Dear Editor,

Thanks sincerely for your handling our manuscript titled "**Mechanistic insights into nitric acid-enhanced iodic acid particle nucleation in the upper troposphere and lower stratosphere**" (MS No.: egusphere-2025-1194) and for giving us the opportunity to refine it. For the reviewer's further expert comments, we have tried to address them from a more comprehensive perspective and provide detailed point-by-point responses to the Referee #3's comments below.

Referee comments:

The authors have adequately addressed many of my concerns, and the manuscripts shows good improvement.

However, there are still one point I would like addressed before, the reasons for it not being addressed may be due to my comment being a bit too vague in the previous round, for which I apologize.

Response: We sincerely thank the reviewer for the positive feedback. The improvement of the manuscript has greatly benefited from your valuable suggestions provided in the previous round, which are also insightful for guiding our future research. Herein, we apologize for not fully understanding and addressing the reviewer's comment earlier. We hope that our current reply can address the issue as thoroughly as possible.

Comment 1:

Regarding the choice of method:

1) I will once again bring up the relativistic nature of iodine, because the authors validate their results against CCSD(T) with both their chosen DLPNO-CCSD(T) and the benchmark CCSD(T) using pseudo-potentials. I.e. they are using a non-relativistic Hamiltonian and then incorporating the relativistic effects using a pseudo-potential. The Peterson pseudo-potential used was fitted to experimental values for small diatomic molecules. It should (at least partially) include both scalar and coupling effects (specifically SOC).

What I aimed to convey in my previous comments was that the authors should check whether

or not using a pseudo-potential to take the relativistic effects into account is "good enough" compared to using for example a scalar-relativistic Hamiltonian with or without spin-orbit coupling corrections added on top. I would assume this to be more accurate given that the systems studied here are significantly larger and contain many intermolecular bonds.
The authors use ORCA, which has both ZORA and DKH scalar-relativistic Hamiltonians defined, beware that they require the special ZORA and DKH basis sets with extra functions in the core region.

Response: The reviewer's expertise in theoretical methods is admirable. This is a critical and helpful point – thanks for bringing it up.

In our theoretical calculations, the relativistic nature of iodine was addressed using the small-core pseudopotential developed by Peterson et al., which was fitted to scalar relativistic all-electron data and experimental results for small iodine-containing diatomic molecules. It has been widely and successfully applied in studies of heavy main-group elements, including iodine-containing systems (Peterson et al., 2003). Nevertheless, the reviewer's concern is that combining the Peterson pseudo-potential with the CCSD(T) or DLPNO-CCSD(T) methods may introduce uncertainties in the calculations, since the two methods adopt non-relativistic Hamiltonian.

According to the reviewer's comment, we first employed the scalar relativistic method recommended by the reviewer: ZORA-DLPNO-CCSD(T) method with the ma-ZORA-def2-TZVPP (for H, O, and N atoms) + SARC-ZORA-TZVPP (for I atom) basis set to calculate the energies of $(IA)_1(NA)_1$, $(IA)_1(NH_3)_1$, and $(IA)_1(NA)_1(NH_3)_1$ clusters studied in the manuscript. To assess the differences caused by different levels of theory, we compared these results with those from using the DLPNO-CCSD(T) method combined with the Peterson pseudo-potential, as adopted in our manuscript.

As listed in Table R1, the differences in electronic energies between the DLPNO-CCSD (T)-based and ZORA-DLPNO-CCSD(T)-based approaches range from 1.4 to 2.7 kcal mol^{-1}, depending on the specific cluster. The range of deviations is comparable to that observed by Engsvang et al. (1.2 – 2.5 kcal mol^{-1}) when comparing small-core ECPs with scalar relativistic

Hamiltonians in iodine-containing systems (Engsvang, Wu and Elm, 2024). Accordingly, it indicates that there are certain differences between the energies obtained from the two levels of theory.

Table R1. Electronic formation energies of the $(IA)_1(NA)_1$, $(IA)_1(NH_3)_1$, and $(IA)_1(NA)_1(NH_3)_1$ clusters calculated at the DLPNO-CCSD(T)/aug-cc-pVTZ(-PP) and the ZORA-DLPNO-CCSD(T)/ma-ZORA-def2-TZVPP (for H, O, and N atoms) + SARC-ZORA-TZVPP (for the I atom) levels of theory, along with the corresponding energy differences.

Clusters	$\Delta E_{\text{aug-cc-pVTZ-PP}}$	ΔE_{ZORA}	$\Delta\Delta E$
$(IA)_1(NA)_1$	-16.4	-13.7	2.7
$(IA)_1(NH_3)_1$	-14.4	-13.0	1.4
$(IA)_1(NA)_1(NH_3)_1$	-34.7	-32.1	2.6

To further evaluate the reliability of different levels of theory, iodine-related experimental data is employed here as a reference standard for computational accuracy. Peterson et al. (2003) demonstrated that the pseudopotential-based CCSD(T)/cc-pVnZ-PP (n = T, Q, 5) approach predicts the dissociation energy of I_2 with deviations of 4.1 – 9.4 kcal mol^{-1} from experimental results. In our calculations using a similar pseudopotential basis set (aug-cc-pVTZ-PP), the deviation is found to be 6.6 kcal mol^{-1}. For comparison, we also calculated the dissociation energy of I_2 at the ZORA-CCSD(T)/SARC-ZORA-TZVPP level of theory; however, the resulting deviation from the experimental value is slightly larger, at 7.5 kcal mol^{-1}. This indicates that calculations at both levels of theory—including theoretically appealing ZORA-based scalar relativistic treatment—exhibit the deviations from experimental values.

Taken together, accurate modeling of iodic acid cluster formation requires appropriate theoretical calculations of formation free energies and experimental benchmarks, which are currently lacking for iodine clusters and warrants future investigation. In fact, the DLPNO-CCSD(T)/aug-cc-pVTZ(-PP) level of theory has been widely used in the study of iodic acid nucleation and provides a good description of the observed cluster concentrations and formation

rates (He et al., 2023; Zhang et al., 2022). The resulting agreement between the theoretical results and experimental nucleation rates measured in the CLOUD chamber demonstrates the applicability of this level of theory in studies of iodic acid nucleation (Notably, we agree with the reviewer's viewpoint regarding the discussion of this agreement. For more details, please refer to our response to Comment 2.). From a theoretical standpoint, the reviewer's suggested ZORA-based method, being theoretically advanced, should be prioritized in upcoming studies. We sincerely thank the reviewer once again for their professional advice and patient review.

Comment 2:

2) This is more of a personal gripe. Feel free to disagree and there is no need for a response here or in the article:

"This pseudo-potential has been successfully applied in other iodine-containing NPF nucleation studies (citations)"

The cited studies are all computational / combined computational and experimental work, where they aim to develop models that can explain systems that are quite complicated from a computational point of view (even though they are very simple / isolated systems compared to the real atmosphere) I find that, using the fact that their results overall agree with the values reported by the experimentalists in complicated experiments, is a flawed way of evaluating whether or not our methods are valid.

This is because whenever we do a calculation, we make many choices of approximations which can contribute to both an underestimation and an overestimation in the final results. Thus a simplified model with the right choices can get the right result. But one should be careful to consider how it can transfer to other systems but also more importantly larger / more complicated systems. For example if you neglect some sources of nucleation in the computational model, it could be compensated for (or covered up) by a choice of QC method which may overestimate the stability of the systems, this may give the correct result in the given study and in future studies if the same neglect is made. However, if one was to try to improve upon the computation by for example adding all the nucleation pathways, one would suddenly find that they are massively overestimating the nucleation, and that they were overestimating

the importance of the pathway previously considered. Thus as long as we run simplified models neglecting pathways, we should always expect to undershoot the experimental values (to a degree) and not agree with them. But what we will be able to say would be how much of the experimental results can be explained by the pathway considered.

If we are to compare to experiments for validation, the experiments should be designed such that we can actually extract detailed information from it and separate different effects. It is my opinion that if you have to use QC data to extract information from an experiment, that information can not be used as a proper validation of the QC method.

Response: We thank the reviewer for the insightful comments on theoretical studies of nucleation. We highly agree with these important points raised. The good agreement between theoretical simulations and experimental observations may result from the mutual cancellation of various input uncertainties, such as overestimations or underestimations caused by specific approximations. Accordingly, the consistency between theory and experiment as direct evidence of methodological validity has inherent limitations. For a meaningful validation of quantum chemical methods, experimental design should be able to effectively distinguish various effects and quantitatively extract detailed information for validation. Otherwise, as the reviewer rightly noted, such experimental results may not serve as a direct benchmark for evaluating the accuracy of the theoretical approach.

Reference:

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