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Comment on acp-2021-1074

Anonymous Referee #2

Referee comment on "Kinetics of OH□+□SO_2□+□M: temperature-dependent rate coefficients in the fall-off regime and the influence of water vapour" by Wenyu Sun et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-1074-RC2, 2022

This manuscript presents experimentally determined rate coefficients for OH+SO2 over a range of atmospherically relevant conditions (T = 220–333 K, p = 14–742 Torr N_2 and xH_2O = 0 – 0.2). This reaction plays a key role in the sulfur-controlled particle formation in the Earth's atmosphere, and, similar to research from the same group into OH + NO_2, warranted updating to include the rate coefficient enhancement when considering H_2O as a third body collision partner of the $HOSO_2$* association complex.

There is a large body of experimental work presented herein using a combination of N_2 and H_2O bath gases to parameterize the rate coefficient. The authors find that H_2O is >5 times more efficient a collision partner compared to N_2, which is significant. Much care was taken to characterize the negligible effect of SO_2 photolysis at 248 nm on the rate coefficient measurement which possibly affected previous determinations of the rate coefficient in He. This included laser energy dependencies, spectroscopic [SO_2] measurements and utilizing HONO as an alternative OH source at 351 nm; a very thorough and meticulous investigation.

This work is rounded off by looking at the overall impact this new parameterization has on the determination of the title rate coefficient, where the authors show there is a significant discrepancy compared to current parameterizations in the recommended IUPAC/NASA literature throughout the troposphere and stratosphere.

I recommend this article for publication with only a few (very) minor comments below.

- Table 1/Line 255: I think the inclusion of RSD is a good tool for us to judge the goodness-of-fit and should be potentially adopted by others, however R^2 is somewhat meaningless for non-linear regressions. Additionally, the correlation coefficient, R, and the coefficient of determination, R^2, are not the same, as stated in the caption.
- Figure 9/S1: Perhaps the red open-square in the legend could be made to line up with

the other open squares for clarity?

- Figure S2: These altitude profiles represent the change in the "dry" rate coefficient, correct? I think it would be good to clarify the ~5% increase in the rate coefficient before the effect of water vapor is included when comparing the data to the current IUPAC/NASA profiles. This is really only important in the lower lower part of the atmosphere, but would highlight the compounding effect of the water vapor collision efficiency in the following modelling section.
- L368 and Fig 13. Over what altitude range are these results integrated when considered "at the Earth's surface" and/or "near the Earth's surface", as quoted from the main text and figure caption respectively?