<p style="text-align:center">Responses to reviewers</p>

Reviewer comments are in **bold**. Our responses are labelled with [R] and authors' actions with [A]. Line numbers in the responses correspond to the revised manuscript with track-changes. Modifications to the manuscript are in blue.

Reviewer 1

Zhou et al. describe a series of laboratory flow-tube experiments analyzing sulfate formation via heterogeneous reaction of SO2 and several types of photo-active organic particles. The results are interesting, demonstrate the utility of a novel analytical method (single-particle aerosol mass spectrometry) for observing particle-phase sulfate formation, and add to the rapidly growing body of works exploring atmospheric sulfate formation. I believe this paper merits publication in ACP after several major and minor comments are addressed, potentially involving additional experimentation. My comments are outlined below.

> [R0] We thank the reviewer for the valuable feedback and constructive suggestions. Detailed responses are given below.

Major comments

I believe the authors need to more clearly highlight the apparent role of RH in these experiments and to more thoroughly explore the role that RH plays in the observed reactions. At line 221 the authors discuss that vanillin-coated particles produced substantially less sulfate at 20% RH relative to the 80% RH used in other experiments. RH therefore seems to be an important factor in affecting organic photosensitizer-initiated sulfate formation, but RH isn't mentioned as a factor in the abstract or the experimental description in the introduction. More thoroughly investigating the role that variable RH has on photosensitizer-initiated SO2 oxidation would be very important to better understanding the significance of this pathway in ambient environments. Additionally, at line 158 the authors discuss potential SO2 oxidants and note the possibility for oxidants that form from H2O; does the apparent RH dependence point to H2O as a secondary oxidant source following initial photo-excitation?

> [R1] Thank you for your comments. We agree that the role of RH in the experimental system should have been better addressed. Firstly, the reaction between photoexcited SO_2 molecules and H_2O can produce secondary OH radicals (Kroll et al., 2018). However, this reaction played a negligible role in this study because we did not see effective sulfate formation in the control experiment using BA-coated particles as

seeds in the presence of SO_2 (Figure 2). Furthermore, Corral Arroyo et al. (2018) also reported that the particle-phase photosensitized radical production was promoted at higher RH due to the presence of more water as plasticizers and reduced particulate viscosity. In our system, the photosensitizers have low solubility and hygroscopicity, resulting in limited available dissolved VL to trigger photosensitization and possibly limited dissolved SO_2. In addition, lower RH could result in higher particulate viscosity, which hinders molecular diffusion and reaction (Kroll et al., 2018; González Palacios et al., 2016; Corral Arroyo et al., 2018). We have added this information to the text. In this study, the low RH experiments were conducted for the externally mixed VL and nitrate system to study whether the relative atmospheric importance of particulate photosensitization and nitrate photolysis are still the same as those under high RH conditions, given that nitrate concentration in droplets may be much higher under low RH. We found that sulfate formation was on VL-coated particles but not on externally mixed nitrate particles under both high and low RH conditions (Figure 4 and Figure S10). Quantitative examinations of the RH-dependent sulfate formation for photosensitization reaction is useful for future work.

[A1] We have added the potential RH effect on the photosensitized reaction after line 271: "When RH decreased to 20%, a significant reduction in the average RPAs from 0.26 to 0.002 was observed for VL-coated particles (Figure S10), attributable to the fewer dissolved VL for sulfate formation since VL has low solubility and hygroscopicity and the limited SO_2 dissolution (Liu et al., 2021b). In addition, lower RH could result in higher particulate viscosity, which hinders molecular diffusion and reaction (Kroll et al., 2018; González Palacios et al., 2016; Corral Arroyo et al., 2018). A systematic study of the effect of RH on the particle-phase photosensitized reaction is desirable. Overall, sulfate formation was found on VL-coated particles but not on externally mixed nitrate particles at both high and low RH in our study."

I have several questions about sulfate signal variability, mass spectral variability inherent to the SPAMS, and particle size.

Line 110, section 2.2: how much variability are there in SPAMS spectra? E.g., how much variability in absolute peak area would be expected for monodisperse sulfate particles? What is the expected detection efficiency of the SPAMS for the observed size ranges of particles? Is it possible that any of the presented results are biased from low number statistics due to low particle detection efficiency and/or low numbers of particles? Does particle-phase water have any effect on desorption/ionization and RPAs/APAs? Even if some of these aspects of the SPAMS have been discussed in more detail previously some discussion here is necessary to fully understand and evaluate the presented results.

[R2] The relative peak area (RPA) of sulfate in photosensitizer coated particles has an average standard deviation of 11% across different size bins (Figure S7). The absolute peak area is more sensitive to the variability in ion intensities associated with particle-laser interactions than RPA (Gross et al., 2000; Hatch et al., 2014), and therefore it is not estimated here. The ionization efficiency of SPAMS to detect atmospheric aerosol particles in the size range of 250-2000 nm was above 30% on average (Li et al., 2011). Taking the ionization efficiency into consideration, the number of detected/ionized particles for each experiment condition was around 1000-3000, which is sufficient for systematically identifying the heterogeneous reaction products (Liang et al., 2022; Qi et al., 2019). Before entering the SPAMS, the particles passed through a diffusion dryer to reduce the matrix effects from water (Neubauer et al., 1998).

[A2] To better understand the results, more details of the SPAMS have been added after line 130: "The sized particles were then desorbed and ionized by a pulsed 266 nm laser (0.5 mJ), which was triggered at the precise time on the basis of the particle velocities. The produced positive and negative molecular fragments were analyzed by a Z-shaped bipolar time-of-flight mass spectrometer (Pratt et al., 2009; Li et al., 2011). The ionization efficiency of SPAMS to detect 250-2000 nm atmospheric aerosol particles was above 30% on average (Li et al., 2011). The number of ionized particles for each experiment condition was around 1000-3000, sufficient for systematically identifying the heterogeneous reaction products (Liang et al., 2022; Qi et al., 2019). Furthermore, each experiment was repeated, as reflected in Figure S6. Single particle size and mass spectral analysis were performed using the Computational Continuation Core (COCO) toolkit based on MATLAB software. The number percentage and relative peak area (RPA, defined as the fractional contribution of the targeted ion peak area to the sum of all ion peak areas) were applied to indicate the variations of the amount of different species (e.g., sulfate) in individual particles (Hu et al., 2022). Sulfate-containing particles were distinguished by m/z -97 [HSO_4^-] or m/z-96 [SO_4^-] (Guazzotti et al., 2001; Liang et al., 2022). In addition, an adaptive resonance theory based neural network algorithm (ART-2a) (Li et al., 2011) was used to separate and cluster particles in external and internal mixtures according to the similarities in individual mass spectra of single particles. Before entering the SPAMS, the particles passed through a diffusion dryer to reduce the matrix effects from water (Neubauer et al., 1998)."

There seems to be a lot of spread in the sulfate RPAs within the experiments (Line 146/Figure 2). Do the authors have a theory for this spread? Is SO2 oxidation less efficient on some particles? Is there substantial spread in flow tube residence time? Is this just due to particle-to-particle variation in SPAMS ionization?

[R3] The spread in the sulfate RPA for a specific experimental condition in Figure 2 is mainly due to the RPA differences for particles of different sizes (Figure S7). As we have discussed in line 257 that the reactive uptake comprises the diffusion of SO_2 molecules, followed by oxidation of SO_2 at/near the surface or in the bulk of the particles. The decreased sulfate RPA with increasing particle size suggested the photosensitized sulfate formation at/near the surface of VL-coated particles, probably due to the prevalence of surface reactions or diffusional limitations of SO_2 in larger particles, especially in the poorly hygroscopic and potentially viscous VL matrix. Even though the sulfate RPA was size dependent, it generally exhibited the same descending order of DMB>VL>SyrAld>BA in each size bin (Figure S7). In Figure 2, the RPA and number percentage for each specific experimental condition was calculated by taking an average of RPAs and number percentages in different size bins in Figure S7.

[A3] For clarity, we had added after line 170 that "Although the coating thickness estimated by particle size increase spanned a wide range from 100 nm to 2.2 μm, the number percentage and RPA of sulfate generally exhibited the same trend for the studied photosensitizers in each size bin (Figures S7). Figure 2 shows the average RPA of sulfate (circles) and the number percentage of sulfate-containing particles (diamonds) in DMB-, VL-, SyrAld- and BA-coated particles at dark and different UV intensities in the presence of SO_2, and the corresponding SO_2 consumption normalized by the average total particle surface area concentration before and after UV irradiation in the OFR detected by SPAMS (crosses). The RPA and number percentage of sulfate for each experimental condition were calculated by taking the average of those values in different size bins in Figure S7. Hence the potential uneven coating thickness has been incorporated in the averages, which show consistent trends in Figure 2. The average number percentages of sulfate-containing particles in DMB- and VL- coated particles are considerably higher (> 84%) under both I_1 and I_4 UV irradiances than under dark (< 2%). SyrAld-coated particles gave a slightly lower percentage of sulfate-containing particles of 43% and 83% at I_1 and I_4 UV irradiances. Upon increase of photon flux densities (I_1 to I_4), the RPA of sulfate increases for DMB-, VL- and SyrAld-coated particles, which is in line with the enhanced normalized SO_2 consumptions. The number percentage and RPA of sulfate exhibited a similar descending order of DMB>VL>SyrAld>BA in each size bin (Figure S7). Our observed trend of sulfate formation potential is in line with the secondary organic aerosol mass yield for syringol oxidation by $^3C*$ of DMB (114%), VL (111%) and SyrAld (78%) in the literature (Smith et al., 2016; Smith et al., 2014)."

On lines 172-174 the authors discuss an apparent size component to the efficiency of sulfate formation. Figure S4 clearly shows that the SPAMS sizing effectively captures the expected size distribution of the PSLs, but what size range do organic-coated particles span before sulfate formation begins? To put another

way, how uniform is the population size distribution after becoming coated in organics? Do these results suggest that sulfate formation occurred unevenly across the particle population? Are there any instrumental factors that may influence the apparent size-dependent sulfate production efficiency? E.g., is it possible that larger particles are only partially ionized by the SPAMS and this skews the observed RPAs?

[R4] [A4] We did not obtain a uniform population for the organic-coated particles. However, we indeed considered the effect of the particle size on the sulfate RPA and please see details in the response [R3]. For the instrumental factor, the laser energy used in this study was 0.5 mJ, which is widely used and sufficiently strong to ionize ambient and laboratory-generated particles (Li et al., 2022; Zhang et al., 2023). Furthermore, Liu et al. (2021a) reported that ionic peak integrity was the best when the laser energy was about 0.5 mJ.

At lines 209-211 the authors discuss the difficulties in using absolute peak areas to draw conclusions about sulfate signal. Are there circumstances where it would be feasible to translate the absolute peak area to some mass (or mass range) of sulfate and therefore be more quantitative about the amount of sulfate present in a particle? Would this be possible after observing APAs of size-selected sulfate particles and taking into account particle sizes measured by the SPAMS? Alternatively, is there a way to be reasonably quantitative about sulfate production rate from the studied photosensitizers, based on measurements like the amount of depleted SO2 and particle surface area?

[R5] Single-particle mass spectrometry instruments can characterize the composition of individual aerosol particles in real-time. Their unique ability to determine the mixing state of the particles enables qualitative assessment of chemical transformation based on the mass spectra of single particles but not the average composition of an ensemble of particles. However, quantitative measurements by single-particle mass spectrometry systems are inherently problematic because ion formation from laser desorption-ionization is not a well-controlled process and gives rise to considerable particle-to-particle variability (Froyd et al., 2019; Hinz and Spengler, 2007). Recently, some studies have attempted to quantify the mass fractions for chemical species in single particles by combing collocated measurements of single particle mass spectrometry and HR-ToF-AMS measurements (Healy et al., 2014). In our current study, using SPAMS alone is subject to different sensitivities for chemical species due to differences in their ionization and matrix effects and therefore cannot provide a quantitative sulfate production rate. However, our focus is to report the possibility of aerosol phase SO_2 oxidation by model biomass burning photosensitizers at single particle level and compare the relative atmospheric importance of particulate photosensitization and nitrate

photolysis in sulfate formation. We thank the reviewer for the suggestions of using the measured SO_2 depletion for further analysis. However, we cannot rule out SO_2 dissolution without oxidation to form sulfate. We agree that the quantitative information about sulfate production rate from photosensitizers is valuable and will be the subject of our future work. We have also modified the title of the paper to emphasize that our analysis is based on the single particle mixing state, but not mass concentration analysis.

[A5] We have added after line 283 that "The quantitative sulfate production rate via aerosol phase SO_2 oxidation by model photosensitizer is limited by SPAMS measurements in the current study, which focuses of single particle mixing state analysis. Further quantitative studies would be useful."

We have modified the title of the paper as follows: Sulfate formation via aerosol phase SO2 oxidation by model biomass burning photosensitizers: 3,4-dimethoxybenzaldehyde, vanillin and syringaldehyde using single particle mixing state analysis

The authors note on lines 174-176 that the sulfate formation efficiency follows a similar trend as SOA formation from reaction between the three photosensitizers and syringol. What did the authors of the previous works attribute the difference in SOA production to? Would this be reasonable within the current system? Are there any other reasonable parameters that would influence the efficacy of SO2 oxidation by these photosensitizers? E.g., absorption spectra, quenching efficiency, particle phase state or physical attributes.

[R6] [A6] We have added the potential reasons for the different sulfate formation efficiency after line 185: "Specifically, DMB has a higher quantum yield and longer lifetime of $^3C^*$ compared to VL (Felber et al., 2021), which can result in a higher sulfate formation efficiency. On the other hand, the direct photodegradation rate constant was higher for SyrAld than VL, likely suppressing the concentration of SyrAld in droplets/ particles and the photosensitized oxidation (Smith et al., 2016). However, photosensitization is still a research field for atmospheric chemistry with broad uncertainties (Felber et al., 2021). Further quantitative work on the quantum yield, lifetime, and the decay and quenching rate constants of the $^3C^*$ is needed."

Minor comments

General: I suggest adding subsections to the "Results and Discussion" to more clearly organize the different materials in this section, as some of the transitions within and between paragraphs are abrupt.

[R7] [A7] Thank you for your suggestions and we have organized the paragraph and added subtitles.

Line 58: what properties make vanillin a typical aromatic carbonyl sensitizer? Or is it just a photosensitizer that's often used in studies?

[R8] [A8] An important class of photosensitizers is aromatic carbonyl compounds (Felber et al., 2021). Vanillin is an aromatic carbonyl and is well-known and widely used in photosensitization studies (Mabato et al., 2022; Felber et al., 2021; Smith et al., 2016).

Lines 85-86: is the estimated organic coating thickness shown anywhere?

[R9] [A9] This has been mentioned in line 170. Although the coating thickness estimated by particle size increase spanned a wide range from 100 nm to 2.2 μm, the number percentage and RPA of sulfate generally exhibited the same trend for the studied compounds in each size bin (Figures S7).

Line 151: what is the presence of (minor) sulfate under dark conditions attributed to?

[R10] [A10] The negligible sulfate formation in the dark may be due to the autooxidation of SO_2 by oxygen.

Line 155: are any sulfite (SO3) signals observed in the mass spectra? It doesn't appear so based on Figure 1 but it's a little difficult to tell. Would sulfite signals be expected to be visible while examining heterogeneous SO2 oxidation?

[R11] [A11] we observed rather small m/z -80[SO_3^-] peak (i.e., RPA < 0.06) in the mass spectra. However, it is more likely due to fragmentation of the formed sulfate rather than dissolved SO_2, as it is only observed under UV conditions but not dark. Almost no sulfate formed under dark conditions.

Line 179: can the O2-free environment influence any aspect of the ionization process?

[R12] [A12] Like other typical mass spectrometers, the pumping scheme inside the SPAMS ensures the high vacuum environments with the pressure of 5×10^{-5} Torr in the sizing region and 7×10^{-7} Torr in the

mass spectrometer region, where ionization process takes place (Li et al., 2011). Therefore, the O$_2$ free environment would not influence the ionization process.

Line 181: although the absolute changes in RPA are smaller for syringaldehyde particles, is the relative change similar to that for vanillin and DMB? Additionally, do the results in N2 imply that direct 3C* oxidation of SO2 can occur but is slower than pathways with O2?

[R13] Figure 3 compared the distribution of RPA for DMB-, VL- and SyrAld-coated particles under air and N$_2$ conditions, and it is clear that replacing air by pure N$_2$ substantially shifted the distribution of RPA for DMB- and VL-coated particles toward the lower end, while SyrAld-coated particles exhibited slight changes. More specifically, when replacing air by pure N$_2$, the number fraction of particles with sulfate RPA large than 0.2 decreased by more than 40% for DMB- and VL- coated particles (I$_4$) but by only 14% for SyrAld-coated particles. Our results suggested the involvement of O$_2$ and the potential important role of secondary oxidants in sulfate formation and also the lower ability of direct 3C* oxidation of SO$_2$ to produce large sulfate RPA. The relative importance of the direct 3C* and secondary oxidants in sulfate production varies among the different compounds, as reflected by the distribution of sulfate RPA in Figure 3. For example, secondary oxidants could be more important in the DMB system than the SyrAld system.

[A13] We modified the sentence on line 224: "Upon the increase of UV intensity (from I$_1$ to I$_4$), the number fraction of particles with sulfate RPA larger than 0.2 only slightly increased in N$_2$-saturated conditions, and particles with RPA of 0-0.2 dominated the population, indicating the lower ability of direct ^{3}C* oxidation of SO$_2$ to produce large sulfate RPA. The relative importance of the direct 3C* and secondary oxidants in sulfate production varies among the different compounds, as reflected by the distribution of sulfate RPA in Figure 3. For example, secondary oxidants could be more important in the DMB system than the SyrAld system."

Line 186: specify what type of system Wang et al. (2020) was exploring.

[R14] [A14] We have added related information in line 229 as follows: "In contrast, Wang et al. (2020) reported that switching from air to N$_2$ resulted in similar S(IV) oxidation rates, indicating that the direct reaction of SO$_2$ with ^{3}C* was more significant than that with the secondary oxidants for 4-(benzoyl)benzoic acid."

Lines 188-189: have similar variations in 3C* reactions rates from different sources towards the same analyte been observed previously?

[R15] [A15] Yes. **Wang et al. (2020)** observed different reaction rate constants between 3C* from different sources and SO_2, with xanthone exhibiting the highest rate constant and followed by acetophenone, flavone and 4-(benzoyl)benzoic acid. We have added this reference.

Line 193: can the decrease in organic ion RPA also be consistent with ion scavenging by newly produced sulfate?

[R16] [A16] No, as the decrease in RPA of parent ions in Figure S8 was indicated by their peaks in the positive spectra, whereas sulfate was detected in negative mass spectra. This has been mentioned in the figure caption.

Line 195: the location of the material following "Note…" seems odd and incongruous with the rest of the paragraph.

[R17] [A17] We agree that the phase state information mentioned here does not fit the paragraph, and therefore we have moved this information to the method part. Please see details in the next [R18].

Lines 195-199: the authors seem to be implying that they do not expect the organic-coated PSLs to undergo substantial growth at the RH values used. If this is correct, please state so directly. Any other statements the authors intend to make here on particle physical characteristics should be clearly stated.

[R18] [A18] We apologize that the location of the particle phase state discussion (originally in lines 195-199) led to confusion. The original lines 195-199, which better fit the method part, have been moved to line 99 as follows. In addition, we have added discussions: "Depending on the experiment, the RH in the OFR was regulated at ~80% or 20% to achieve different content of aerosol water by passing HEPA-filtered and activated-carbon-denuded compressed air or pure N_2 through water bubblers. Note that the photosensitizers may be (polymorphic) solid or semi-solid due to their low solubility and hygroscopicity, even at 80% RH (Kavuru et al., 2016; Hussain et al., 2001). For example, Mochida and Kawamura (2004) reported that pyrolysis products of lignin with -COOH, including vanillic acid and syringic acid, showed no hygroscopic growth even at RH of more than 90%. They also proposed that other pyrolysis products with chemical structures such as –CHO may have even lower hygroscopicity than –COOH and would not show measurable particle growth. Though we could not observe the phase states of the particles, both aerosol liquid water in (partially) deliquescent particles and surface adsorbed water content on solid particles at 80% RH were expected to be higher than at 20% RH (Rubasinghege and Grassian, 2013)."

Line 203: to clarify, are the vanillin-coated particles here still PSLs?

[R19] [A19] Yes, VL-coated particles are VL coated on the PSL condensation nuclei.

Line 205: would pH and the identity of the NO3- counterion (e.g., H+, NH4+) potentially influence SO2 oxidation?

[R20] Yes, SO_2 dissolution is not favorable under acidic environments (Gen et al., 2019a), so the counterion could play a role directly through pH. However, at 80% RH, the pH of KNO_3 particles was 6.38±0.07, comparable to that of VL (pH = 6.15±0.12). Thus, pH-dependent partitioning of SO_2 is not expected to play an important role in the different sulfate formation observed for KNO_3 and VL in this study. Furthermore, since the solubility of SO_2 may be limited in the acidic nitrate particles such as ammonium nitrate, the sulfate formation in KNO_3 particles could represent an upper limit of contribution from nitrate photolysis in the atmosphere. Another potential impact of counterion on SO_2 oxidation is via the ionic strength of the solution (Liu et al., 2021b). Divalent cations (e.g., Ca^{2+}) afford higher ionic strength than monovalent cations (e.g., Na^+), but the interaction between Ca^{2+} and nitrate will shift the nitrate absorption band away from actinic wavelengths with increasing concentration (i.e., ionic strength) (Roca et al., 2008). Nevertheless, divalent cations were not used in our experiments and hence ionic strength variations due to the use of different counterions do not affect our conclusion that photosensitization prevails nitrate photolysis in SO_2 oxidation in our experimental conditions.

[A20] We have added the pH information after line 266, "At 80% RH, the pH of KNO_3 particles was 6.38±0.07, comparable to that of VL (pH = 6.15±0.12). Thus, pH-dependent partitioning of SO_2 is not expected to play an important role in the different sulfate formation observed for KNO_3 and VL in this study."

Line 210: is there any possibility for the different photosensitizers/organic particle matrices to lead to different sulfate ionization efficiencies and RPAs?

[R21] Matrix effect inherently exists in SPAMS measurements, which limits the SPAMS to provide quantitative results. Lacking robust accurate absolute concentration measurements, the relative intensity has been accepted to qualitatively represent chemical composition variations on particles (Gross et al., 2000; Li et al., 2017). We also noted that the variation in relative peak area (RPA) was smaller than in the absolute peak area (APA), even though some studies found that the RPA values may also be affected by the inherent variability of particle compositions due to matrix effects within particles (Reinard and Johnston, 2008).

[A21] We have added the potential matrix effect after line 255: "However, APA is more sensitive to the variability in ion intensities associated with particle-laser interactions than RPA (Gross et al., 2000; Hatch et al., 2014; Zhou et al., 2022). The variation in RPA was smaller than that in the APA, even though some studies found that the RPA values may also be affected by the inherent variability of particle compositions due to matrix effects within particles (Reinard and Johnston, 2008; Zhou et al., 2016)."

Line 214: it's not clear that the KNO3 particles are deliquesced. Freney al. (2009) observed continuous growth with increasing RH for KNO3 particles and a deliquescence RH of 90% for dried particles (in line with prior works cited in Freney et al.). Therefore, I don't believe the direct comparison to the sulfate formation in aqueous droplets used in Gen et al. (2019) is valid, and this comparison and discussion of photosensitizer vs nitrate SO2 oxidation should be caveated with this information.

[R22] [A22] The KNO_3 wet aerosols were generated using an atomizer (TSI 9032), and introduced to the OFR (80% RH) without passing a dryer (as shown in Figure S2b). It has been reported that more than 96% of the KNO_3 particles from nebulization exhibit no efflorescence relative humidity (ERH) (Freney et al., 2009; M.-J. Lee, 2011). Therefore, we considered the KNO_3 particles were deliquescent.

Line 224: is there a reason to suspect that oxalic acid/KNO3 mixtures might affect SO2 oxidation differently than pure KNO3 particles?

[R23] [A23] When mixed with organics, the physicochemical properties of nitrate particles such as pH may change, which may, in turn, affect the nitrate photolysis effectiveness. The oxalic/KNO_3 mixtures represent a slightly more complicated nitrate photolysis system that contains one of the most abundant water soluble organic compounds. No sulfate formation was observed in oxalic/ KNO_3 particles, just as in pure nitrate particles, but we did not speculate on the detailed mechanism.

Line 238-239: "qualitatively more efficient" under the studied conditions: wet aerosols at 80% RH.

[R24] [A24] We have added the studied experimental conditions.

Line 250: are photosensitizers emitted or formed in non-BB environments, for example urban environments where multifunctional aromatics are common emissions and high NOx levels are common?

[R25] [A25] Yes, photosensitizer particles exist in urban environments. Polycyclic aromatic hydrocarbons (PAHs) as constituents of urban grime act as potential photosensitizers (Gomez Alvarez et al., 2012; Vione

et al., 2006). Furthermore, Wang et al. (2021) reported that naphthalene-derived secondary organic aerosols exhibited interfacial photosensitizing properties.

Reviewer 2

Zhou et al. investigated the sulfate formation from aerosol SO_2 oxidation by model biomass burning photosensitizers. The authors show clear evidence that biomass burning-derived photosensitizer particles can induce photosensitized oxidation of SO_2. The results will advance our understanding of sulfate formation pathways and therefore meet the metric for publication in ACP. I have some minor comments for the authors' consideration.

[R0] We thank the reviewer for the valuable feedback and constructive suggestions. Detailed responses are given below.

Line 25: S(IV) is often used to represent dissolved species of SO_2. Can the authors confirm that the aerosol particles in this study are in the liquid phase?

[R1] [A1] We have discussed the phase state of photosensitizer particles at line 100, though we could not directly observe it. It is expected that there is always surface adsorbed water or bulk phase water in partially dissolved VL particles, in which SO_2 will form S(IV). We would like to keep this terminology.

Lines 85-86: Are the particles uniformly coated? It would be helpful to provide the size distribution information of the coated particles.

[R2] We did not obtain a uniform population for the organic-coated particles. However, we indeed considered the effect of the particle size on the sulfate RPA. The coating thickness estimated by particle size increase spanned a wide range from 100 nm to 2.2 μm, and different particle sizes may have effects on the sulfate RPA. As we have discussed in line 258 that the reactive uptake comprises the diffusion of SO_2 molecules, followed by oxidation of SO_2 at/near the surface or in the bulk of the particles. The decreased sulfate RPA with increasing particle size suggested the photosensitized sulfate formation at/near the surface of VL-coated particles, probably due to the prevalence of surface reactions or diffusional limitations of SO_2 in larger particles, especially in the poorly hygroscopic and potentially viscous VL matrix. Even though the sulfate RPA was size dependent, it generally exhibited the same descending order of DMB>VL>SyrAld>BA in each size bin (Figure S7). The RPA and number percentage for each specific experimental condition in the main text (e.g., Figure 2) were calculated by taking the average of those values in different size bins in Figure S7. Hence the potential uneven coating thickness has been incorporated in the averages, which show consistent trends in Figure 2.

[A2] For clarity, we had added after line 170 that "Although the coating thickness estimated by particle size increase spanned a wide range from 100 nm to 2.2 μm, the number percentage and RPA of sulfate generally exhibited the same trend for the studied photosensitizers in each size bin (Figures S7). Figure 2 shows the average RPA of sulfate (circles) and the number percentage of sulfate-containing particles (diamonds) in DMB-, VL-, SyrAld- and BA-coated particles at dark and different UV intensities in the presence of SO_2, and the corresponding SO_2 consumption normalized by the average total particle surface area concentration before and after UV irradiation in the OFR detected by SPAMS (crosses). The RPA and number percentage of sulfate for each experimental condition were calculated by taking the average of those values in different size bins in Figure S7. Hence the potential uneven coating thickness has been incorporated in the averages, which show consistent trends in Figure 2. The average number percentages of sulfate-containing particles in DMB- and VL- coated particles are considerably higher (> 84%) under both I_1 and I_4 UV irradiances than under dark (< 2%). SyrAld-coated particles gave a slightly lower percentage of sulfate-containing particles of 43% and 83% at I_1 and I_4 UV irradiances. Upon increase of photon flux densities (I_1 to I_4), the RPA of sulfate increases for DMB-, VL- and SyrAld-coated particles, which is in line with the enhanced normalized SO_2 consumptions. The number percentage and RPA of sulfate exhibited a similar descending order of DMB>VL>SyrAld>BA in each size bin (Figure S7). Our observed trend of sulfate formation potential is in line with the secondary organic aerosol mass yield for syringol oxidation by $^3C^*$ of DMB (114%), VL (111%) and SyrAld (78%) in the literature (Smith et al., 2016; Smith et al., 2014)."

Lines 131-137: The authors tend to attribute the sulfate formation to SO_2 oxidation at the aerosol surface. However, the increase of SO_2 consumption with the increase in surface area cannot rule out the possibility of bulk phase reactions. Can the authors provide more insights on whether the reaction occurs at the surface or in the bulk?

[R3] In Figure 4, we found an overall inverse relationship between the sulfate RPA and particle size for VL-coated particles, which indicated that the relative sulfate content increased with the particle surface to volume ratio. This points to the importance of reactions on/near the surface, though we cannot exclude the existence of reactions in the inner bulk.

[A3] We have clarified this in the text as follows (lines 257-262): "The reactive uptake comprises the diffusion of SO_2 molecules, followed by oxidation of SO_2 at/near the surface or in the bulk of the particles. The decreased sulfate RPA with increasing particle size suggested the photosensitized sulfate formation at/near the surface of VL-coated particles, probably due to the prevalence of surface reactions or diffusional limitations of SO_2 in larger particles, especially in the poorly hygroscopic and potentially viscous VL matrix.

We cannot exclude the occurrence of bulk phase reaction in the organic moiety, though it was likely less efficient than the surface reaction."

Line 138: Can the authors explain why only slight SO$_2$ consumption was observed in the presence of SyrAld-coated particles? The aerosol pH is also important to SO$_2$ oxidation. Is the pH of these particles similar?

[R4] The pH of the DMB, VL and SyrAld particles were measured as 6.01±0.06, 6.15±0.12, 5.97±0.10, respectively. Although acidic environments would suppress SO$_2$ uptake, it was not applicable in the comparison of results of these photosensitizer particles, which are similarly neutral. SyrAld-coated particles show slight SO$_2$ consumption, which was consistent with its considerably lower average RPA and number percentage of sulfate-containing particles (Figure 2), than the DMB- and VL- coated particles. In general, we found that the sulfate formation potential (RPA and number percentage) exhibited the descending order of DMB>VL>SyrAld, which is in line with the secondary organic aerosol mass yield for syringol oxidation by ^{3}C* of DMB (114%), VL (111%) and SyrAld (78%) in the literature (Smith et al., 2016; Smith et al., 2014).

[A4] We have added the potential reasons for the different sulfate formation efficiency after line 185: "Specifically, DMB has a higher quantum yield and longer lifetime of ^{3}C* compared to VL (Felber et al., 2021), which can result in a higher sulfate formation efficiency. On the other hand, the direct photodegradation rate constant was higher for SyrAld than VL, likely suppressing the concentration of SyrAld in droplets/ particles and the photosensitized oxidation (Smith et al., 2016). However, photosensitization is still a research field for atmospheric chemistry with broad uncertainties (Felber et al., 2021). Further quantitative work on the quantum yield, lifetime, and the decay and quenching rate constants of the ^{3}C* is needed."

We have added pH information after line 183: "The pHs of the DMB (6.01±0.06), VL (6.15±0.12) and SyrAld (5.97±0.10) particles were similar."

Lines 202-203: Are the size distribution of particles similar for VL-coated and KNO$_3$ particles?

[R5] [A5] As shown in Figure 4, both VL-coated particles and KNO$_3$ particles spanned a wide size range from around 400 to 2500 nm. However, it was clear that KNO$_3$ particles exhibited an RPA of 0 over the full-size range, while VL-coated particles exhibited an average sulfate RPA of 0.26.

Lines 221-223: What is the role of RH? If it is due to the fewer dissolved VL, then it means that the particle is in the liquid phase. Is it in contrast to the discussion in lines 195-199?

[R6] Firstly, the reaction between photoexcited SO_2 molecules and H_2O can produce secondary OH radicals (Kroll et al., 2018). However, this reaction played a negligible role in this study because we did not see effective sulfate formation in the control experiment using BA-coated particles as seeds in the presence of SO_2 (Figure 2). Furthermore, Corral Arroyo et al. (2018) also reported that the particle-phase photosensitized radical production was promoted at higher RH, due to the presence of more water as plasticizers and reduced particulate viscosity. In our system, the photosensitizers have low solubility and hygroscopicity, resulting in limited available dissolved VL to trigger photosensitization and possibly limited dissolved SO_2. In addition, lower RH could result in higher particulate viscosity, which hinders molecular diffusion and reaction (Kroll et al., 2018; González Palacios et al., 2016; Corral Arroyo et al., 2018). We have added this information to the text. In this study, the low RH experiments were conducted for the externally mixed VL and nitrate system to study whether the relative atmospheric importance of particulate photosensitization and nitrate photolysis are still the same as those under high RH conditions, given that nitrate concentration in droplets may be much higher under low RH. We found that sulfate formation was on VL-coated particles but not on externally mixed nitrate particles under both high and low RH conditions (Figure 4 and Figure S10). This analysis was not in contrast to the phase state discussion, as both aerosol liquid water in (partially) deliquescent particles and surface adsorbed water content on solid particles at 80% RH were expected to be higher than at 20% RH (Rubasinghege and Grassian, 2013).

We apologize that the location of the particle phase state discussion (originally in lines 195-199) led to confusion. We have moved it to 100, which better fits the method part.

[A6] We have added the potential RH effect on the photosensitized reaction after line 272: "When RH decreased to 20%, a significant reduction in the average RPAs from 0.26 to 0.002 was observed for VL-coated particles (Figure S10), attributable to the fewer dissolved VL for sulfate formation since VL has low solubility and hygroscopicity and the limited SO_2 dissolution (Liu et al., 2021b). In addition, lower RH could result in higher particulate viscosity, which hinders molecular diffusion and reaction (Kroll et al., 2018; González Palacios et al., 2016; Corral Arroyo et al., 2018). A systematic study of the effect of RH on the particle-phase photosensitized reaction is desirable. Overall, sulfate formation was found on VL-coated particles but not on externally mixed nitrate particles at both high and low RH in our study."

The original lines 195-199, which better fit the method part, have been moved to line 99 as follows. In addition, we have added discussions: "Depending on the experiment, the RH in the OFR was regulated at ~80% or 20% to achieve different content of aerosol water by passing HEPA-filtered and activated-carbon-denuded compressed air or pure N_2 through water bubblers. Note that the photosensitizers may be (polymorphic) solid or semi-solid due to their low solubility and hygroscopicity, even at 80% RH (Kavuru et al., 2016; Hussain et al., 2001). For example, Mochida and Kawamura (2004) reported that pyrolysis products of lignin with -COOH, including vanillic acid and syringic acid, showed no hygroscopic growth even at RH of more than 90%. They also proposed that other pyrolysis products with chemical structures such as –CHO may have even lower hygroscopicity than –COOH and would not show measurable particle growth. Though we could not observe the phase states of the particles, both aerosol liquid water in (partially) deliquescent particles and surface adsorbed water content on solid particles at 80% RH were expected to be higher than at 20% RH (Rubasinghege and Grassian, 2013)."

Lines 214-217: Are these results applicable to ambient conditions? Does this indicate that nitrate photolysis plays a negligible role in sulfate formation in ambient conditions?

[R7] [A7] Nitrate photolysis was found to be significant in triggering sulfate formation in the ambient (Gen et al., 2019b; Zheng et al., 2020). Moreover, our study implies that photosensitization could be an even more effective pathway than nitrate photolysis contributing to sulfate formation. The residence time in the OFR may be too short (~ 2.5 min) to show effective sulfate formation via nitrate photolysis.

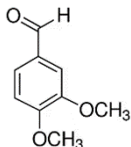
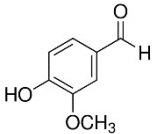
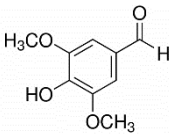
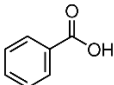
Reviewer 3

This manuscript describes studies of aqueous phase oxidation of sulfur dioxide by three photosensitizers, and for comparison, a non-photosensitizing organic compound and the nitrate ion. The organic compounds are common components of biomass burning plumes, including some phenolic and some non-phenolic species. The authors show that photosensitizer-mediated oxidation of SO_2 is much faster than by nitrate photolysis. Pure N2 is also substituted for air in some experiments to provide some clues about the reaction mechanism. These results suggest that SO2 oxidation by the secondary oxidants (singlet oxygen ($^1O_2$), superoxide ($O_2^{\cdot-}$), hydroperoxyl radical ($\cdot HO_2$), and $\cdot OH$) produced by reaction of the triplet species with O2 is much more significant than direct reactions between $^3C + SO_2$. These results are of interest especially to those studying the puzzle of rapid sulfur oxidation in polluted regions, which is especially notable in humid areas with high aerosol loading. I recommend publication after minor revision to address the following comments and questions.

[R0] We thank the reviewer for the valuable feedback and constructive suggestions. Detailed responses are given below.

The manuscript cites two earlier studies of photosensitizer-induced S(IV) oxidation (Wang et al. 2020 and 2021). Looking at these earlier studies, it appears that Wang et al. (2020) studied humic acid, ambient aerosol particles, and 4-benzoyl benzoic acid, while Wang et al. (2021) studied naphthalene-derived secondary compounds, so this manuscript advances our knowledge of photosensitizer-induced S(IV) oxidation by testing three photosensitizing aldehyde species, both phenolic and non-phenolic, plus a non-photosensitizing acid species for comparison. However, readers would benefit from a clearer explanation of how the current study builds on these earlier works in the introduction. This would also help readers to better understand the statement (page 8 line 188) where the authors try to rationalize the conflicting results about the importance of secondary oxidant species between the current study and that of Wang et al. (2020).

[R1] Thanks for the suggestions.

[A1] We have added more related background information in the introduction as follows (lines 62-69): "However, only limited studies focused on the role of biomass burning-derived photosensitizers in S(IV) oxidation. Wang et al. (2020) reported that photosensitized chemistry involving the humic fraction of aerosols during Chinese haze events could explain a significant fraction of the observed sulfate formation, which highlighted the potential photosensitizing properties played by biomass burning particles. Naphthalene, emitted primarily from fossil fuel combustion and biomass burning, can be oxidized by

hydroxyl radicals to form secondary organic aerosol (SOA), which was observed to possess interfacial photosensitizing properties (Wang et al., 2021). These recent studies have advanced our understanding of the photosensitized processes, but the types of photosensitizers from biomass burning are diverse and their properties are complex, limiting us from further assessing the importance of photosensitized sulfate formation in the dynamic ambient atmosphere. In this study, we investigate sulfate formation via aerosol phase SO_2 oxidation by biomass burning-derived aromatic carbonyl photosensitizers, including both non-phenolic (3,4-dimethoxybenzaldehyde, DMB) and phenolic photosensitizers (vanillin, VL and syringaldehyde, SyrAld) with similar molar absorptivity at atmospheric relevant wavelengths (Figure S1, Supporting information), in an oxidation flow reactor (OFR) utilizing a single particle aerosol mass spectrometer (SPAMS). Nitrate photolysis has been reported as a typical sulfate formation pathway initiated by particulate photoactive compounds, similar to photosensitization (Gen et al., 2022). The objectives of this study are to semi-quantitatively evaluate the extent of sulfate formation in photosensitizer particles and qualitatively compare the relative atmospheric importance of particulate photosensitization and nitrate photolysis in sulfate formation."

It would be helpful to have the chemical structures of the studied compounds given somewhere in the manuscript or SI along with a listing of which compounds are photosensitizers and which are phenolic. Currently, the latter bits of information are split between the Introduction and the Methods sections, making it difficult for readers to notice or understand the close structural relationships between the different VOCs selected for study.

[R2] Thanks for the suggestions.

[A2] We have added after line 85 in the method that: "The structures of the chemicals used are provided in Table S2.", and added Table S2 in the supporting information.

Table S2 Chemical formula, structure, molar mass and property of the chemicals used in this study.

Chemical compound	Formula	Structure	Molar mass (g mol^{-1})	Property[a]
3,4-dimethoxybenzaldehyde	$C_9H_{10}O_3$		166.17	non-phenolic photosensitizer

vanillin	$C_8H_8O_3$		152.15	phenolic photosensitizer
syringaldehyde	$C_9H_{10}O_4$		182.17	phenolic photosensitizer
benzoic acid	$C_7H_6O_2$		122.123	non-photosensitizer

[a]The Photosensitizing properties are derived from the literature (Smith et al., 2015, 2016; Smith et al., 2014).

p. 8 line 188: This sentence is the authors' only attempt at resolving the significant differences in results between Wang et al. 2020 and the current work. Yes, they studied different photosensitizing compounds. However, given what is known about triplet carbon states and photosensitization, does it make sense that the aldehyde photosensitizers in the current work reacted with SO2 mostly via secondary oxidants, while the carboxylic acid photosensitizers in the earlier study reacted directly with SO2? Some further discussion here could be very valuable.

[R3] Figure 3 compared the distribution of RPA for DMB-, VL- and SyrAld-coated particles under air and N_2 conditions, and it is clear that replacing air by pure N_2 substantially shifted the distribution of RPA for DMB- and VL-coated particles toward the lower end, while SyrAld-coated particles exhibited slight changes. Our results suggested the involvement of O_2 and the potential important role of secondary oxidants in sulfate formation and also the lower ability of direct 3C* oxidation of SO_2 to produce large sulfate RPA. The relative importance of the direct 3C* and secondary oxidants in sulfate production varies among the different compounds, as reflected by the distribution of sulfate RPA in Figure 3. For example, secondary oxidants could be more important in the DMB system than the SyrAld system. In addition to the aldehyde functional group, the effects of other different functional groups should still be considered (Mabato et al., 2023). For instance, the phenolic structure and the number of methoxy groups, etc. Therefore, we think that our understanding of the effects of different functional groups of the photosensitizer on the reactivity of 3C* is far from being generalized. In any case, future studies on the physicochemical properties of photosensitizers are required to better understand the impact of photosensitized reactions.

[A3] We modified the sentence on line 224: "Upon the increase of UV intensity (from I_1 to I_4), the number fraction of particles with sulfate RPA larger than 0.2 only slightly increased in N_2-saturated conditions, and particles with RPA of 0-0.2 dominated the population, indicating the lower ability of direct $^3C^*$ oxidation of SO_2 to produce large sulfate RPA. The relative importance of the direct 3C* and secondary oxidants in sulfate production varies among the different compounds, as reflected by the distribution of sulfate RPA in Figure 3. For example, secondary oxidants could be more important in the DMB system than the SyrAld system."

We have also added after line 186 that: "Specifically, DMB has a higher quantum yield and longer lifetime of $^3C^*$ compared to VL (Felber et al., 2021), which can result in a higher sulfate formation efficiency. On the other hand, the direct photodegradation rate constant was higher for SyrAld than VL, likely suppressing the concentration of SyrAld in droplets/ particles and the photosensitized oxidation (Smith et al., 2016). However, photosensitization is still a research field for atmospheric chemistry with broad uncertainties (Felber et al., 2021). Further quantitative work on the quantum yield, lifetime, and the decay and quenching rate constants of the $^3C^*$ is needed."

p. 9 lines 195 – 199: This argument about solubility, phase, and reactivity is confusing. The authors note that vanillic acid and syringic acid have no measurable hygroscopic growth due to water uptake at 90% RH, and that the three aldehyde photosensitizers are less hygroscopic than these two acids, suggesting that they may therefore be solid or semi-solid phase aerosol particles at the range of RH used in this study. From the preceding parts of the paragraph, the authors appear to be using this aerosol phase argument as a possible explanation of the lower reactivity of vanillin and syringaldehyde. However, DMB is clearly less hygroscopic than vanillin or syringaldehyde, and by this argument it should be the least reactive of the three. In any case, how this aerosol hygroscopicity information ties in to the rest of the paper is not spelled out.

[R4] [A4] The purpose of this sentence is to describe the probable phase states of photosensitizer-coated particles instead of explaining the observed discrepancy in sulfate production for the three photosensitizers. To explain the lower sulfate formation efficiency for VL and SyrAld than DMB, we have added after line 186: "Specifically, DMB has a higher quantum yield and longer lifetime of $^3C^*$ compared to VL (Felber et al., 2021), which can result in a higher sulfate formation efficiency. On the other hand, the direct photodegradation rate constant was higher for SyrAld than VL, likely suppressing the concentration of SyrAld in droplets/ particles and the photosensitized oxidation (Smith et al., 2016). However,

photosensitization is still a research field for atmospheric chemistry with broad uncertainties (Felber et al., 2021). Further quantitative work on the quantum yield, lifetime, and the decay and quenching rate constants of the $^3C^*$ is needed."

The original lines 195-199, which better fit the method part, have been moved to line 100. In addition, we have added after line 99 that "Depending on the experiment, the RH in the OFR was regulated at ~80% or 20% to achieve different content of aerosol water by passing HEPA-filtered and activated-carbon-denuded compressed air or pure N_2 through water bubblers. Note that the photosensitizers may be (polymorphic) solid or semi-solid due to their low solubility and hygroscopicity, even at 80% RH (Kavuru et al., 2016; Hussain et al., 2001). For example, Mochida and Kawamura (2004) reported that pyrolysis products of lignin with -COOH, including vanillic acid and syringic acid, showed no hygroscopic growth even at RH of more than 90%. They also proposed that other pyrolysis products with chemical structures such as –CHO may have even lower hygroscopicity than –COOH and would not show measurable particle growth. Though we could not observe the phase states of the particles, both aerosol liquid water in (partially) deliquescent particles and surface adsorbed water content on solid particles at 80% RH were expected to be higher than at 20% RH (Rubasinghege and Grassian, 2013)."

Supplement p 2 line 23: Was the transmission of the quartz glass vial measured through just one wall, or all the way through the vial (both walls)? If the latter, the transmission of light to the inside of the vial may be closer to 95%, necessitating a smaller photon flux correction factor.

[R5] [A5] The transmission of the quartz glass vial was measured through one wall. This information has been added to SI.

Technical corrections

p. 7 line 146: this sentence is unclear. What "considerable difference" is being referred to, that between average RPA and NP, between different VOCs, between dark and UV conditions, or between one of those things and the SO2 consumption? The context of surrounding sentences does not fully resolve the meaning of this sentence.

[R6] [A6] We have deleted "a considerable difference in" to make the sentence clear and it is revised as follows: "Figure 2 shows the average RPA of sulfate (circles) and the number percentage of sulfate-containing particles (diamonds) in DMB-, VL-, SyrAld- and BA-coated particles at dark and different UV intensities in the presence of SO_2, and the corresponding SO_2 consumption normalized by the average total particle surface area concentration before and after UV irradiation in the OFR detected by SPAMS (crosses)."

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