Comment on acp-2021-1074

Anonymous Referee #1

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-RC1, 2022

The manuscript reports on an experimental kinetic study of the OH + SO$_2$ + M reaction. The experiments were performed in a pulsed laser photolysis (PLP)/laser-induced fluorescence (LIF) setup with OH production from photolysis of H$_2$O$_2$, HNO$_3$, or HONO and time-resolved detection of OH with LIF. Rate constants were determined under pseudo-first order conditions with respect to OH. The excess concentration of SO$_2$, which is critical for the second- and third-order rate constants, was carefully determined with UV absorption spectroscopy. Neat N$_2$ or mixtures of N$_2$ with H$_2$O were used as bath gases, and it was found that H$_2$O is a particular efficient collider leading to a notably increased rate constant. In general the rate constants were found to be in the falloff range at the chosen conditions (T = 220–333 K, p = 14–742 Torr), and their pressure dependence was parameterized in terms of Troe expressions. These results were implemented in the chemistry part of an atmospheric general circulation model to assess the influence of atmospheric water content. It was found that the atmospheric lifetime of SO$_2$ is probably lower than previously assumed in nearly all regions of the atmosphere.

Overall, this manuscript is a fine piece of work combining very carefully performed laboratory experiments with adequate parameterizations of rate constants and atmospheric modeling calculations. The scientific problem addressed is timely, and the methods used are adequate and state-of-the-art. The results are carefully discussed and compared with those from other works, and the paper is excellently written. There is almost nothing to complain. Hence, I recommend acceptance of the manuscript for ACP after minor, mainly technical revisions.

The following points should be considered by the authors before acceptance:

General: The authors should carefully check the consistent use of rate constant symbols. Sometimes the temperature dependence $(T/300)^n$ is included in the rate constant, sometimes it is not (cf. e.g. the use of $k_{1,0}^{N2}$ in the abstract and introduction section and its use in eqs. (3–6). Also, in the abstract, nothing is said about the T dependence of $k_{1,0}^{H2O}$ whereas the temperature exponent o = 4.90 on page 11 (bottom). This must be corrected. Also better use $(T/300 \text{ K})^n$ instead of $(T/300)^n$ etc.

lines 58, 183, 312: Shouldn't "photo-excitation of SO_2" better read "photo-dissociation of SO_2"?

line 61: Check parentheses in rate constant symbols.

line 97: In line 92, the volume of the quartz reactor is given (500 cm^3). So it would be better to give the flow rate for typical T and p also in units cm^3 s^{-1} instead of cm s^{-1}. The reader does not know the length of the reactor. Are with these flow rates really fresh(!) gas samples photolyzed at each laser pulse (with 10 Hz repetition rate)?

eq. (5): One (in the denominator is missing.