

Interactive comment on “Exploring the atmospheric chemistry of

O₂SO₃⁻ and assessing the maximum turnover number of a ion catalysed H₂SO₄ form

Anonymous Referee #2

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In this work, the authors present a density functional theory-based study of the reactions of O₂SO₃⁻ with O₃ and their implications for the atmosphere. It is a nice work, well-written, with appealing results, and an adequate level of calculation. The authors have experience in the field and I have only few minor (and a major) critiques. Then, I recommend this manuscript for publication in Atmos. Chem. Phys. Discuss., although some revisions are requested before this work can be considered publishable. In the incoming paragraphs, I enclose some comments, which I can think that they can be useful for the authors to do an improved version of this manuscript: a) The authors used the new CAM-B3LYP functional and in the computational details section, they cite two articles, which show that CAM-B3LYP is superior to B3LYP with respect to deter-

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mining activation energies for a range of typical chemical reactions. These two articles didn't consider systems with triplet multiplicity, some additional references about the goodness of the CAM-B3LYP functional for triplet and open-shell systems can be very useful for the potential reader of this article. b) In the computational details section, it is indicated the methodology used to evaluate the reaction rate constants. The authors have considered the symmetry of these systems to evaluate the reaction rate constants (it is not clear in the text) ? Moreover, they have considered the different stable (and almost isoenergetic according to the text) configurations of the dehydrated and hydrated cluster decomposition mechanism and O₂SO₃⁻ oxidation reaction rate constants ? c) In the section 3.1 of self-dissociation, the authors correctly point out a discrepancy between the calculated and measure [SO₃⁻]:[O₂SO₃⁻] ratios. They explain this difference considering that the SO₃⁻ can be stabilized by more than one water or that the sources and sinks of SO₃⁻ and O₂SO₃⁻ induces a dynamic rather than a thermal equilibrium. This paragraph is very interesting and deserves more emphasis (even to open the discussion about new and more accurate experimental measures). d) As a suggestion for the incoming works, they need to increment the basis set to aug-cc-pv(T+d)z basis set, which can have important effects, e.g. evaluation of the electron affinity of SO₃ and SO₃⁻. e) A small misprint in the page 30185 "when evaluating Reaction (??)". f) The authors reported increment free energy values, although it is not indicated the pressure and temperature considered (I guess it is 298° K and 1 atm.). The authors have considered the possibility to study the stability of these systems at different altitudes of the Earth's Atmosphere ? g) My major comment is in the section 3.3.1 formation of O₃SO₃⁻. The authors note in the page 310187 "at standard conditions the de- and monohydrated energy barriers are 27.1 and 39.6 kJmol⁻¹ respectively, implying the water is significantly hindering the oxygen transfer due to destabilization of the transition state, see Fig. 3". This sentence is true for the most stable configuration considered, however at the beginning of the section 3.2 the authors note that the hydrated O₂SO₃-O₃ has at least 10 stable configurations within 10 kJmol⁻¹. For instance, one of this almost isoenergetic configuration will have the water and ozone molecules in different

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sides of O_2SO_3^- , i.e. the effect of the water will be different than the structure of Figure 5a and my guess is that in this configuration the energy barriers of the de- and mono-hydrated energy barriers will be similar. This fact can have relevant implications for the conclusions derived from this work. h) The authors have considered the possibility of a transition state in the formation of $\text{SO}_5\text{-O}_3$ and $\text{SO}_5\text{-WO}_3$ complexes? Which is the binding energy of these complexes ? i) A table with a summary of the relative energies, enthalpies, and free energies of these reactions will help to follow the results reported in this article.

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