A potential source of atmospheric sulfate from O2 --induced SO2 oxidation by ozone

Authors are Narcisse Tchinda Tsona and Lin Du

Recommendation: This paper is publishable subject to minor revisions noted. Further review is not needed.

Comments: The authors have theoretically studied the role of the superoxides such as O2- in SO2 oxidation. The simulations were performed using a combination of DFT and CC levels of theory (CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ). Calculations were performed in the gas phase with and without one water molecule. Two possible mechanisms for the titled reaction were suggested and considered.

It is well known, that sulfur oxidation products play an important role in the atmosphere: formation of secondary aerosols, clouds and acid rains. Therefore, this theoretical work is an important contribution to a better understanding of the total mechanism of atmospheric sulfuric acid formation. I recommend publication this paper in the Atmospheric Chemistry and Physics Discussions after minor revisions.

Page 1, line 18. Misspelling the word “modelling”. It does not need double LL.

Page 3, line 9. Does not need a dot in the middle of sentences “with O3. in”

Page 6, line 10. Delete the empty space between “4. 5”

Page 12, line 16. Need to add a negative charge to the formula O2SOO.

1) In the Methods section, please, mention what multiplicity and charge did you use for the calculations of considered systems.

2) Did you perform IRC (intrinsic reaction coordinate) analysis, to prove that all your saddle points from the same PES (Pre-reactive complex – TS – Products)? If not, you should do it.

3) Do you think that just one water molecule is it a sufficient model to simulate liquid phase? Authors can additionally apply PCM models to the monohydrated system. Probably, in this case, the reaction will run spontaneously, without pre-reactive complex and TS (now, authors have a situation where in the case monohydrated system the energy of TSW2 is lower than the energy of the pre-reactive complex RCW2).

4) Please, add [Units] to the mentioned constants in Eq. 4 and 5 (for q, h, ε0 etc.