Manuscript No.: ACP-2026-68

Title: In Situ Real-Time Determination of SO_2 Photochemical Oxidation in Nanoscale Sea Salt Aerosols based on Dark-Field Microscopy

We thank the anonymous referees for their valuable and constructive comments/suggestions on our manuscript. We have revised the manuscript accordingly and please find our point-to-point responses below.

Comments by Anonymous Referee #1:

General Comments:

This study proposes an in situ real-time measurement method based on dark-field microscopy to investigate the photochemical oxidation of SO_2 in nanoscale sea-salt aerosols. By combining the hygroscopic GF with the ZSR mixing rule, the authors successfully retrieve single-particle reaction kinetics and reveal a non-monotonic dependence of the reaction rate on particle size. The method is innovative, and the research falls within the scope of ACP. However, the scientific significance and the completeness of the experimental design require further clarification and strengthening. Acceptance is recommended after addressing the following points.

Response: We thank the reviewer for the constructive comments and valuable suggestions. Following the reviewer's recommendations, we have revised the manuscript to clarify the scientific significance of this study and strengthen the description of the experimental design. Point-to-point responses to the reviewer's comments are provided below, and the corresponding revisions have been incorporated into the manuscript.

Major comments:

1) *While this study achieves in situ observation of reaction kinetics for individual nano-aerosol particles—a notable methodological advance—what specific atmospheric chemistry problem does it aim to solve? For instance, does it target the mechanism of rapid sulfate formation during haze episodes? How do the findings directly improve existing atmospheric chemistry models or pollution assessments?*

Response: We thank the reviewer for this important question. The primary objective of this study is to investigate the size-dependent kinetics of heterogeneous SO_2 oxidation in nanoscale sea salt aerosols. Rapid sulfate formation in atmospheric particles—such as that

observed during haze episodes—has been widely reported, yet the controlling mechanisms and kinetic parameters remain uncertain, particularly at the nanoscale. Most previous studies derive heterogeneous reaction rates from bulk solutions or micrometer-sized droplets, while atmospheric aerosols frequently exist in the submicron and nanoscale range.

In this size regime, geometric factors such as surface-to-volume ratio and surface curvature may influence gas uptake and interfacial mass transfer, but experimental constraints on these effects remain limited. By combining dark-field microscopy with hygroscopic growth analysis, this work provides in situ kinetic measurements for individual NaCl particles in the 50–400 nm size range. The observed non-monotonic size dependence of sulfate formation rates suggests that nanoscale geometric effects can influence heterogeneous SO_2 oxidation. These findings provide experimental constraints on size-dependent sulfate formation processes and may help improve the representation of heterogeneous sulfur oxidation in atmospheric chemistry models.

2) *In this study, the hygroscopic G) of particles is derived from grayscale intensity using dark-field microscopy, and reaction kinetics are inferred based on the ZSR rule. To verify the reliability of the optical method, please provide the measured hygroscopic GF results for pure NaCl particles under the same experimental conditions (e.g., RH range 25%–85%) and compare them with theoretical models (e.g., E-AIM) or classical HTDMA data. If direct measurements were not performed, please specify whether GF parameters for NaCl from validated literature were adopted and discuss their applicability within your optical measurement system.*

Response: We thank the reviewer for this helpful suggestion. In response, we have added a comparison between the hygroscopic GF of monodisperse 100 nm NaCl particles measured using our dark-field microscopy method and the predictions from the thermodynamic model E-AIM under the same RH conditions.

3) *In Section 2.2 and Figure 3b, you state that IC measurements provided independent validation of the GF-based kinetic analysis, showing a "consistent linear trend" when plotting $\ln(C_0/C)$ versus time. However, the manuscript does not provide a clear, step-by-step explanation of how the IC*

data (presumably aqueous concentrations of anions like sulfate or chloride from filter extracts) were converted into the dimensionless ln(C_0/C) values used in Figure 3b

Response: We thank the reviewer for pointing out this lack of clarity. In response to this comment, we have added a detailed description of the data processing procedure in the revised manuscript (Lines 270-284), including the step-by-step derivation showing how the IC measurements were converted into the dimensionless *ln(C_0/C)* values used in Figure 3b.

4) *The SO_2 concentration used in the experiments (200 ppm) is much higher than typical atmospheric background levels (usually ppb). The authors explain this is necessary to obtain sufficient signal within the experimental timeframe. However, could this affect the representativeness of the reaction mechanism (e.g., surface adsorption, oxidation pathways)? Were validation experiments conducted at lower, more atmospherically relevant concentrations to confirm the applicability of the derived kinetic parameters?.*

Response: We thank the reviewer for this important comment. We acknowledge that the SO_2 concentration used in the primary experiments is substantially higher than typical atmospheric levels. This concentration was selected to ensure sufficient signal-to-noise ratio and to enable time-resolved observation of the reaction kinetics within a practical experimental timescale.

To evaluate whether the elevated SO_2 concentration affects the observed reaction behavior, we conducted an additional control experiment using 100 nm NaCl particles at a lower SO_2 concentration of 20 ppm under otherwise identical conditions (85 % RH and UV irradiation). The corresponding results have been added to the Supplementary Information (Fig. S20). The apparent first-order rate constant decreased from 0.6523 h^{-1} at 200 ppm SO_2 to 0.2254 h^{-1} at 20 ppm SO_2, indicating a slower reaction rate at lower SO_2 concentration.

Importantly, the reaction remained well described by first-order kinetics at 20 ppm SO_2. Although the reaction proceeded on a longer timescale, the overall evolution of sulfate formation and NaCl consumption was qualitatively consistent with that observed at 200 ppm when the observation period was extended sufficiently. These results suggest

that the elevated SO_2 concentration primarily affects the reaction timescale and absolute rate, rather than fundamentally altering the kinetic behavior observed in this study.

We have added a discussion of these results in the revised manuscript (Lines 280–294) and Supplementary Information.

Comments by Anonymous Referee #2:

General Comments:

This manuscript details a method using dark-field microscopy for in situ real-time measurement of photochemical oxidation of SO_2 in individual nanoscale aerosol particles. Hygroscopic growth factors and the Zdanovskii-Stokes-Robinson rule are employed to determine first-order kinetics for sodium chloride aerosols ranging in size from 50-400 nm, revealing a non-monotonic dependence of the reaction rate constant on particle size. Additionally, the study investigates the effect of organic coatings on oxidation reaction rates. The method is certainly novel and an appropriate topic for ACP, however I have several questions and points of confusion that should be addressed prior to acceptance.

Response: We thank the reviewer for the constructive comments and for recognizing the novelty and relevance of this work. We also appreciate the reviewer's careful reading and for pointing out several questions and areas that require clarification. Following these comments, we have revised the manuscript to improve the clarity of the data analysis, better explain the experimental design and underlying assumptions, and strengthen the presentation of the results and their interpretation. Point-by-point responses to the reviewer's comments are provided below, and all corresponding revisions have been incorporated into the manuscript.

Major comments:

1) *I found it difficult to follow the method for calculating the rate constant as detailed in the experimental section, and then subsequently challenging to connect the presentation of kinetic data in the results with the described calculations. There were several mislabeled variables (see Minor Comments for examples) or new variables introduced in the discussion that were not defined in the method (specifically $ln(C_0/C)$. Most of my confusion re: calculations will be*

alleviated by correcting equation/variable labels and clarifying how plotted variables in Figures 3-5 were determined, but as it currently is presented, the method for data analysis is unclear and needs to be addressed.

Response: We thank the reviewer for this careful reading and for pointing out the lack of clarity in the presentation of the data analysis procedure. We have revised the section 2.4 of the manuscript to improve the transparency and consistency of the kinetic analysis. The rewritten Section 2.4 is provided in Lines 160 – 204 of the revised manuscript.

Specifically, the calculation procedure for deriving the rate constant has been reorganized and described in a clearer, step-by-step manner. All variables used in the analysis (including $ln(C_0/C)$) will be explicitly defined upon first introduction, and their physical meanings will be clarified. In addition, we will carefully check and correct mislabeled variables and ensure consistency between the Methods section and the presentation of results in Figures 3 – 5.

Furthermore, we will expand the description of how the plotted quantities were obtained from the experimental measurements, including the derivation from hygroscopic GF data to the kinetic parameters. These revisions are intended to eliminate ambiguity and ensure that the data processing workflow is transparent and reproducible.

2) *The primary conclusions regarding the non-monotonic dependence of the SO_2 reaction rate constant on particle size rely on a comparison of the experimental GFs of NaCl particles with E-AIM calculated GFs of NaCl and $NaHSO_4$ particles. Comparison to experimental GFs for NaCl and $NaHSO_4$ particles or literature GFs under similar environmental parameters would lend greater validity and confidence to the results presented in this work.*

Response: We thank the reviewer for this valuable suggestion. To strengthen the validity of the GF-based analysis, we have supplemented the manuscript with experimentally measured hygroscopic GFs for both NaCl and $NaHSO_4$ particles under comparable environmental conditions. The experimental results have been included and compared with the corresponding E-AIM model predictions.

The experimental hygroscopic GF measurements for pure NaCl particles have been added to the revised manuscript (Lines 155 – 159), while the corresponding measurements for pure $NaHSO_4$ particles are provided in the Supplementary Information (Fig. S21). In both

cases, the experimental results show good agreement with the E-AIM predictions, providing additional confidence in the applicability of the hygroscopicity-based approach adopted in this study.

These additions further support the reliability of the GF calculations and strengthen the basis for the subsequent kinetic analysis and interpretation of the particle-size dependence of the reaction rate.

3) *How might this method be applied to cover a scope of more atmospherically relevant conditions, such as lower SO_2 concentrations or lower RH?*

Response: We thank the reviewer for this important question regarding the broader applicability of the method. We acknowledge that atmospheric conditions often involve lower SO2 concentrations and a wider range of RH. The present study focuses on the retrieval of reaction kinetics and the investigation of curvature effects. To better resolve these effects and enhance the observability of the reaction behavior, relatively elevated SO2 concentrations and high RH conditions were employed.

To evaluate the applicability of the method under less extreme conditions, we performed an additional experiment at 20 ppm SO_2 using 100 nm NaCl particles. The reaction remained consistent with first-order kinetics, although the apparent rate constant decreased from 0.6523 h^{-1} to 0.2254 h^{-1}. When the observation period was extended sufficiently, the overall kinetic evolution remained similar to that observed at 200 ppm SO_2, demonstrating that the methodology can be applied under lower SO_2 concentrations. These additional results and the associated discussion have been incorporated into the revised manuscript (Lines 280 – 294).

Future work will extend this approach to lower SO_2 concentrations, a broader RH range, and more atmospherically relevant aerosol systems. The ability of the method to continuously monitor single-particle hygroscopic evolution in situ makes it particularly suitable for investigating heterogeneous reaction kinetics under realistic environmental conditions.

Minor Comments:

1) *Figure 1: Misspelling of 'diffusion dryer' in graphic labels.*
2) *Line 100: The text refers to Figure 2.1 – should it be Figure 1?*
3) *Line 115: Please define the acronym 'OVF'.*

4) Line 150: Should the section title read '2.4 Calculation of Reaction Rate'?

5) Line 178: Should the defined variables be C_0, Ct? I do not see CT in either equation (7) or (8).

6) Figure 2/Line 210: The text refers to a red curve representing fresh NaCl particles in Figure 2, but the curve in reference is actually blue?

7) Lines 240-250: The text refers to $ln(C/C_0)$ but the corresponding Figure 3 (and later discussion) refers to $ln(C_0/C)$.

8) Line 350: The text referring to Figure 5 discusses $ln(C_0/C)$ values, but they are not represented in the figure?

9) Figure 5: The figure caption refers to a shaded area denote 95% confidence intervals, but there does not appear to be a shaded area in the figure.

Response: We thank the reviewer for the careful reading of the manuscript and for pointing out these minor errors and inconsistencies. We have carefully revised the manuscript to correct all typographical errors, inconsistencies in figure labeling, and unclear definitions. Specific revisions are detailed below:

1) The spelling of "diffusion dryer" in Figure 1 has been corrected.

2) The figure reference in Line 100 has been corrected to the appropriate figure.

3) The acronym "OVF" (organic volume fraction) has been defined upon first use in the Line 21.

4) The section title has been corrected to "2.4 Retrieval of reaction progress and kinetic parameters".

5) The variable notation has been corrected for consistency, and the definitions of C_0 and Ct are now clearly stated in both the text and equations.

6) The color description of the curve in Figure 2 has been corrected to blue.

7) The notation for the logarithmic expression has been corrected to $ln(C_0/C)$ to ensure consistency between the text and figures.

8) The description of Figure 5 has been revised to accurately reflect the data presented.

9) The figure caption has been revised to be consistent with the figure.

Comments by commenter:

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_2 oxidation," which are too vague. Is the SO_2 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 term "UV-catalyzed SO_2 oxidation" used in the original manuscript was overly general and did not adequately describe the photochemical process investigated in this work.

The observed sulfate formation is interpreted within the framework of chloride-mediated photochemical oxidation of dissolved S(IV) species in aqueous NaCl droplets under UV irradiation. The primary objective of this study is to quantify the apparent reaction kinetics of SO_2 oxidation in nanoscale sea-salt aerosols rather than to directly identify the elementary reaction pathways or reactive intermediates.

We emphasize that the proposed mechanism is inferred based on consistency with previous studies (Zhang et al., 2023) of illuminated saline aerosols and is used here as a conceptual framework for interpreting the observed sulfate formation. Because reactive intermediates were not directly measured in the present study, we avoid overinterpreting the detailed radical chemistry .

2) *Does O_2 exist in the gas phase of the multiphase reaction system? Based on the Methods section, I infer that the gas phase consists of SO_2, N_2, and water vapor. The authors should explain why O_2 (or air) was excluded from the system. This exclusion does not reflect realistic atmospheric conditions. In addition, O_2 may play an important role in chloride-mediated SO_2 photooxidation. As shown by Cao et al. (2024), Cl radicals are generated through photoactivation of [Cl- ... H3O+...O_2] adducts rather than by direct activation of Cl- ions.*

Response: We thank the reviewer for this insightful comment. We acknowledge that O_2 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_2, N_2, and water vapor, and O_2 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 (Lines 105-107). 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_2 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_2 and TiO_2 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_2 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 have added a discussion of this point in the revised version (Lines 90-91).

4) *The SO_2 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_2 concentrations and examining how the kinetics scale with SO_2 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_2 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.

In response, we conducted an additional control experiment using 100 nm NaCl particles at 20 ppm SO_2 under otherwise identical experimental conditions. The corresponding hygroscopic growth measurements and kinetic analysis have been included in the Supplementary Information (Fig. S20). The apparent first-order rate constant decreased from 0.6523 h^{-1} at 200 ppm SO_2 to 0.2254 h^{-1} at 20 ppm SO_2, confirming that the absolute reaction rate depends on SO_2 concentration. These additional results and the associated discussion have been incorporated into the revised manuscript (Lines 280 – 294).

Nevertheless, the reaction remained well described by first-order kinetics at both concentrations. Furthermore, when the observation period was extended sufficiently, the temporal evolution of sulfate formation and NaCl consumption exhibited similar behavior at 20 ppm and 200 ppm SO_2. These results indicate that the elevated SO_2 concentration mainly affects the characteristic timescale of the reaction rather than the underlying kinetic framework.

We agree that a systematic parameterization of reaction kinetics over a wider range of SO_2 concentrations would be valuable for quantitative atmospheric extrapolation. Such experiments are beyond the scope of the present study but will be the subject of future work. We have clarified this limitation and added the new low-concentration results to the revised manuscript.

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 $\ln(C/C_0)$ 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.

Regarding the approximately linear increase in sulfate concentration shown in the original Figure 3a, the original manuscript only presented data over the reaction period of 0 – 3.5 h, which mainly corresponds to the early stage of the reaction, during this period, NaCl consumption remains limited and the sulfate concentration increases approximately linearly with time. We agree that this may give the impression that the reaction does not follow first-order behavior. In the revised manuscript, we have extended the observation period to 5 h. The updated results show a clear slowdown in sulfate formation after approximately 4 h, with the system gradually approaching a plateau. This behavior is consistent with progressive reactant depletion and supports the first-order kinetic interpretation derived from the $\ln(C_0/C)$ analysis.

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_2 by H_2O_2?

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 has been revised to clarify that this refers to the oxidation of SO_2 by H_2O_2.

Lines 47 – 48: We thank the reviewer for this suggestion. The description of the work by Angle et al. has been 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” has been checked and corrected in the figure.

Additional technical corrections requested by the editor

In addition to the revisions addressing the referee and community comments, we have implemented the technical corrections suggested by the editor as follows:

1) All figures and tables provided in the Supplement have been cited in the main text.

2) The spelling error in Fig. S19 has been corrected.

3) The sections of Code and data availability, Author contributions, and Competing interests have been added to the manuscript.

We appreciate the editor’s guidance and believe that these corrections have improved the completeness and clarity of the manuscript.