Responses to Referee #1'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 #1's comments are summarized below:

Jing Li and co-authors have performed computational simulations on HIO_3-HNO_3-NH_3 clustering relevant to UTLS (upper troposphere - lower stratosphere) new-particle formation, including also some comparisons to H_2SO_4-HNO_3-NH_3 clusters. This is a highly relevant and timely topic for atmospheric chemists and physicists. For example, there is an ongoing discussion, even debate, on the relative roles of iodine oxyacids (HIO_3, HIO_2) versus iodine oxides (e.g. I_2O_5) in promoting particle formation. Engsvand and Elm recently showed, using similar methods as the authors, that in combination with bases such as amines, the latter are more efficient (https://chemrxiv.org/engage/chemrxiv/article-details/67b4894bfa469535b9db7fa5). However, the present manuscript suggests that this comparison should probably be broadened to include also species like HNO_3, which might possibly interact more favourably with the oxyacids (or not, this remains to be seen). Overall, the article is generally well written and easy to follow, the simulation methods are broadly appropriate (I especially commend the authors for both thinking carefully about appropriate temperature-dependent boundary settings, and also reporting these so clearly), and I'm happy to recommend publication of the study in ACP. I only have some minor questions and comments that I'd like the authors to briefly address.

Response: Thanks sincerely for the reviewer's professional and positive comments. We have revised the manuscript accordingly. The detailed point-to-point responses are listed as follows.

Scientific (minor) issues

1) Concerning the discussion of temperature on page 2, any gas-to-particle nucleation mechanism will be more efficient at low temperatures if the concentrations of participating vapors are kept constant. This follows straight from the lesser role of entropy at lower temperatures. The catch is that most potentially nucleating vapor concentrations (in the real world, if not always in simulations or laboratory experiments) also tend to decrease (often very strongly) with temperature. Is the IA-driven mechanism somehow especially efficient in this regard? For example, is it known that IA concentrations in the air decrease less with temperature compared to other potentially nucleating vapours? Or does the IA-related nucleation rate at constant concentrations increase much more steeply with decreasing temperature than most competing nucleation rates? Just saying that it is shows "remarkable efficiency" at low temperatures doesn't really say that much, the same is arguably true for almost any mechanism. Please elaborate on this.

Response: We appreciate the reviewer's insightful comment. Indeed, the enhanced nucleation at lower temperatures largely stems from reduced entropic contribution, which generally applies to all gas-to-particle nucleation processes when vapor concentrations are kept constant. Due to limited field observations of IA, it remains unclear whether the concentration decay of IA is slower than that of other vapors. Nonetheless, existing research has shown that the influence of temperature on nucleation varies between different systems. He et al. (2021) reported that iodic acid-driven nucleation exhibits strong temperature sensitivity, as evidenced by "the nucleation rate increases rapidly as the temperature falls from 10 °C to -10 °C". In comparison, the increase in nucleation rate for the sulfuric acid-ammonia (H_2SO_4-NH_3) system is much smaller, thereby showing less sensitivity to temperature changes.

To clarify the temperature dependence of different systems, we simulated the cluster formation rates of the studied IA-involved system (IA–NA–NH_3) and SA–NH_3 systems, under the different temperatures (T = 240 K and 220 K), within the same acid concentration range (10^5 – 10^6 molec. cm^{-3}). As shown in Fig. R1, when the temperature decreases from 240 K (dashed lines) to 220 K (solid lines), the cluster formation rate of the IA–NA–NH_3 system (red lines) increases by up to four orders of magnitude, while that of the SA–NH_3 system (blue lines) increases by only about one order of magnitude. It can be seen that IA-driven nucleation processes display greater sensitivity to temperature changes. These findings align well with the reviewer's valuable insight that, "the IA-related nucleation rate at constant concentrations increase much more steeply with decreasing temperature" than the competing SA–NH_3 system, which is a typical nucleation system at high altitudes. Accordingly, the stronger temperature dependence may render IA-driven nucleation more efficiently under cold atmospheric conditions.

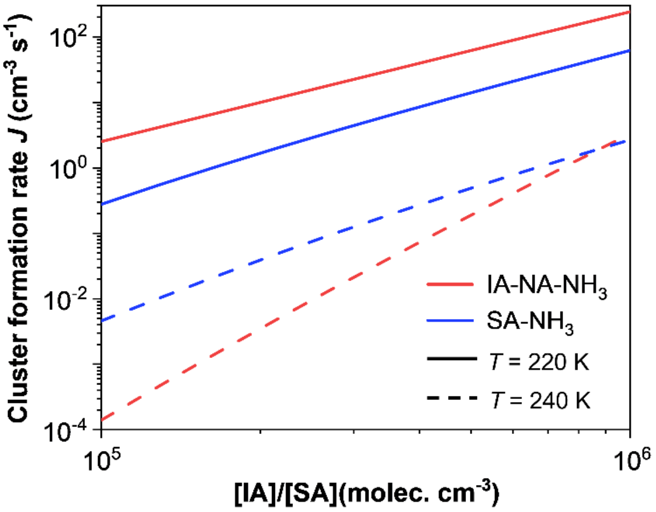

Figure R1. Cluster formation rate J (cm^{-3} s^{-1}) as a function of [IA]/[SA] of IA–NA–NH_3 and SA–NH_3 system at the conditions of $T = 220 – 240$ K, CS = 10^{-4} s^{-1}, [NA] = 1×10^{10} molec. cm^{-3}, and [NH_3] = 3×10^8 molec. cm^{-3}.

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2) The authors use a aug-cc-pVTZ basis set (and the associated pseudopotential) for I atoms, and a 6-311++G(3df,3pd) basis set for other atoms (C, O, N, H). Previously, the use of imbalanced basis sets (specifically, large basis sets on I atoms and small basis sets on other atoms) has been shown to lead to catastrophically large biases in favour of forming bonds with iodine, see e.g. Finkenzeller et al, https://www.nature.com/articles/s41557-022-01067-z, for a discussion on this. Now, the difference in size between 6-311++G(3df,3pd) and aug-cc-pVTZ is not that dramatic, for example for C atoms its 39 vs 46 basis functions. So I don’t expect the present results to be qualitatively incorrect because of this issue - especially as the final energies are then corrected by coupled-cluster calculations, which do consistently use the same basis set for all atoms. However, a few test calculations comparing e.g. the structures and binding energies (both pure DFT energies and coupled-cluster corrected energies on top of structures optimised with different basis sets) of the smallest HIO_3 - containing clusters obtained with the authors’ approach, and with aug-cc-pVTZ for all atoms (with the PP for iodine of course) also at the DFT stage, might be warranted, to check whether the bias in the present results is negligible or not.

Response: The reviewer’s suggestion is highly professional and well-taken, as the results of quantum chemical calculations have a substantial impact on subsequent ACDC simulations. Thus, it is necessary to examine the potential bias introduced by the chosen imbalanced basis set.

Our earlier work (Rong et al., 2020) includes benchmarking tests obtained with four different basis sets: aug-cc-pVDZ (for non-I atom) + aug-cc-pVDZ-PP (for I atom), aug-cc-pVTZ (for non-I atom) + aug-cc-pVTZ-PP (for I atom), 6-311++G(3df,3pd) + aug-cc-pVDZ-PP (for I atom), and 6-311++G(3df,3pd) + aug-cc-pVTZ-PP (for I atom). The results showed that, for the studied IA-containing clusters, such as $(IA)_2$, $(IA)_1(SA)_1$, and $(IA)_1(NH_3)_1$, the *RMSD* (root mean square deviation, an index of structural difference) between the optimized structures using different basis sets was less than 0.1 Å. This indicates that the structural differences among the clusters optimized with the adopted imbalanced (6-311++G(3df,3pd) + aug-cc-pVTZ-PP) and aug-cc-pVTZ(-PP) basis sets are almost negligible.

Nevertheless, given the differences in the studied systems, we recalculated the IA-containing clusters studied in this work, evaluating both structural and energetic deviations, according to the reviewer's suggestion. Herein, the small IA-containing clusters such as $(IA)_1(NA)_1$, $(IA)_1(NH_3)_1$, and $(IA)_1(NA)_1(NH_3)_1$, were optimized at 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. To further evaluate the energy differences, the single-point energies of these clusters optimized using different basis sets were calculated at DLPNO-CCSD(T) /aug-cc-pVTZ(-PP) and CCSD(T)/aug-cc-pVTZ(-PP) levels of theory. The detailed analysis is provided below and can be found on pages 6-7 in the revised Supporting Information.

"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)).

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

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 geometry 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):

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

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, $\Delta G_{\text{CCSD(T)}}$ 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.”

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 *ω*B97X-D/6-311++G(3df,3pd) (for H, O, and N atoms) + aug-cc-pVTZ-PP (for I atom) and *ω*B97X-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)//*ω*B97X-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)//*ω*B97X-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)//*ω*B97X-D/6-311++G(3df,3pd) (for H, O, and N atoms) + aug-cc-pVTZ-PP (for I atom) level of theory.

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3) Just to confirm: when the collision rates are multiplied by 2.3 to account for long-range attractions, also the evaporation rates go up by the same fact, right? (They should, by detailed balance, equation S2 in the authors own supplement. I.e. I just want the authors to confirm that the multiplication by 2.3 is applied to both the collision and the evaporation rates.)

Response: We thank the reviewer for the thorough review and deeply respect the expertise in the field. This is indeed an important point that should be addressed in the manuscript. As noted by the reviewer, the multiplication factor of 2.3 was applied to both the collision and evaporation rates, as the two are related through the principle of detailed balance, as described in Eq. (S2). of our Supplementary Information.

$$\gamma_{(i+j)\to i} = \beta_{i,j} \frac{P_{\mathrm{ref}}}{k_B T} \exp\left(\frac{\Delta G_{i+j} - \Delta G_i - \Delta G_j}{k_B T} \right), \tag{S2}$$

where $\gamma_{(i+j)\to i}$ is evaporation rate coefficient, $\beta_{i,j}$ the collision rate coefficient, P_{ref} is the reference pressure (1 atm), and ΔG_i is the Gibbs free energy of the formation of cluster i.

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4) Concerning the discussion in section 3.2, of course the nucleation rate goes up with the concentration of participating species. This is inevitable and obvious. Thus it is not an actual discussion-worthy result that J goes up ("exhibits a positive correlation") with [IA], or that the J rate with NA present is higher than the rate of the otherwise identical system with NA absent. Now, the numerical values themselves are of course interesting, e.g. the fact that even 1E9 per cm3 of NA substantially increases the rate is a valid results. But please reformulate this so that mathematically inevitable consequences of how ACDC works are not reported as novel or "notable" results.

Response: We thank the reviewer for the helpful suggestion, which helps the manuscript better focus on content of greater interest to the readers. And we fully agree with the reviewer that fixed trend is not an actual discussion-worthy result, and that the emphasis should instead be placed on the numerical values. Accordingly, we have revised the analysis in Section 3.2 (lines 164-166, page 7 in the revised manuscript) on cluster formation rates as follows:

"As illustrated in Fig. 3a, at T = 220 K, CS = 10^{-4} s^{-1}, [IA] = 10^5 – 10^6 molec. cm^{-3}, and [NH_3] = 3 × 10^8 molec. cm^{-3}, NA exhibits a significant enhancing effect on IA–NH_3 nucleation. Even when the NA concentration is as low as 10^9 molec. cm^{-3}, it can enhance J(IA–NH_3) by up to a factor of 6, increasing from 0.3 to 1.8 cm^{-3} s^{-1}."

Technical or language issues:

-Figure 5b. How can the two pie charts corresponding to NA=1E9 and IA=1E6 (2nd pie chart from the left in both rows) be different? NH_3, T, CS are the same in these runs, as are NA and IA - why are the branching ratios different? Is this a typo, or a bug, or what?

Response: Thanks for the reviewer's carefulness. This is indeed a typographical error — the NA concentration in the conditions for the lower row of pie charts should be 10^{10} molec. cm^{-3}. We have corrected this accordingly.

-The last sentence on page 1 (ending with "undisclosed") seems to be missing some words, should this be "has led to… REMAINING undisclosed"? Also, the word choice is odd: "undisclosed" implies purposeful keeping of secrets (by a sentient actor, typically a human), while what the authors presumably mean is that this facet of the natural world has simply not yet been discovered or understood.

Response: According to the reviewer's suggestion, the phrase "has led to…undisclosed" has been corrected to "has led to…remaining undiscovered" in the lines 30-31 on page 1 of the revised manuscript.

-Page 6, it's trivially true that SA-NA-NH_3 clusters do not form halogen bonds - they do not contain halogen atoms! The first sentence on page 6 thus sounds a bit odd, and could use some rephrasing. (The general point that XBs make the IA-containing clusters substantially stronger is of course valid and worth making, I'm just commenting on the formulation here.)

Response: Accordingly, we have rephrased the first sentence on page 6 (lines 142-144 of the revised manuscript) as follows:

"In the IA–NA–NH_3 system, the presence of IA introduces XBs, allowing NA to be stabilized simultaneously by HBs, XBs, and electrostatic interactions. In contrast, in the SA–NA–NH_3 cluster, a typical high-efficiency system in the UTLS, NA only participates in HB formation and the protonation of NH_3."

Reference：

He, X.-C., Tham, Y. J., Dada, L., Wang, M., Finkenzeller, H., Stolzenburg, D., Iyer, S., Simon, M., ¨rten, A. K., Shen, J., Roerup, B., Rissanen, M., Schobesberger, S., Baalbaki, R., Wang, D. S., Koenig, T. K., Jokinen, T., Sarnela, N., Beck, L. J., Almeida, J., Amanatidis, S., Amorim, A., Ataei, F., Baccarini, A., Bertozzi, B., Bianchi, F., Brilke, S., Caudillo, L., Chen, D., Chiu, R., Chu, B., Dias, A., Ding, A., Dommen, J., Duplissy, J., Haddad, I. E., Carracedo, L. G., Granzin, M., Hansel, A., Heinritzi, M., Hofbauer, V., Junninen, H., Kangasluoma, J., Kemppainen, D., Kim, C., Kong, W., Krechmer, J. E., Kvashin, A., Laitinen, T., Lamkaddam, H., Lee, C. P., Lehtipalo, K., Leiminger, M., Li, Z., Makhmutov, V., Manninen, H. E., Marie, G., Marten, R., Mathot, S., Mauldin, R. L., Mentler, B., Moehler, O., Mueller, T., Nie, W., Onnela, A., Petaja, T., Pfeifer, J., Philippov, M., Ranjithkumar, A., Saiz-Lopez, A., Salma, I., Scholz, W., Schuchmann, S., Schulze, B., Steiner, G., Stozhkov, Y., Tauber, C., Tome, A., Thakur, R. C., Vaisanen, O., Vazquez-Pufleau, M., Wagner, A. C., Wang, Y., Weber, S. K., Winkler, P. M., Wu, Y., Xiao, M., Yan, C., Ye, Q., Ylisirnio, A., Zauner-Wieczorek, M., Zha, Q., Zhou, P., Flagan, R. C., Curtius, J., Baltensperger, U., Kulmala, M., Kerminen, V.-M., Kurten, T., Donahue, N. M., Volkamer, R., Kirkby, J., Worsnop, D. R. and Sipila, M.: Role of iodine oxoacids in atmospheric aerosol nucleation, Science, 371, 589–595, http://doi.org/10.1126/science.abe0298, 2021.

Rong, H., Liu, J., Zhang, Y., Du, L., Zhang, X. and Li, Z.: Nucleation mechanisms of iodic acid in clean and polluted coastal regions, Chemosphere, 253, 126743, http://doi.org/10.1016/j.chemosphere.2020.126743, 2020.