helpful comments on our manuscript **"Mechanistic insights into nitric acid-enhanced iodic acid particle nucleation in the upper troposphere and lower stratosphere"** (MS No.: egusphere-2025-1194). We have revised the manuscript carefully according to reviewers' comments. The point-to-point responses to the Referee #3's comments are summarized below:

Jing Li and coworkers have investigated the nucleation behavior of the combined iodic acid (IA), nitric acid (NA), and ammonia (AM) systems up to hexamers. They have done this under upper tropospheric and lower stratospheric conditions. They compare this with the already studied, equivalent systems with iodic acid replaced by sulfuric acid (SA). These types of combined systems are relevant to study due to the complexity of the real world atmosphere, where different chemical species can either work in synergy enhancing their nucleation beyond what two separate nucleation pathways can provide, or they can hinder further nucleation reducing the total nucleation.

This paper suggests that nitric acid can play a vital role in enhancing the nucleation exhibited by iodic acid, and that when studying iodine-driven nucleation outside of the lower troposphere / boundary layer one should keep the impact of this in mind.

<u>Overall, I will recommend publication, with the caveat that the following concerns regarding the discussion of the results are addressed, I have seen the first review, and have tried to avoid reiterating any concerns discussed there unless I had something extra to add:</u>

Response: We sincerely thank for the reviewer's careful review of our manuscript, as well as the valuable and positive comments.

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1) **Regarding the concentrations used:**

The authors have found different studies from literature detailing concentration measurements from different parts of the atmosphere. I would recommend that the authors have a more detailed discussion of this in the methods section, where they go through exactly what has been measured

in different areas of the troposphere and stratosphere. This is because the authors cite works with for example measurements that just reach the lower troposphere of IA, but uses measurements from the upper troposphere / lower stratosphere for NA. Please correct if I am wrong, but the beginning of the free troposphere is a few kilometers above ground (depending on the local conditions), while the upper troposphere is quite vaguely defined, but could potentially be several kilometers higher, or is it just the free troposphere up to the tropopause?

Thus, I would like a more specific and detailed discussion of where you use concentrations directly, and where exactly they have been measured, and where you have to assume that for example the concentration in the upper troposphere is equivalent to the concentration at the start of the free troposphere. That is, what kind of concentration ranges are measured where in the atmosphere.

Response: This is a very insightful point – thanks for bringing it up. In this study, the adopted precursor concentrations were set in ACDC simulations based on results from field observations and model simulations. Following the reviewer's suggestion, we have added the relevant analysis in the revised manuscript (lines 164-189, page 7-8). For the convenience of review, we have copied the corresponding statement below:

"To further evaluate the nucleation efficiency of the IA–NA–NH$_3$ system, we performed ACDC simulations to calculate cluster formation rates (J, cm^{-3} s^{-1}) under the UTLS conditions. The concentrations of the nucleation precursors (IA, NA, and NH$_3$) used in this study were primarily based on currently available field observations and model simulation data.

Concentration of IA. Sipilä et al. (2016) reported that atmospheric IA concentrations range from 10^6 to 10^8 molec. cm^{-3} during new particle formation events at the Mace Head site in the boundary layer. Moreover, Salignat et al. (2024) reported an average IA concentration of 2.9×10^5 molec. cm^{-3} at the Maïdo Observatory (2150 m above sea level) over the Indian Ocean, with peak values reaching up to 3.3×10^6 molec. cm^{-3}. Although, to our knowledge, gaseous IA levels at higher altitudes have not yet been reported, vertical profiles of IO radicals, a key intermediate in IA formation, are available across different elevations. Importantly, CLOUD experimental evidence shows a strong correlation between IA concentrations ([IA]) and IO radical levels, and IA formation of this process appears to be insensitive to variations in O$_3$, H$_2$O, and temperature

(Finkenzeller et al., 2023). Notably, the mixing ratio of IO radicals exhibits minimal variation with altitude, particularly above 2 km (Saiz-Lopez et al., 2014; Karagodin-Doyennel et al., 2021). This suggests that at high altitudes, IA might exhibit similar concentrations at ~2 km altitude (~10^6 molec. cm^{-3}), although lower IA levels are also possible. This issue warrants further investigation in future studies. Given the limited field observations of IA concentrations in the UTLS, this study adopts an IA concentration range of 10^5 to 10^6 molec. cm^{-3}, which are comparable to or even lower than those observed at around 2 km altitude.

Concentration of NA. NA mixing ratios at an altitude of approximately 10 km range from 100 to 2500 pptv, with average values exceeding 1000 pptv (Singh et al., 1996). Meanwhile, theoretical model investigations indicated that NA mixing ratios in the upper troposphere range from 0.1 to 2 ppbv (Laaksonen et al., 1997). In addition, gas-phase NA concentrations in the tropical lower stratosphere that were typically 0.1 ppbv or lower (Popp et al., 2006). Therefore, based on the environmental conditions such as temperature and pressure in the UTLS, the concentration of NA in this study was set over a broad range, from 10 pptv to 10 ppbv (10^8 – 10^{11} molec. cm^{-3}).

Concentration of NH$_3$. Based on satellite observations and high-altitude aircraft measurements, NH$_3$ mixing ratios in the upper troposphere over the Asian monsoon region can reach up to 30 pptv as a three-month average, and up to 1.4 ppbv in hotpots (Höpfner et al., 2016; Höpfner et al., 2019). Accordingly, the NH$_3$ concentration was set to 30 pptv in this study, based on the typical conditions of the UTLS. Under these conditions, specifically at a temperature of 220 K and a pressure of 0.2 atm, 30 pptv corresponds to 3×10^8 molec. cm^{-3}.”

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2) **Regarding the choice of method:**

I am missing some discussion on the expected accuracy of the quantum chemical calculations carried out in the study. For example, DLPNO-CCSD(T) with a triple zeta basis set is often used in lieu of the "gold-standard" CCSD(T), but how accurate is it for heavy atoms such as iodine where relativistic effect can start to become relevant. Is it expected to overestimate, or underestimate, and if so, do we have any knowledge of how much? You also use a pseudo-potential for iodine, how accurate is this choice of simplification for clusters, is it known? If not,

please explicitly say that you assume transferability of benchmark results from other chemical species if that is the case.

As the other reviewer has pointed out, you also mix basis sets within the same calculation (6-311++G(3df,3pd) and aug-cc-pVTZ-PP), which one should be careful of. aug-cc-pVTZ is defined for the other atoms too, why not use that one?

Thus in general, I would like to see the "Quantum Chemistry Calculation" sections expanded, with a discussion of how the different assumptions used in your study affects your final binding energies, because we have to make some assumption / simplifications to make the calculations feasible. However, it is important to keep in mind the accuracy of the QC, because even small errors can significantly affect the ACDC nucleation rate.

Furthermore, if a choice of method is simply based on precedence / to be comparable to other results, this should be explicitly laid out.

Response: Thanks for the professional suggestions.

Item 1) from the reviewer: I am missing some discussion on the expected accuracy of the quantum chemical calculations carried out in the study. For example, DLPNO-CCSD(T) with a triple zeta basis set is often used in lieu of the "gold-standard" CCSD(T), but how accurate is it for heavy atoms such as iodine where relativistic effect can start to become relevant. Is it expected to overestimate, or underestimate, and if so, do we have any knowledge of how much?

Response: Indeed, the prior benchmark study has compared the calculations by CCSD(T) and DLPNO-CCSD(T) methods and found that, for closed-shell systems involved in hydrogen atom transfer reactions, the differences in calculated barrier heights at DLPNO-CCSD(T)/aug-cc-pVnZ and CCSD(T)/aug-cc-pVnZ (n = D, T, and Q) levels of theory consistently remain below ~0.8 kcal mol^{-1} (Mallick, Roy and Kumar, 2020). Following the reviewer's suggestion, we additionally calculated the single-point energies (ΔE) of the most stable structures of $(IA)_1(NA)_1$, $(IA)_1(NH_3)_1$, and $(IA)_1(NA)_1(NH_3)_1$ clusters obtained in this study at the CCSD(T)/aug-cc-pVTZ(-PP) level of theory. These results were then compared with those obtained at the DLPNO-CCSD(T)/aug-cc-pVTZ(-PP) level of theory. The results of comparison are presented in Table S7.

Item 2) from the reviewer: You also use a pseudo-potential for iodine, how accurate is this choice of simplification for clusters, is it known? If not, please explicitly say that you assume transferability of benchmark results from other chemical species if that is the case.

Response: Considering that the iodine atom is a heavy atom with many inner-shell electrons, a small-core (28 electrons) relativistic pseudopotential (aug-cc-pVTZ-PP with ECP28MDF) is employed for iodine atom in this study to enable efficient calculations. More importantly, Peterson et al. (2003) demonstrated that the errors associated with the use of small-core pseudopotentials are negligible relative to all-electron calculations, with bond length deviations of less than 0.006 Å and dissociation energy discrepancies below 0.3 kcal mol^{-1}. This pseudo-potential has been successfully applied in other iodine-containing NPF nucleation studies (Xia et al., 2020; He et al., 2021; Zhang et al., 2022; Ma et al., 2023).

Item 3) from the reviewer: As the other reviewer has pointed out, you also mix basis sets within the same calculation (6-311++G(3df,3pd) and aug-cc-pVTZ-PP), which one should be careful of. aug-cc-pVTZ is defined for the other atoms too, why not use that one?

Thus in general, I would like to see the "Quantum Chemistry Calculation" sections expanded, with a discussion of how the different assumptions used in your study affects your final binding energies, because we have to make some assumption / simplifications to make the calculations feasible. However, it is important to keep in mind the accuracy of the QC, because even small errors can significantly affect the ACDC nucleation rate.

Furthermore, if a choice of method is simply based on precedence / to be comparable to other results, this should be explicitly laid out.

Response: As the reviewer correctly pointed out, the mixed basis set used in this study was primarily intended to maintain consistency with our previous work. To validate the reliability of the adopted mixed basis set (6-311++G(3df,3pd) and aug-cc-pVTZ-PP), we conducted a series of benchmark calculations. In addition, we carried out a comparative analysis of the CCSD(T) and DLPNO-CCSD(T) methods to address the reviewer's concerns regarding methodological accuracy. In response to the reviewer's request, we have included a summary of the benchmark results in the "Quantum Chemical Calculations" section to assist readers in understanding the computational choices. And the corresponding details are provided in the revised Supporting

Information (pages 6-7). For the convenience of the review, we have copied the corresponding analysis as following:

"To confirm that the structures of the most stable clusters optimized at ωB97X-D/6-311++G(3df,3pd) (for H, O, and N atoms) + aug-cc-pVTZ-PP (for I atom) level of theory are reasonable, three clusters ((IA)$_1$(NA)$_1$, (IA)$_1$(NH$_3$)$_1$, and (IA)$_1$(NA)$_1$(NH$_3$)$_1$) were optimized by ωB97X-D functional with 6-311++G(3df,3pd) (for H, O, and N atoms) + aug-cc-pVTZ-PP (for I atom) and aug-cc-pVTZ (for H, O, and N atoms) + aug-cc-pVTZ-PP (for I atom) basis sets. And the optimized cluster structures with different basis sets were compared by calculating the root-mean-square deviations (*RMSD*, the index of the difference between the two structures, is calculated as Eq. (S3)).

$$RMSD = \sqrt{\frac{1}{N}\sum_i^n [(x_i - x_i')^2 + (y_i - y_i')^2 + (z_i - z_i')^2]}, \quad \text{(S3)}$$

where (x_i, y_i, z_i) and (x_i', y_i', z_i') are the coordinates of the atom i of two structures optimized with two different basis sets, respectively. As shown in Table S7, the *RMSD* between the structures of any one of three clusters are lower than 0.1 Å, indicating that the differences among structures of clusters optimized with two different basis sets are negligible.

Besides, to test the effects of the chosen basis set on the Gibbs free energy of cluster formation (ΔG, kcal mol^{-1}), the optimizations and frequencies calculations of (IA)$_1$(NA)$_1$, (IA)$_1$(NH$_3$)$_1$, and (IA)$_1$(NA)$_1$(NH$_3$)$_1$ clusters were performed by ωB97X-D functional using 6-311++G(3df,3pd) (for H, O, and N atoms) + aug-cc-pVTZ-PP (for I atom) and aug-cc-pVTZ (for H, O, and N atoms) + aug-cc-pVTZ-PP (for I atom) basis sets, respectively. The final Gibbs free energies are calculated by Eq. (S4):

$$\Delta G_{\text{DLPNO–CCSD(T)}} = \Delta G_{\text{thermal}}^{\omega\text{B97X–D}} + \Delta E_{\text{DLPNO–CCSD(T)}}, \quad \text{(S4)}$$

The thermal contributions ($\Delta G_{\text{thermal}}^{\omega\text{B97X–D}}$) were obtained from calculations using two different basis sets. Subsequently, the single-point energies ($\Delta E_{\text{DLPNO-CCSD(T)}}$) of the corresponding optimized clusters were calculated at the DLPNO-CCSD(T)/aug-cc-pVTZ(-PP) level of theory. The final Gibbs free energies ($\Delta G_{\text{DLPNO-CCSD(T)}}$) were derived by combining the thermal contributions with the single-point energies, and the differences between the two basis sets ($\Delta\Delta G_{\text{DLPNO-CCSD(T)}}$) were then evaluated. Furthermore, to assess the accuracy of the DLPNO-

CCSD(T) method employed for single-point energy calculations, a comparison was conducted against the results obtained using the more accurate CCSD(T) method. Here, $\Delta G_{\mathrm{CCSD(T)}}$ denotes the energy calculated at the CCSD(T)/aug-cc-pVTZ(-PP)//ωB97X-D/6-311++G(3df,3pd) (for H, O, and N atoms) + aug-cc-pVTZ-PP (for I atom) level of theory. As presented in Table S7, the $\Delta\Delta G$ values for the three clusters are less than 1 kcal mol^{-1}, suggesting that the differences in the calculated Gibbs free energies obtained using the two basis sets, i.e., 6-311++G(3df,3pd) (for H, O, and N atoms) + aug-cc-pVTZ-PP (for I atom) and aug-cc-pVTZ (for H, O, and N atoms) + aug-cc-pVTZ-pp (for I atom), are minimal. Moreover, the energy differences after the correction of DLPNO-CCSD(T) and CCSD(T) methods are also minor, suggesting that the DLPNO-CCSD(T) method provides sufficiently reliable results compared to the "gold standard" CCSD(T) results.

In summary, these benchmarks sufficiently proved the reliability of methods used in this study, and therefore the results and conclusions of our study are reliable and convincing."

Table S7. Structural *RMSD* (in Å) and Gibbs free energy (in kcal mol^{-1}) comparisons of $(IA)_1(NA)_1$, $(IA)_1(NH_3)_1$, and $(IA)_1(NA)_1(NH_3)_1$ clusters at different levels of theory.

Clusters	*RMSD*	$\Delta G_{\mathrm{DLPNO\text{-}CCSD(T)}}$[1]	$\Delta G_{\mathrm{DLPNO\text{-}CCSD(T)}}$[2]	$\Delta\Delta G_{\mathrm{DLPNO\text{-}CCSD(T)}}$	$\Delta G_{\mathrm{CCSD(T)}}$
$(IA)_1(NA)_1$	0.005	-4.90	-4.42	0.50	-4.92
$(IA)_1(NH_3)_1$	0.004	-3.85	-3.12	0.73	-3.79
$(IA)_1(NA)_1(NH_3)_1$	0.023	-9.23	-9.06	0.17	-9.78

RMSD is the structural differences of the clusters optimized at the ωB97X-D/6-311++G(3df,3pd) (for H, O, and N atoms) + aug-cc-pVTZ-PP (for I atom) and ωB97X-D/ aug-cc-pVTZ (for H, O, and N atoms) + aug-cc-pVTZ-PP (for I atom) levels of theory. [1] $\Delta G_{\mathrm{DLPNO\text{-}CCSD(T)}}$ is the Gibbs free energy calculated at the DLPNO-CCSD(T)/aug-cc-pVTZ(-PP)//ωB97X-D/6-311++G(3df,3pd) (for H, O, and N atoms) + aug-cc-pVTZ-PP (for I atom) level of theory. [2] $\Delta G_{\mathrm{DLPNO\text{-}CCSD(T)}}$ is the Gibbs free energy calculated at the DLPNO-CCSD(T)/aug-cc-pVTZ(-PP)//ωB97X-D/aug-cc-pVTZ (for H, O, and N atoms) + aug-cc-pVTZ-PP (for I atom) level of theory. $\Delta\Delta G_{\mathrm{DLPNO\text{-}CCSD(T)}}$ is the energy differences between the two basis sets. $\Delta G_{\mathrm{CCSD(T)}}$ is the energy calculated at the CCSD(T)/aug-cc-pVTZ(-PP)//ωB97X-D/6-311++G(3df,3pd) (for H, O, and N atoms) + aug-cc-pVTZ-PP (for I atom) level of theory.

3) Further on the choice of method:

You say that you do spin-orbit coupling calculations using a specific DFT functional, however, you do not directly say how this is done, just that is done in Gaussian. Please comment further on what methods Gaussian is using to do this, because there is a veritable ocean of different ways to calculate SOC even if you restrict it to using DFT.

Response: The reviewer's suggestion is valuable for improving the readability of the manuscript. It helps to refine the computational details, providing readers with a clearer understanding of the data sources and allowing for a better assessment of data reliability.

It is well known that for systems containing heavy atoms, such as iodine in this study, which belongs to the fifth period, relativistic effects must be taken into account. The relativistic effects can be divided into scalar relativistic effects and spin-orbit coupling (SOC). In this study, the scalar relativistic effects have been effectively accounted for by the adopted pseudopotential basis set (aug-cc-pVTZ-PP), while the SOC effects arising from iodine were treated by the dhf-TZVP-2c basis set, which includes scalar potential and spin-orbit potential. Here, the effects of SOC on the binding energy of all IA-containing clusters, defined as ΔE_{SOC}, was calculated as follows:

$$\Delta E_{SOC} = E_2 - E_1$$

where E_2 and E_1 represent the single-point energies calculated with and without spin-orbit potential, respectively, as obtained using the Gaussian 16 program, which supports such two-component relativistic DFT calculations. Accordingly, the ΔE_{SOC} term represents the energy difference resulting from the inclusion or exclusion of SOC effects.

To ensure that readers are informed of the computational details and can reproduce the results, we have included a detailed description of this procedure in the Supporting Information (page 4), as follows:

"The spin-orbit coupling (SOC) correction energies for all iodine-containing clusters were calculated using the Gaussian 16 software (Frisch et al., 2016), which supports two-component relativistic DFT calculations. SOC effects arising from iodine were accounted for using the dhf-TZVP-2c basis set. The SOC contribution to the binding energy of each IA-containing cluster, defined as ΔE_{SOC}, was calculated as follows:

$$\Delta E_{SOC} = E_2 - E_1$$

where E_2 and E_1 represent the single-point energies calculated with and without spin-orbit potential, respectively. E_1 was calculated at the ωB97X-D/6-311++G(3df,3pd) (for H, O, and N atoms) + dhf-TZVP-2c (for I atom) level of theory. E_2 was performed by adding the "g" keyword to the method (i.e., at the gωB97X-D level). Accordingly, the ΔE_{SOC} term represents the energy difference resulting from the inclusion or exclusion of SOC effects."

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4) On the size of simulation system:

You calculate clusters with up to 6 monomers, however the nucleation rate derived from ACDC can be highly dependent on this choice. Thus an evaluation / discussion of the impact of this choice would be prudent, see for example: https://doi.org/10.1021/acs.jpca.3c00068. I don't expect you to do any calculations, but I recommend discussing what possible changes that increasing the simulation system further could bring. I.e. would we expect it to have converged to the "true" nucleation rate?

Response: We appreciate the insightful and rigorous comments from the reviewer. Indeed, system size plays a role in determining the calculated cluster formation rate. As the system size increases, the rate generally decreases (Kubecka et al., 2023). Hence, the manuscript should clarify whether the system size used in this study is sufficient to capture the "true" nucleation behavior, in order to avoid the reader's confusion.

Kulmala et al. (2013) have reported that the critical cluster size range for atmospheric nucleation lies between 1.1 and 1.9 nm. In our study, the largest clusters included in the simulations consist of up to 6 molecules, corresponding to a size of ~1.2 nm, which falls within this reported nucleated cluster size range. In addition, the largest included clusters need to be stable enough. In other words, the clusters outside the simulated system do not significantly re-evaporate back into the system. For our study, the largest cluster consists of six molecules and reaches the critical size (~1.2 nm), where the collision rate surpasses the evaporation rate (see the collision-to-evaporation rate ratio in the "Boundary settings in ACDC simulation" section of the Supporting Information for details). These clusters are thus considered stable enough to satisfy the boundary conditions in ACDC simulations, indicating that the system size is large

enough. It is also explained in detail at https://github.com/tolenius/ACDC/blob/main/ACDC_M anual_2022_11_18.pdf

We sincerely thank the reviewer once again for this important suggestion from the reader's perspective. Furthermore, to make the results clearer, we have rephrased "nucleation rate" as "cluster formation rate" in the revised manuscript.

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5) **On the sulfuric acid comparison system:**

Maybe I just did not notice, but you only cite/refer to the SA-NA-AM system in your introduction. I think you are comparing to the experimentally derived nucleation rates (and later experimentally derived concentrations), but to be honest this was / is quite unclear to me. So please clarify that you are doing this, either in your methods or directly in the discussion.

Response: We thank the reviewer for highlighting this critical point. We apologize for not explaining this clearly in the original manuscript, which may have led to confusion. In fact, in Fig. 3(b), we compared the simulated cluster formation rates of the IA–NA–NH$_3$ and SA–NA–NH$_3$ systems. The presented simulation results were calculated at a consistent level of theory, with simulation parameters such as precursor concentration, temperature, and condensation sink (CS) corresponding to the experimental conditions. To avoid misunderstanding, we have refined the relevant analysis in the revised manuscript (lines 211-213, page 9) as following:

"…, we simulated J for the IA–NA–NH$_3$ and SA–NA–NH$_3$ systems and conducted a comparative analysis...".

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6) **On the discussion of the cluster formation rate:**

In general for the enhancement strength, you define the enhancement as the ratio of the nucleation rate with NA and the one without. I disagree on this choice of definition, because unless NA is actively hindering (and is doing it enough to counteract potential NA-AM nucleation) the nucleation you will always have an enhancement of 1 or above with this definition. Likewise, if you add 10^{11} more molecules that can collide, then it is probable that even a small amount will stick even if it is for a brief period of time, if this happens on the

boundary clusters, you would find that the clusters cross the boundary and contribute to nucleation. Thus it should always be larger than 1. It is just measuring the logical consequence of adding more molecules to the system, with the potential to capture if it hinders nucleation significantly.

I would suggest that this type of discussion of enhancement would be more suitable if you compared: IA-NH$_3$ and NA-NH$_3$ nucleation co-occurring (i.e. non-interacting nucleation) compared with the simulation of IA-NA-AM (i.e. interacting nucleation). Thus the ratio: J(IA-NA-AM)/(J(IA-AM)+J(NA-AM)) would measure what I would refer to as enhancement. With the caveat that running two entirely separate nucleation simulations does not give the same results as a simulation with two separate nucleation channels. However, this is not possible in ACDC as far as I remember.

As the other reviewer suggested, a reformulation of this section is in order.

Response: We agree with the reviewer's valuable insight that the previously defined enhancement R consistently exceeds 1. After careful consideration, we also find the reviewer's definition to be more appropriate. Accordingly, we have updated the definition of R (Eq. (S5)) as follows:

$$R = \frac{J\left(\left[\mathrm{IA}\right]=10^6, \left[\mathrm{NA}\right]=x, \left[\mathrm{NH}_3\right]=y\right)}{J\left(\left[\mathrm{IA}\right]=10^6, \left[\mathrm{NA}\right]=0, \left[\mathrm{NH}_3\right]=y\right)+J\left(\left[\mathrm{IA}\right]=0, \left[\mathrm{NA}\right]=x, \left[\mathrm{NH}_3\right]=y\right)}.$$
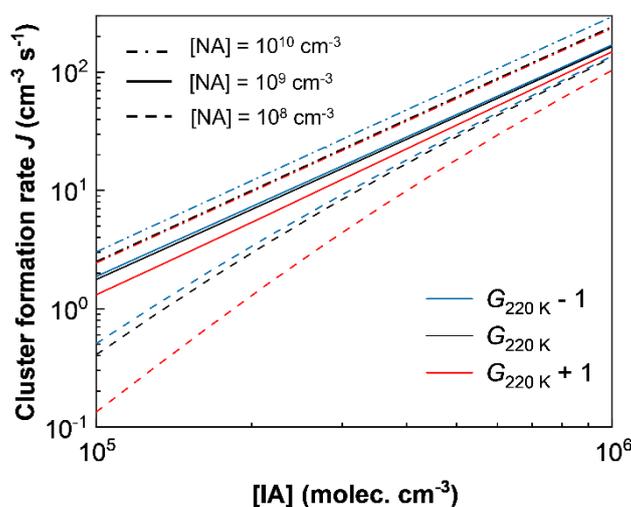
Moreover, based on the revised results of R, we have updated the corresponding figure and its description in the revised manuscript accordingly. We would like to once again thank the reviewer for the professional suggestion, and this new definition of enhancement strength will be highly beneficial for our future research.

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7) Further on the discussion of the cluster formation rate:

Many of your differences are well within one order of magnitude in e.g fig 3a. How accurate would you expect the ACDC calculations to be, given your choice of QC method?

Likewise for fig. 3b, how significant is this difference, compared to the uncertainties in the input QC?

Response: As correctly noted by the reviewer, the quantum chemical calculations of Gibbs free energy inherently introduce a certain level of uncertainty in ACDC simulations. To assess the impact of the uncertainty on the cluster formation rate (J), we systematically investigated how variations in Gibbs free energy (ΔG) affect J. Specifically, based on the benchmark results discussed earlier, the ΔG uncertainty was found to be within ~1 kcal mol^{-1}. Therefore, we assessed the sensitivity of J by artificially increasing or decreasing the ΔG by 1 kcal mol^{-1}. The figure below presents the uncertainty analysis results of J at $T = 220$ K, CS $= 10^{-4}$ s^{-1}, [IA] $= 10^5 - 10^6$, [NA] $= 10^8 - 10^{10}$, and [NH$_3$] $= 3 \times 10^8$ molec. cm^{-3}.

Figure S6. Cluster formation rate J as a function of [IA] $= 10^5 - 10^6$ molec. cm^{-3}, with different energy of ΔG_{220K} (black line), $\Delta G_{220K} - 1$ (blue line), $\Delta G_{220K} + 1$ (red line), at $T = 220$ K, CS $= 10^{-4}$ s^{-1}, [IA] $= 10^5 - 10^6$, [NA] $= 10^8 - 10^{10}$, and [NH$_3$] $= 3 \times 10^8$ molec. cm^{-3}.

Here, we have added the results of J under different Gibbs free energy to the revised Supporting Information, and for the convenience of the review, we have copied Fig. S6 and the corresponding analysis (lines 199-205 page 8 in the revised manuscript) as following:

"In addition, considering the potential uncertainties in quantum chemical calculations, we also investigated the effect of the uncertainty in the calculated ΔG on the cluster formation rate J. As shown in Fig. S6, under NA concentrations ranging from 10^8 to 10^{10} molec. cm^{-3}, adjusting the ΔG_{220K} of clusters by subtracting 1 kcal mol^{-1} results in a minor variation in J. Although an increase in ΔG_{220K} by adding 1 kcal mol^{-1} may cause a slight offset in J values, the DLPNO method tends to underestimate binding energies to some extent, indicating that the present results

($J_{\Delta G220K}$) are at a low limit. Therefore, the scenario of adding 1 kcal mol^{-1} may be unlikely to occur. Taken together, the uncertainty of calculated quantum chemistry does not significantly impact the conclusions of this study."

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8) Line 213:

"This finding indicates that the IA–NA–NH$_3$ ternary pathway dominates in regions where IA level is limited, while NA is abundant, aligning well with the conditions in the focused UTLS. More broadly, such scenario characterized by scarce IA and rich NA also exists in higher atmosphere, such as ~20 km (i.e., the bottom of near space). This NA-enhanced mechanism is likely a vital source of fresh particles in this region."

I guess, but how much ammonia is going to be present there?

Response: Thanks for the reviewer's comment. Indeed, ammonia is widely present in the upper troposphere and lower stratosphere (UTLS). The mixing ratio of ammonia vapor in the Asian monsoon upper troposphere can reach up to 30 pptv, and as high as 1.4 ppbv in hotspot regions (Höpfner et al., 2016; Höpfner et al., 2019). Moreover, ammonia signals are also detected above 20 km, although the associated uncertainties are large, making it difficult to provide specific values (Höpfner et al., 2016).

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Extra comments:

Line 52: In your citation for the gas-phase mixing ratios of NA you cite Popp et al, who do measurements in the lower stratosphere. However you also cite Wang et al 2023, which is the paper: "Mechanistic understanding of rapid H$_2$SO$_4$-HNO$_3$-NH$_3$ nucleation in the upper troposphere". I assume this is a mistake? The Wang et al. study does cite papers that have conducted measurements / modeling that could support the argument, however, then you should cite those papers directly.

Response: Thanks. According to the reviewer's suggestion, we have revised the reference for the gas-phase mixing ratios of NA on page 2, line 52 in the revised manuscript.

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Line 58: You choice of systems is exclusively 1:1 or acid-dominated. While there has been indications elsewhere that this is the case, I would prefer it if you comment on this choice of systems. Not necessarily much, but it would be prudent to comment on the fact that you don't allow any base dominated clusters (at least this is how I read it).

Response: In this work, all the studied clusters have a number of acid molecules greater than or equal to that of base molecules. Previous studies have shown that clusters containing one additional acid molecule are generally more stable than those containing one additional base molecule (Xie and Elm, 2021). According to the reviewer's suggestion, we have included the following analysis in the revised manuscript (lines 119-122, page 4):

"Furthermore, all clusters investigated in this study comprise an equal or greater number of acid molecules relative to base molecules, as previous studies have demonstrated that such compositions generally exhibit enhanced thermodynamic stability (Xie and Elm, 2021)."

Reference:

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