

Journal: Atmospheric Chemistry and Physics (ACP)

Title: Exploring the atmospheric chemistry of O_2SO_3^- and assessing the maximum turnover number of ion catalysed H_2SO_4 formation

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Dear Ari Laaksonen

Atmospheric Chemistry and Physics Editor

I reviewed the above paper and you can see my idea in the follow.

Best Regards

Comments to the Authors

The authors report a theoretical study of the catalytic oxidation of SO_2 to SO_3 using $\text{SO}_3^-(\text{H}_2\text{O})_{\geq 5}$ at the CAM-B3LYP and CCSD(T) levels of theory. Then, they predict rate of reactions, the total turnover number and conclude the maximum fraction of H_2SO_4 using this method.

I think that the topics of the research will be of interest and this manuscript may be published after major revisions. I recommend that it should be revised taking into account the following main comments:

1. It is well accepted that for period-3 atoms such as S, additional functions are necessary. I would then expect the author to have used the aug-cc-pV(T+d)Z basis rather than aug-cc-pVTZ.
2. All the parameters and procedures used in the dynamics calculation should be specified so other researchers can repeat and check their results. In this paper, the details of rate constants calculation for the reaction mechanism are not exactly defined. While, the calculation of rate constant using TST theory as shown in equation 2 in the paper, need to known transition state physical properties such as structure, energetic properties, and vibrational frequencies especially imaginary frequency, I cannot find any numerical data in the main paper or supplementary data. Suggested in the new table in supporting information at least vibrational frequencies of transition state are tabulated. If they added Cartesian coordinate of all species, it is the best.
3. The spin multiplicity of all species is singlet except oxygen atom which is triplet. This reaction is forbidden in photochemical method. So, the authors should be clarifying the spin multiplicity of species and relaxation step of oxygen molecule from singlet to triplet in the final product. As we know, oxygen molecule has two singlet excited state.
4. In this work, I find some van der Waals interactions. I cannot accept the van der Waals interaction between sulfur atom of $\text{O}_3\text{SO}_2\text{W}$ and central oxygen atom of ozone (see figure 2 for the interaction length of 3.53 Å). My suggestion is explanation of any interaction

using atom in molecule calculation, AIM, or NBO analysis or added a sentence with this concept “ all of interactions are confirm using atom in molecule (or NBO) analysis”

Minor comments:

- a. Gibbs free energy explains the stability of specie. I think don't have any formalism to imply free energy related to the lifetime (kinetic parameter) of specie. If no, please add reference. (see line 16 page 30184)
- b. In line 8 page 30185, what is the meaning of question marks?
- c. The first paragraph of page 30186, line 2 to 3 “Assuming that the540 cm⁻¹.” need to references.
- d. Are the thermodynamic parameters in standard form? If yes, please add standard symbol, (0), in superscript of thermodynamic parameters. If no, clarify temperature.
- e. In supplementary data, the authors told “transition state energies are given in table SI-2” but I don't find them.
- f. The molecular symmetry of known species is added in the next of molecules.
- g. It seems the authors don't calculated basis set superposition error. In this work, it is necessary that calculated and added to the energetic parameters of species.
- h. I am not native English, so I haven't any idea for the English level of paper.