

**Manuscript No.:** ACP-2026-68

**Title:** In Situ Real-Time Determination of SO<sub>2</sub> Photochemical Oxidation in Nanoscale Sea Salt Aerosols Based on Dark-Field Microscopy

We thank the commenter for the valuable and constructive comments on our manuscript. We will revise the manuscript accordingly. Please find our point-to-point responses below.

**Major comments:**

1) *The authors need to clarify which photochemical mechanism is being investigated in this work. The manuscript uses terms such as “UV-catalyzed SO<sub>2</sub> oxidation,” which are too vague. Is the SO<sub>2</sub> conversion driven by photoactivation of chloride, such as that reported by Cao et al. (JACS 2024, 146, 1467–1475)? If so, I suggest that the authors explicitly state the targeted reaction mechanism in the Introduction or at the beginning of the Results section. The relevant chemical equations and the corresponding kinetic expression derived from the proposed mechanism should also be clearly presented.*

**Response:** We thank the reviewer for this important comment. We agree that the description “UV-catalyzed SO<sub>2</sub> oxidation” in the original manuscript was not sufficiently specific. In the revised manuscript, we have clarified that the reaction is interpreted as a chloride-mediated photochemical oxidation process occurring in the aqueous phase of NaCl droplets under UV irradiation.

We have added a more explicit description of the proposed reaction pathways in the Introduction and at the beginning of the Results section, including representative reactions involving reactive chlorine species based on relevant literature (e.g., Cao et al., 2024).

Corresponding kinetic expressions have also been included to better support the interpretation of the observed kinetics. We note that the mechanism is inferred based on consistency with previous studies, rather than directly resolved in this work.

2) *Does O<sub>2</sub> exist in the gas phase of the multiphase reaction system? Based on the Methods section, I infer that the gas phase consists of SO<sub>2</sub>, N<sub>2</sub>, and water vapor. The authors should explain why O<sub>2</sub> (or air) was excluded from the system. This exclusion does not reflect realistic atmospheric conditions. In addition, O<sub>2</sub> may play an important role in chloride-mediated SO<sub>2</sub> photooxidation.*

*As shown by Cao et al. (2024), Cl radicals are generated through photoactivation of [Cl- ... H3O+ ... O2] adducts rather than by direct activation of Cl- ions.*

**Response:** We thank the reviewer for this insightful comment. We acknowledge that O<sub>2</sub> can play an important role in chloride-mediated photochemical oxidation pathways, particularly in facilitating radical formation and propagation, as suggested in previous studies (e.g., Cao et al., 2024).

In the present study, the carrier gas consists of SO<sub>2</sub>, N<sub>2</sub>, and water vapor, and O<sub>2</sub> was not intentionally introduced. This design was adopted to control experimental variables and to better highlight geometric effects, particularly those related to particle size and curvature.

We have clarified this point in the revised manuscript and emphasized that the present results should be interpreted as reflecting a simplified system, where geometric and interfacial effects can be examined more clearly. The influence of O<sub>2</sub> on the reaction mechanism and kinetics will be an important direction for future work.

3) *How do the authors rule out the influence of the substrate? Both SiO<sub>2</sub> and TiO<sub>2</sub> can act as effective photocatalytic materials under UV irradiation. It is therefore possible that the substrate contributes to the conversion of S(IV). Moreover, if the reaction occurs partly or predominantly at the liquid–solid interface, for example in the contact region between the droplet and the substrate, the observed reaction rate could also increase with droplet size simply because larger droplets have a greater contact area with the substrate.*

**Response:** We thank the reviewer for raising this important point. To minimize potential substrate-induced effects, the SiO<sub>2</sub> substrate used in this study is coated with a thin inert gold layer, which effectively suppresses direct photocatalytic activity from the underlying material.

This surface treatment reduces the likelihood that the observed reaction is driven by substrate photocatalysis. In addition, the observed size-dependent trends are more consistent with aerosol geometric factors (e.g., surface-to-volume ratio and curvature effects) rather than scaling with the droplet – substrate contact area.

Similar surface treatment strategies have been employed in our previous work. This aspect was not explicitly emphasized in the original manuscript, and we will add a discussion of this point in the revised version.

4) *The SO<sub>2</sub> concentration used in the experiments (200 ppm) is extremely high. This is approximately three to four orders of magnitude higher than concentrations encountered even during severe air pollution episodes. The authors should consider repeating the experiments over a range of SO<sub>2</sub> concentrations and examining how the kinetics scale with SO<sub>2</sub> concentration. Without such*

*parameterization, it is difficult to assess whether the measured kinetics can be meaningfully extrapolated to atmospherically relevant conditions.*

**Response:** We thank the reviewer for this important comment. We acknowledge that the SO<sub>2</sub> concentration used in this study (200 ppm) is significantly higher than typical atmospheric levels. This concentration was selected to ensure sufficient signal-to-noise ratio.

We agree that reaction kinetics may depend on SO<sub>2</sub> concentration, and therefore the absolute rate constants reported here should not be directly extrapolated to ambient conditions. Instead, the primary focus of this study is on relative trends, particularly the dependence of reaction kinetics on particle size and surface properties.

We will include additional control experiments conducted at lower SO<sub>2</sub> concentrations to evaluate whether the reaction kinetics exhibit significant dependence on SO<sub>2</sub> levels and to assess the robustness of the observed trends under more atmospherically relevant conditions. We will clarify this in the revised supporting information.

5) *I am very confused by the derivation of first-order kinetics from the presented data. As stated in the manuscript, first-order kinetics should be reflected by an exponential decay in NaCl concentration. However, Figure 3d appears to show an exponential increase in C, rather than a decay. In addition, at the initial condition (t = 0), why is ln(C/C<sub>0</sub>) equal to zero rather than one? Furthermore, the sulfate concentration shown in Figure 3a increases approximately linearly with time, rather than following the type of exponential behavior expected for first-order kinetics. These observations seem inconsistent with the authors' kinetic interpretation and should be clarified carefully.*

**Response:** We thank the reviewer for this careful reading and for pointing out the confusion regarding the kinetic analysis. We have clarified this point in the revised manuscript.

In Figure 3d, the plotted quantity represents sulfate concentration, which is a reaction product. Therefore, its increase with time reflects product formation and can exhibit an exponential growth behavior, rather than decay.

For the logarithmic analysis,  $\ln(C_0/C)$  is used to describe the decay of the reactant (NaCl). At the initial condition ( $t = 0$ ),  $C = C_0$ , and thus  $\ln(C_0/C) = \ln(1) = 0$ , which is consistent with the definition.

The approximately linear increase in sulfate concentration shown in Figure 3a corresponds to the early stage of the reaction, during which the reactant concentration does not decrease significantly. Under such conditions, the reaction rate is effectively independent of reactant depletion, and the product formation appears quasi-linear over time.

We have revised the text and figure descriptions to clearly distinguish between reactant decay and product formation, and to improve the consistency of the kinetic interpretation.

**Minor Comments:**

- 1) *Line 43: Do the authors mean oxidation of SO<sub>2</sub> by H<sub>2</sub>O<sub>2</sub>?*
- 2) *Lines 47–48: The authors may wish to reconsider their interpretation of the work by Angle et al. In that study, the kinetics were derived from Raman measurements of changes in reactant or product concentrations, rather than from the evolution of ionic strength.*
- 3) *Figure 1: Please check the spelling of “diffusion dryer.”*

**Response:** We thank the reviewer for the careful reading and for these helpful minor comments. We will revise the manuscript accordingly, as detailed below:

Line 43: The text will be revised to clarify that this refers to the oxidation of SO<sub>2</sub> by H<sub>2</sub>O<sub>2</sub>.

Lines 47 – 48: We thank the reviewer for this suggestion. The description of the work by Angle et al. will be revised to more accurately reflect that the reaction kinetics were derived from Raman measurements of changes in reactant and/or product concentrations, rather than from the evolution of ionic strength.

Figure 1: The spelling of “diffusion dryer” will be checked and corrected in the figure.