This is an interesting and new submission investigating the formation of organic sulfur compounds through the SO2 initiated (photo)chemistry of PAHs and DMSO at the air-water interface. A series of advanced analytical tools are employed to identify the products of these chemical interactions. This study is in line with previous investigations of the same group.

The fact that SO2 and/or PAHs could trigger photochemistry at the air/water interface is a topic that certainly falls with the scope of ACP, this is why I would certainly recommend the publication of this manuscript once the authors have dealt with the comments below.

We would like to thank the reviewer for the constructing and encouraging comments.

While the title stresses the photochemical aspects of the chemistry presented, the actual text is a bit vague about the importance or not of the dark chemistry during the experiments (some figures in the SI points towards some active dark chemistry as well which is finally quite surprising for the poly-aromatic compounds). The same comment applies to the relative importance of the photochemistry of SO2 and PAHs. The text mentions that the SO2 dominates but pathway B stresses another possibility. It would be helpful if the authors could elaborate more on the relative importance of each pathway to avoid any confusion for the reader.

The reviewer is right that SO_2 reaction with PAHs/DMSO in absence of light can lead to the formation of product compounds. In dark, SO_2 can form π complexes with C=C bonds of PAHs upon ring opening which may undergo transformation to diradical organosulfur intermediates which in turn upon reaction with dissolved O_2 can lead to production of reactive oxygen species (ROS) such as OH radical. (Shang et al., 2016) These π complexes can absorb UV/Vis light depending on the double bond substitutions, leading to photoactivation and formation of product compounds (Passananti et al., 2016). The formation of diradical organosulfur intermediates and ROS have been suggested for reactions of SO_2 with alkenes and fatty acids (Shang et al., 2016, Pasananti et al., 2016), but here we suggest that the same mechanism may occur for the reaction of SO_2 with PAHs. While the SO_2 addition to the C=C bond would be responsible for the organic sulfur compounds, the CHO oxidation products could be explained by radical chain reactions triggered by ROS (Shang et al., 2016, Passananti et al., 2016) Additionally, the photosensitized degradation of DMSO initiated by excited triplets of PAHs can explain the formation of CHOS and CHO compounds. However, it is difficult to distinguish which mechanism is prevalent in the environment. Here, we suggest a mechanism that SO_2 may indeed proceed on PAHs by SO_2 addition on C=C bonds and it is supported by theoretical calculations of the reaction Gibbs energies, based on the information obtained from the detected tentative products. We show however, that under our experimental conditions, $^3SO_2^*$ oxidation of PAHs would prevail over PAH photodegradation and would lead to sulfur-containing PAHs. In this study highest number of observed CHOS compounds was observed upon reaction of SO_2 with PAHs/DMSO highlighting the importance of the involved SO_2.

We added the following paragraph in the revised version of the manuscript including the cited papers:

"Alternatively, SO_2 can form π complexes with C=C bonds of PAHs upon ring opening, which may undergo transformation to diradical organosulfur intermediates which in turn can react with dissolved O_2 leading to production of reactive oxygen species (ROS) such as OH radical. (Shang et al., 2016) The formation of diradical organosulfur intermediates

and ROS have been suggested for reactions of SO_2 with alkenes and fatty acids (Shang et al., 2016, Passananti et al., 2016), but here we suggest that the same pathway may occur for the reaction of SO_2 with PAHs. While the SO_2 addition to the C=C bond would be responsible for the OSs, the CHO oxidation products could be explained by radical chain reactions triggered by ROS (Shang et al., 2016, Passananti et al., 2016)"

If excited SO2 would create some OH radicals in the liquid phase it would certainly be scavenged by DMSO due to its very high concentration (it is used as cosolvent), with little interplay with the PAH photochemistry. In other, is there any synergy between PAH and SO2 or are the experiments looking at the PAH/DMSO and SO2/DMSO chemistry with finally no interaction.

The excited triplet of SO_2 ($^3SO_2^*$) can form OH radical as suggested by Martins-Costa et al., 2018 and Kroll et al., 2018

$^3SO_2^* + H_2O \rightarrow OH + HOSO$ R-1

Alternatively, OH radicals can be also formed without assistance of light. Namely, SO_2 can form π complexes with C=C bonds of PAHs which may undergo transformation to diradical organosulfur intermediates which react with dissolved O_2 leading to formation of reactive oxygen species (ROS) such as OH radical. (Shang et al., 2016) While the SO_2 addition to the C=C bond would be responsible for the CHOS, the CHO oxidation products could be explained by radical chain reactions triggered by ROS (Shang et al., 2016, Passananti et al., 2016)

The reviewer is right that there is a high probability that OH is scavenged by DMSO due to its high concentration but the observed CHO compounds point out to the implication of ROS, thus OH radical in their formation through oxidation of PAHs.

We added the following paragraph to clarify this:

"Alternatively, SO_2 can form π complexes with C=C bonds of PAHs upon ring opening, which may undergo transformation to diradical organosulfur intermediates which in turn can react with dissolved O_2 leading to production of reactive oxygen species (ROS) such as OH radical. (Shang et al., 2016) The formation of diradical organosulfur intermediates and ROS have been suggested for reactions of SO_2 with alkenes and fatty acids (Shang et al., 2016, Passananti et al., 2016), but here we suggest that the same pathway may occur for the reaction of SO_2 with PAHs. While the SO_2 addition to the C=C bond would be responsible for the OSs, the CHO oxidation products could be explained by radical chain reactions triggered by ROS (Shang et al., 2016, Passananti et al., 2016)"

Finally, more experiments are need to clarify which mechanism would be prevalent in the real-life environment.

The chemical scheme involving PAH is not fully clear to the reviewer, as it seems that S(IV) is oxidized to S(VI) without any real explanation.

We supplemented the oxidation pathway in the Scheme 1 and added the following sentence to clarify this:

“The S(IV) in sulfite group of $C_{10}H_6O_3S$ (10) would first undergo oxidation by the strong oxidizing agents in the system to result in more stable S(VI) in $C_{10}H_8O_3S$ (12).”

Also, section 3.2 mixes some discussion on the actual results and the atmospheric context of the study. Some reediting here would certainly help the reader.

We shifted one part (atmospheric context) of the discussion in section 3.2 to the section “Atmospheric Implications” (see revised version of the manuscript).

Finally, while this reviewer recognizes the need to perform such experiment at high concentrations. The observations made here cannot directly be used for realistic outdoors conditions. Therefore, some discussions on how to extrapolate these finding to authentic atmospheric conditions would beneficial for the manuscript.

We are currently estimating the importance of the suggested chemistry here under environmentally relevant conditions. We added the following paragraph in the section “Atmospheric Implications”:

“Based on the observed emission rates of OSs in this study, we estimate emission fluxes of MSA, and MSIA, among others, considering realistic environmental conditions, SO_2 mixing ratios ranging between 2 ppb and 50 ppb, surface UV-VIS irradiation, surface microlayer coverage with PAHs/DMSO, and surface wind speeds, (Brüggemann et al., 2018) to account the potential impact of the heterogeneous SO_2 (photo)chemistry with PAHs/DMSO, on the aerosol production in marine boundary layer, which results will be published elsewhere.”

Reviewer 2:

In this work, the authors investigated the formation of compounds including orgaosulfur compounds through SO2 initiated photochemistry of PAHs and DMSO. Mass spectrometric data and reaction mechanims supported by theorteical calcultions are given to support the formation of observed products in the gas and aqueous phase. The results of this work provide greater insight into the sources of atmoshpheric sulfur compounds formed through light induced heterogeneous processesing of SO2 with PAHs/DMSO at air/water interface. I support the publication of this work with a few minor comments below.

We would like to thank the reviewer for the constructing and encouraging comments.

Line 145, "The applied mixing ratio of 800 ppb would probably amplify the intensity of the detected product compounds, but the formation profiles would still remain the same as in the case of smaller SO2 mixing ratios." In addition to the reaction pathways, can the authors further elaborate if the formation and volatilation of reaction products (e.g. the detection of the gas phase products) would be affected by the high concentrations of the reactants applied in the study?

The mixing ratio applied in this study of 800 ppb is similar with the mixing ratio of 500 ppb in the previous study. However, even if much lower SO_2 mixing ratios were applied the same compounds would be formed but probably with lower signal intensities. Future model studies should reveal the levels of the formed organic sulphur compounds under

realistic environmental conditions i.e. SO_2 concentration, PAHs and DMSO concentrations etc.

As we mentioned above the goal was to suggest an alternative formation pathway of organic sulfur compounds in the atmosphere. The suggested reaction mechanism tentatively describes the process of formation of these compounds in the gas and in the aqueous phase.

We are currently estimating the importance of the suggested chemistry here under environmentally relevant conditions. We added the following paragraph in the section "Atmospheric Implications":

"Based on the observed emission rates of Oss in this study, we estimate emission fluxes of MSA, and MSIA, among others, considering realistic environmental conditions, SO_2 mixing ratios ranging between 2 ppb and 50 ppb, surface UV-VIS irradiation, realistic surface microlayer coverage with PAHs/DMSO, and surface wind speeds, (Brüggemann et al., 2018) to account the potential impact of the heterogeneous SO_2 (photo)chemistry with PAHs/DMSO, on the aerosol production in marine boundary layer, which results will be published elsewhere."

Line 221, " we tentatively identified a number of unsaturated multifunctional molecules and OSs released in the gas phase from the reaction of SO2 with either DMSO or PAHs/DMSO, which are summarized in Table S5." Again, will the detection of gas-phase products be affected by the choice of the reactant concentrations?

We performed test experiment by using 50 ppb of SO_2 and the same product compounds with similar profiles were obtained. However, we are unable to carry out experiments with lower DMSO concentration and for this reason we are currently modeling the laboratory data by using environmentally relevant conditions. The model outcomes will be published elsewhere.

Line 234, Figure 1, please check the resolutions of the figures and the reaction scheme.

The resolutions of figures and reaction scheme have been updated.

Line 239, "In this study, we observed rapid formation of MSA, MSIA, MSM, EMS, MSAOH, and ESAOH (Figure 2 and Figure S2)." What are the concentrations of these gas-phase products (e.g. ppb or ppm) and their aqueous phase concentrations?

It is challenging to quantify the observed product compounds because of the lack of standards. However, with the calibrations of EPA TO15 standard gas established before the experiments, we could relatively quantify the products by using benzene as the reference standard. The concentrations of these gas-phase products were 15-20 ppb for MSA, 96-230 ppb for MSIA, 47-240 ppb for MSM, 1.4-2 ppb for EMS, 2-2.3 ppb for MSAOH and 8-18 ppb for ESAOH in the reactions of SO_2 and PAHs/DMSO under light irradiation. Usually, their concentrations were higher in the reactions of light-excited SO_2 and DMSO (around 25 ppb MSA, 210 ppb MSIA, 285 ppb MSM, 2.3 ppb EMS, 3 ppb MSAOH and 23 ppb ESAOH). As these values are based on semi-quantitative analysis we did not add these values in the manuscript.

Line 261, " Here, we show that during daytime the reactions of light-excited SO2 and aqueous DMSO or DMSO/PAHs could represent an important source of gaseous MSA in the atmosphere near the water (ocean, lake and river) surface" What are the yields of the gasoues MSA in different systems?

We are currently modeling the measured emission fluxes to evaluate their importance in the real-life environment. The results will be published elsewhere.

Line 271, "The intensities of the product compounds (Figure 2 and Figure S2) decrease after one hour most probably due to their reaction with SO2 and/or their photodegradation" Please elobarate or show these reactions. What are the kinetics or rates of these reactions?

Determining the kinetics of SO_2 induced degradation of PAHs/DMSO was out of scope in this study. The rates of photochemical degradation of PAHs/DMSO are reported in our previous study by Jiang et al. published in JGR: Atmosphere.

Line 284, "Numerous unsaturated multifunctional molecules and OSs were identified in the liquid phase during the reaction of SO2 with either DMSO or PAHs/DMSO by using FT-ICR-MS. The number of detected product compounds in the aqueous phase was significantly higher compared to those detected in the gas phase, due to very high sensitivity of FT-ICR-MS." What are the concentrations of these aqueous-phase products detected by the FT-ICR-MS? Are they volatile or non-voltiles in the reaction systems?

The same as above. Due to the lack of standards and the limitations of FT-ICR-MS, it is challenging to quantify the observed product compounds. Based on ionization efficiency and the concentrations of target compounds, only relative abundance was acquired by the semi-quantification of ESI FT-ICR-MS. Thus, we are unable to give the concentrations of aqueous-phase compounds. The detected compounds are soluble and they are detected in the aqueous phase. It is not excluded that some of these compounds partition in the gas phase as well. The compounds released in the gas phase were detected in real-time by the use of SPI-TOF-MS.

Line 398, "3.5. Reaction Mechanism of the Gaseous Compounds" As mentioned above, will there be other volatile and gaseous compounds that want to be considered?

Depending on the vapor pressure of the compounds it is not excluded that some other compounds would partition in the gas phase.

Line 416, "These observations highlight the importance of the SO2 oxidation reactions of DMSO and/or PAHs/DMSO at the freshwater and sea surface, or in the liquid films of the aerosol particles, which would represent important source of OSs." What would be the formation yields of these products through SO2 oxidation reactions of DMSO and/or PAHs/DMSO?

We are not sure we can give the formation yields for the aqueous products through SO_2 oxidation reactions of DMSO and/or PAHs/DMSO due to the lack of standards and the limitations of FT-ICR-MS.