Dear Editor,

Thank you very much for your time and effort in handling our manuscript (MS No.: EGUSPHERE-2026-2401) entitled "**Heterogeneous Nitrosation Reactions of Amines Driven by Dinitrogen Tetroxide: A Missing Source of Particulate Nitrosamines**". We are also grateful to the reviewers for the thoughtful, constructive, and insightful comments, which have greatly helped us improve the quality and clarity of the manuscript.

In response to the reviewers' comments and suggestions, we have carefully revised the manuscript and addressed each point in detail. All changes made in the revised manuscript are highlighted in blue for ease of reference. A detailed, point-by-point response is provided below.

Reviewer(s)' Comments to Author:

Response to Referee #1

Referee's general assessment:

Chi et al. present a well-designed theoretical study on the heterogeneous formation mechanisms of carcinogenic nitrosamines at the air–water interface. Using *ab initio* molecular dynamics simulations, the authors demonstrate that amines (MA/DMA) can rapidly react with dinitrogen tetroxide (N_2O_4) at aqueous aerosol surfaces, resulting in the direct formation of particulate nitrosamines and nitrate. This study provides in-depth mechanistic insights into the particulate nitrosamine production in urban atmospheres. Additionally, combination of BOMD and metadynamics simulations enables a precise monitoring of these ultrafast interfacial processes, and the accompanying wave function analyses enhance mechanistic interpretation. Overall, this manuscript is well-designed and contains substantial theoretical results. The obtained theoretical results are of significant importance to atmospheric multiphase chemistry and

aerosol interfacial processes. The reviewer recommends publication of this manuscript in *Atmos. Chem. Phys.* after the following minor concerns are addressed:

Author response: We sincerely thank the referee for the positive evaluation of our manuscript and for the constructive comments and valuable suggestions. We have carefully revised the manuscript accordingly, with all changes highlighted in blue. Our detailed responses to each comment are provided below.

Scientific issues:

Comment S1. Schemes 1 and 2 are very informative and greatly aid the understanding of the proposed reaction mechanisms. However, Scheme 2 (*iii*) should be explicitly referenced and discussed in Section 3.2 to better direct the readers to the mechanistic pathways presented. In addition, the authors should further clarify why the reaction pathway shown in Scheme 2 (*iii*) is not feasible. Notably, the preformed complex involved in Scheme 2 (*iii*) appears to be the same as that shown in Scheme 1 (*ii*). In Scheme 1 (*ii*), collision of this complex with the air–water interface directly leads to nitrosation at the interface. However, this does not adequately explain why hydrolysis cannot occur when the same complex interacts with the air–water interface. A more detailed mechanistic explanation distinguishing the feasibility of nitrosation versus hydrolysis pathways would strengthen the interpretation of the interfacial reaction mechanisms.

Author response: We sincerely thank the referee for this insightful and constructive comment. We agree that a more explicit discussion of Scheme 2 (*iii*) and its relationship to Scheme 1 (*ii*) improves the clarity of the competing interfacial reaction pathways. Accordingly, Scheme 2 (*iii*) has now been explicitly referenced and discussed in Section 3.2. In addition, we have expanded the mechanistic discussion to clarify why the pathway shown in Scheme 2 (*iii*) is kinetically

unfavorable. The corresponding text has been added to Lines 207–218 of the revised manuscript, as follows:

"It is worth noting that the gas-phase pre-reactive complex t-$ONONO_2$–MA/DMA shown in Scheme 2 (iii) is structurally identical to that presented in Scheme 1 (ii). However, when this complex collides with the air–water interface, it preferentially undergoes N-nitrosation rather than hydrolysis. This difference can be understood from the distinct elementary steps involved in the two pathways. In the N-nitrosation pathway (Scheme 1 (ii)), the preformed t-$ONONO_2$–MA/DMA complex already possesses an N···N interaction between the amine and the NO moiety of t-$ONONO_2$. Upon adsorption at the air–water interface, the interfacial environment facilitates the transfer of the NO group to the amine, leading to the formation of the nitrosamine cation. In contrast, the hydrolysis pathway requires nucleophilic attack by interfacial water molecules on the t-$ONONO_2$ moiety, accompanied by concerted solvent-assisted proton transfer. The BOMD trajectories suggest that the pre-existing N···N interaction between the amine and the NO moiety may reduce the accessibility of interfacial water molecules to the reactive site and hinder their adoption of a favorable orientation for nucleophilic attack. Consequently, the preformed gas-phase complex preferentially undergoes N-nitrosation upon collision with the air–water interface, whereas the competing hydrolysis pathway is kinetically disfavored."

Comment S2. It is recommended to cite recent key studies in the "introduction" to offer a clear picture regarding the "reaction-accelerating effect of the air–water interface".

Author response: We sincerely thank the referee for this helpful suggestion. We agree that citing recent key studies on the air–water interface induced reaction acceleration provides important context for the present work. Accordingly, we have incorporated the references into

the Introduction. The corresponding revisions have been made in Lines 58–62 of the revised manuscript:

"This possibility is motivated not only by the inability of existing gas- and aqueous-phase pathways to explain the observed particulate nitrosamine levels, but also by accumulating evidence that MA and DMA exhibit strong interfacial propensity (Deng et al., 2026; Ning et al., 2023, 2024) and that the air–water interface can substantially accelerate a wide range of atmospheric reactions (Chen et al., 2025; Fang et al., 2025; Song et al., 2024; Xie et al., 2024; Zhang et al., 2026)."

Newly added references:

Chen, X., Wan, Z., Bai, Q., Zhu, C., and Francisco, J. S.: HOCl/$ClONO_2$ Catalytic Cycle: Promotion of the Reactive Uptake of N_2O_5 at the Air–Water Interface, J. Am. Chem. Soc., 147, 29215–29222, https://doi.org/10.1021/jacs.5c08347, 2025.

Xie, R., Guo, K., Li, Y., Zhang, Y., Zhong, H., Leung, D. Y. C., and Huang, H.: Harnessing air–water interface to generate interfacial ROS for ultrafast environmental remediation, Nat. Commun., 15, 8860, https://doi.org/10.1038/s41467-024-53289-z, 2024.

Zhang, Y., Yang, X., Gu, J., Liu, Y., Wang, Z., Liu, B., Li, H., and Zhang, X.: H_2O_2-Driven Sulfate Formation at Air–Water Interfaces: Stepwise Mechanism and Accelerated Kinetics, Environ. Sci. Technol., acs.est.5c17902, https://doi.org/10.1021/acs.est.5c17902, 2026.

Comment S3. The conclusion effectively summarizes the key findings. Please explicitly reiterate the "missing source" aspect in the final paragraph to tie it back to the Abstract and resonate with the readers.

Author response: We sincerely thank the referee for this valuable suggestion. We agree that the "missing source" aspect should be explicitly reiterated in the concluding paragraph to better

connect the Conclusion with the Abstract. Accordingly, we have revised the final paragraph to emphasize that the heterogeneous interfacial N-nitrosation mechanism identified in this study represents a previously overlooked source of particulate nitrosamines and may help explain the missing nitrosamine sources reported in atmospheric observations. This revision further reinforces the broader atmospheric significance of our findings. The corresponding changes have been made in Lines 329–333 of the revised manuscript:

"Furthermore, the identified heterogeneous interfacial N-nitrosation pathway represents a previously overlooked source of particulate nitrosamines and may account for the missing sources inferred from atmospheric observations. By incorporating the revealed interfacial N-nitrosation pathway into the established scheme of gas- and aqueous-phase nitrogen chemistry, this study advances and broadens our current understanding of multiphase reactive nitrogen cycling (Fig. 5)."

Comment S4. The environmental implications of simultaneous HONO and nitrate formation deserve further emphasis. The manuscript primarily focuses on nitrosamine production, while the concurrent formation of HONO and nitrate is not strictly discussed. From an atmospheric chemistry perspective, this coupled production pathway could be highly important because it simultaneously influences oxidation capacity, aerosol nitrate burden, and reactive nitrogen cycling. The authors may consider expanding this discussion in the Conclusion section to better highlight the broader implications of the revealed chemistry beyond nitrosamine formation alone.

Author response: We sincerely thank the referee for this valuable suggestion. We agree that the simultaneous formation of HONO and nitrate, together with nitrosamines, represents an important atmospheric implication of the revealed interfacial chemistry. Following the referee's suggestion, we have expanded the Conclusion to explicitly emphasize that the identified

heterogeneous pathway simultaneously produces nitrosamines, HONO, and nitrate, thereby coupling particulate toxicity with atmospheric oxidation capacity, aerosol nitrate formation, and reactive nitrogen cycling. The corresponding changes have been incorporated in Lines 325–328 of the revised manuscript:

"Importantly, the coupled formation of nitrosamines, HONO, and nitrate simultaneously influences particulate toxicity, atmospheric oxidation capacity, aerosol nitrate burden, and reactive nitrogen cycling, thereby extending the atmospheric significance of the identified interfacial chemistry beyond nitrosamine formation alone."

Comment S5. The discussion of HONO-mediated nitrosation could be strengthened to better contextualize its atmospheric significance. Although the HONO + DMA pathway is identified as secondary due to its higher free-energy barrier, the calculated interfacial rate constant is still reported to be 7-8 orders of magnitude faster than the corresponding aqueous-phase value. This represents a remarkably strong interfacial enhancement. The authors may therefore consider discussing under what atmospheric conditions this secondary pathway could nevertheless become important, such as in aged aerosols or HONO-rich nighttime environments.

Author response: We sincerely thank the referee for this insightful comment. We agree that the atmospheric significance of the HONO-mediated nitrosation pathway deserves further discussion. Following the referee's suggestion, we have expanded the discussion in Section 3.3 to clarify that the HONO-mediated pathway may become atmospherically relevant under specific environmental conditions. The corresponding discussion has been added to Lines 256–264 of the revised manuscript.

"Although the HONO-mediated nitrosation pathway is kinetically less favorable than the direct N-nitrosation by N_2O_4 under the investigated conditions, this pathway may become environmentally relevant under specific atmospheric scenarios. In particular, aged aerosols

with prolonged atmospheric residence times and nighttime HONO-rich environments may provide favorable conditions for this secondary pathway, because heterogeneous HONO production and accumulation can increase the availability of HONO at aqueous aerosol surfaces, whereas the concentration of highly reactive N_2O_4 may decrease during aerosol evolution. Under such conditions, interfacial HONO may serve as an important reactive nitrogen reservoir, linking inorganic nitrogen species with particulate organic nitrogen formation through subsequent reactions with amines. Therefore, the HONO-mediated pathway should not be considered merely as a kinetically minor reaction, but rather as a potentially important complementary pathway that contributes to particulate nitrosamine formation under specific atmospheric conditions."

Technical corrections:

6. Typos and non-scientific corrections:

a). Line 73: Add the missing article "the" before "plane-wave basis set": "...while that for the plane-wave basis set was set to 280 Ry."

Author response: Thanks. The revised sentence appears in Lines 84–85 of the revised manuscript:

"The cutoff energy for the Gaussian basis set was set to 40 Ry, while that for the plane-wave basis set was 280 Ry."

b). Section 3.3: In the sentence "Although the calculated energy barrier... is 7.65 kcal mol^{-1}... which is significantly lower...", the relative clause is awkward. Please split this into two sentences or rephrase to "Although the calculated energy barrier is 7.65 kcal mol^{-1}—a value significantly lower than..."

Author response: We sincerely thank the referee for this helpful suggestion. Following this comment, we reassessed the HONO–DMA reaction in the gas and aqueous phases, removed

the corresponding barrier calculations, and revised the discussion. The revised sentence appears in Lines 239–241 of the revised manuscript:

"The calculated energy barrier for this process is 7.65 kcal mol^{-1} (Fig. 4c), corresponding to an interfacial rate constant of 1.67 × 10^{7} M^{-1} s^{-1} at 300 K based on transition state theory (TST)."

c). Table S1: Please specify "Vibrational frequencies" in the header instead of "Calculated frequencies".

Author response: Accordingly, we have revised the header of Table S1 from "Calculated frequencies" to "Vibrational frequencies" in the revised Supporting Information.