Responses to Referee #2's comments

Thank you very much for your handling our manuscript "**Interface-dominated hydroxymethanesulfonate and its isomer formation provides key mechanisms for reconciling the atmospheric sulfur budget gap in polluted and cold environments**" (MS No.: egusphere-2026-388). The point-to-point responses to the Referee #2's comments are summarized below:

Referee #2:

Liu et al. investigated the formation mechanisms of HMS and HMSi in aqueous phase and at air-water/ice interfaces using quantum chemistry calculations with ORCA and BOMD simulations with the CP2K package, and observed a nearly barrierless HMS formation route at air-water/ice interfaces and a competitive formation energy barrier in the bulk aqueous phase. Interestingly, the formation route reverses for the interfacial reactions when the pH drops below 2, which indicates the importance of aerosol acidity in product formation.

In the revised manuscript, the authors have carefully addressed the proposed comments. In particular, the title is moderated, the aerosol pH statement is clarified, additional metadynamics convergence diagostics have been provided, the use of PBE-D3 has been better justified, the initial configurations for the unbiased BOMD trajectories have been clarified, and a conceptual scheme has been added. These changes substantially enhanced the clarity and scientific rigor of the manuscript.

Response: Thanks for the reviewer's professional and valuable comments. We have addressed all comments point by point and made the corresponding revisions in the manuscript. The detailed responses are listed as follows.

Major and Specific Comments:

Comment 1: First of all, although the title has been moderated, the abstract and conclusion still contain claims that exceed what can be demonstrated by molecular simulations alone. For example, the statement that interfacial mechanisms dominate HMS and HMSi formation cannot not quantitatively supported without considering atmospheric flux estimates and chemical transport model computations. I would recommend replacing such language with more cautious wording, such as "may substantially enhance formation" or "may provide efficient pathways for HMS/HMSi formation" which can lower down the tone of the statement.

Response: We sincerely thank the reviewer for this careful and valuable comment. We have rephrased relevant statement cautiously throughout the abstract, introduction, and conclusions to soften the tone of the statement and reflect the mechanistic nature of our findings without implying quantitative atmospheric closure. The corresponding revisions are as follows.

In the Abstract (Page 1, lines 19–21), the “Our findings establish that interfacial mechanisms dominate HMS and HMSi formation in both polluted and cold environments, helping to reconcile model-observation discrepancies in the atmospheric sulfur budget” has been revised to “Our findings suggest that interfacial mechanisms may provide efficient pathways for HMS and HMSi formation in both polluted and cold environments, helping to reconcile model-observation discrepancies in the atmospheric sulfur budget.”

In the Introduction (Page 4, lines 97–98), the phrase “we aim to reveal interfacial-dominated sulfur cycling mechanisms” has been revised to “we aim to reveal interfacial sulfur cycling mechanisms.”

In the Conclusions (Page 15, lines 358–361), the sentence “At air–water interfaces in polluted aerosols, HMS formation proceeds with a dramatically reduced barrier of 0.6 kcal mol^{-1} through stepwise water-mediated proton transfer, while HMSi formation faces a substantially higher barrier of 6.1 kcal mol^{-1}” has been revised to “At air–water interfaces in polluted aerosols, HMS formation proceeds with a substantially reduced barrier of 0.6 kcal mol^{-1} through stepwise water-mediated proton transfer, while HMSi formation faces a higher barrier of 6.1 kcal mol^{-1}, suggesting that interfacial chemistry may substantially enhance HMS formation relative to the bulk aqueous phase.”

We hope these revisions appropriately moderate the tone of our claims while preserving the mechanistic significance of the findings.

Comment 2: Second, the author correctly acknowledged the comment that geometric exposure of the HMS hydroxyl radical may not directly prove enhanced oxidation. However, the conclusion still states that this exposure accelerates conversion to sulfate, which should be aligned with the revisions in the previous chapter and the response letter.

Response: We sincerely thank the reviewer for catching this inconsistency. We agree that the conclusions should be aligned with the more cautious wording adopted in Section 3.5 and in our previous response letter. Accordingly, we have revised the corresponding sentence in the Conclusions to remove the strong claim about accelerated conversion to sulfate. The revision is as follows.

In the Conclusions (Page 15, lines 373–374), the original sentence "This enhanced gas-phase exposure renders HMS more accessible to atmospheric oxidants including hydroxyl radicals, accelerating its conversion to sulfate" has been revised to "This enhanced gas-phase exposure may render HMS more accessible to atmospheric oxidants including hydroxyl radicals, potentially facilitating its interfacial oxidation due to orientation preferences."

Comment 3: Third, the aerosol pH statement has been improved in the Introduction, but the conclusion still refers to strongly acidic regions as encompassing approximately 20% of Earth's surface atmosphere. This should be revised to retain the same spatiotemporal constraints described earlier so as to provide a better implication of spatiotemporal predictions.

Response: We sincerely thank the reviewer for this careful observation. We agree that the conclusions should retain the same spatiotemporal and methodological constraints already adopted in the Introduction. Accordingly, we have revised the corresponding sentence in the Conclusions to align with the more accurate phrasing introduced in the previous round. The revision is as follows.

In the Conclusions (Page 15, lines 364–367), the original sentence "Because strongly acidic regions encompass approximately 20% of Earth's surface atmosphere (Li et al., 2022), this acid-catalyzed pathway addresses previously uncharacterized sulfur sources in marine and polluted continental environments" has been revised to "Based on global surface-layer aerosol pH estimates using annual-mean GEOS-Chem simulations coupled with E-AIM thermodynamic calculations, aerosol pH in the range of −1 to 1 occurs over at least 20% of the global surface area where the model successfully converges (Li et al., 2022)."

Reference:

Li, M., Su, H., Zheng, G., Kuhn, U., Kim, N., Li, G., Ma, N., Poschl, U., and Cheng, Y.: Aerosol pH and Ion Activities of HSO_4^- and SO_4^{2-} in Supersaturated Single Droplets, Environ. Sci. Technol., 56, 12863–12872, https://doi.org/10.1021/acs.est.2c01378, 2022.