

Review of “Exploring the chemical fate of the sulfate radical anion by reaction with sulfur dioxide in the gas phase by N. T. Tsona, N. Bork, and H. Vehkamäki

The original referee's comments, replies included in the revised paper, replies not included in the revised paper and comment made by the referee on the revised manuscript are reproduced in green, red, blue and black, respectively.

The manuscript could probably be publishable; however, I cannot recommend publication of the manuscript in the present form because most of the issues pointed out in the original referee's report have not been addressed properly. I hope that the authors will be able to address these issues quickly and that the manuscript will soon be transformed into an adequate paper that meets the ACP standards.

Specific comments:

1. The authors have mentioned that “PW91 and B3LYP are two of the most popular functionals, but for anionic systems the CAM-B3LYP functional is superior to B3LYP by the inclusion of long-range correction (Yanai et al., 2004)” and choose the CAM-B3LYP as the primary method for the geometry optimization and thermal correction. The authors provide a more detailed explanation of the importance of the “long-range correction” in the case, when strongly bonded ionic clusters are studied, and a clearer justification for the selection of the CAM-B3LYP as the primary computational method. In particular, additional tests/ benchmarks of PW91, B3LYP and CAM-B3LYP methods on $\text{SO}_4^- + \text{H}_2\text{O} \rightarrow \text{SO}_4(\text{H}_2\text{O})$ and $\text{SO}_4^- + \text{SO}_2 \rightarrow \text{SO}_4^-(\text{SO}_2)$ reactions (Table 1) should be included in the revised manuscript. Based on the results presented in Table 1 showing clearly that CAM-B3LYP significantly underestimates the reaction free energies, one could probably conclude that PW91, typically predicting stronger bonding, may be a better choice than both B3LYP and CAM-B3LYP.

This was inserted in line 26, page 12865 Table 1 shows the changes in binding Gibbs free energy and Gibbs free energy barrier with the chosen methods for three representative reactions. It is seen that the performance of the PW91 functional is superior to that of B3LYP and CAM-B3LYP when it comes to clustering reactions. The low energy barrier (3.8 kcal/mol below the initial reactants) predicted by the PW91 functional implies that the formation of SO_3SO_3^- from $\text{SO}_2 + \text{SO}_4^-$ almost proceeds at collision rate. If this is the case, the experimental Gibbs free energy value -6.7 kcal/mol would correspond to the energy change of $\text{SO}_2 + \text{SO}_4^- \rightarrow \text{SO}_3\text{SO}_3^-$ reaction, for which PW91 predicts a Gibbs free energy change of -9.1 kcal/mol, thus overestimating the experiment by 2.4 kcal/mol. It is likely that PW91 is underestimating the energy barrier and to avoid overestimating the atmospheric importance of the $\text{SO}_2 + \text{SO}_4^-$ reaction, we choose the CAM-B3LYP functional for our calculations.”

The authors should state clearly that based on data presented in Table 1, PW91 agrees with the experimental data better than all the other methods used for benchmarking in the present study, including those combining the DFT and single-point high-level *ab initio* corrections.

The authors state that “*It is likely that PW91 is underestimating the energy barrier and to avoid overestimating the atmospheric importance of the $\text{SO}_2 + \text{SO}_4^-$ reaction, we choose the CAM-B3LYP functional for our calculations.*” This statement is solely based on the authors’

assumptions and does not seem to be justified. Moreover, PW91 has not been mentioned in the original manuscript and was not considered by the authors as one of the candidate methods. This means that the statement should be deleted.

In the response, the authors state that

However, PW91 also predicts a very low energy barrier of the SO_2SO_4 - to SO_3SO_3 - conversion, just 2.8 kcal/mol above the SO_2SO_4 - ion complex, i.e. submerged by 3.8 kcal/mol compared to the $SO_2 + SO_4$ - reactants. This is much lower than the predictions by CAM-B3LYP and B3LYP.

Does it imply that CAM-B3LYP and B3LYP are used as reference methods? The PW91 method is clearly in much better agreement with experiments than both CAM-B3LYP and B3LYP methods, while CAM-B3LYP and B3LYP underestimate the cluster stability compared to both the experiments and PW91. However, according to the authors, it looks like the conclusion that PW91 predicts lower barrier height compared to CAM-B3LYP and B3LYP significantly underestimating the cluster stability implies that PW91 predictions are likely wrong.

If the PW91 prediction is correct, this suggests immediate conversion of the SO_2SO_4 - cluster ion into the SO_3SO_3 - ion and the experimental reference energy would, in fact, not be of the $SO_2 + SO_4 \rightarrow SO_2SO_4$ - reaction, but of the $SO_2 + SO_4 \rightarrow SO_3SO_3$ - reaction (unknowing to the experimentalists since the experiments are conducted using mass spectrometry wherein the SO_2SO_4 - and SO_3SO_3 - cluster ions are indistinguishable). However, the latter reaction has a reaction free energy of -9.0 kcal/mol (PW91/aVDZ) clearly suggesting that the experimental value of -6.7 kcal/mol does correspond to $SO_2 + SO_4 \rightarrow SO_2SO_4$ - (6.6 kcal/mol at PW91/aVDZ). This is a strong argument that a significant energy barrier does separate the conversion of SO_2SO_4 - to SO_3SO_3 .

According to the authors, the experimental reaction products are pretty much unknown (“ *SO_2SO_4 - and SO_3SO_3 - are indistinguishable*”). Is there any possibility that measured properties represent those of a mixture of various ($SO_n^{(-a)}SO_k^{(-b)}$), where $a+b=-1$ and $n+k=6$? Also, please, briefly comment on the experimental uncertainties.

2. Based on the data shown in Table 1 one can conclude that in most cases the single point CCSD(T) and CCSD(T)-F12 energy corrections do not seem to systematically improve the quality of the DFT results. The authors should briefly comment on this issue.

We agree that this effect is striking and we replaced the third sentence, last paragraph of page 12866 by the following: “It is well known that entropy and zero point vibrational energy terms based on DFT may be several kcal/mol in error. Here, the sum of these terms by the CAM-B3LYP functional seems about 2.5 to 3 kcal/mol underestimated at $T = 298.15$ K since the most accurate of the four electronic energy corrections leads to underestimating the binding energies by this amount.”

The response is irrelevant to the original Comment 2 and should be deleted. Instead, the authors should make a clear statement that *the single point CCSD(T) and CCSD(T)-F12 energy corrections applied in their study do not improve the quality of the DFT results.*

3. The hydration range ($n = 0-2$) considered in the present paper does not seem to be wide enough to represent the real atmospheric conditions, at which higher hydrates may exist in significant concentrations. Please, explain your choice and comment on the impact of possible uncertainties related to hydration on conclusions made in the present paper.

It is correct that SO_4^- can bind up to five water molecules under typical atmospheric conditions, but after clustering with SO_2 several of these water molecules will evaporate and at $T = 298.15 \text{ K}$ and 50 % relative humidity, the SO_2SO_4^- cluster ion is most likely to be dehydrated. We therefore argue that the range of hydration is adequate for describing the reaction $\text{SO}_2 + \text{SO}_4^- (\text{H}_2\text{O})_n \rightarrow \text{SO}_3\text{SO}_3^- (\text{H}_2\text{O})_n$. This is discussed in section 3.3 of the article, but to avoid misunderstandings this will be further stressed in the revised manuscript.

This commenting should be inserted in line 22, page 12867 “In this work we limit the hydration range to two since several of the water molecules initially bound to SO_4^- will evaporate after collision with SO_2 , leaving the SO_2SO_4^- cluster ion mostly dehydrated as will be discussed in Section 3.3.”

The quality of the hydration analysis is still well below satisfactory. It is well-known that B3LYP typically underestimates the hydration free energies by several kcal/mol. However, the uncertainties in the hydration free energies due to the application of the B3LYP and CAM-B3LYP have not been considered in the revised manuscript. The conclusion that SO_2SO_4^- are likely dehydrated is questionable because the hydration free energies at the CAM-B3LYP level are just 0.5-1.4 kcal/mol below the threshold value of -2.5 kcal/mol. Moreover the hydration strength seems to increase with the hydration number. This means that higher hydrates may present in significant concentrations under the conditions specified in Fig.4. In order to address this issue, the authors should extend the hydration study to $n=3$ and $n=4$. The $\text{SO}_2\text{SO}_4^- (\text{H}_2\text{O})_n$ clusters are quite small and, therefore, this task can be accomplished in less than a week. The authors should also include new data obtained by other methods, say PW91 and RI-MP2, in the comparison of hydration free energies shown in Fig.4. At very least, they should carry out a more comprehensive uncertainty analysis showing how does the propagation of uncertainty of 1 kcal/mol (chemical accuracy limit) affect their conclusions.