

Concerning the research article:

**Exploring the chemical fate of the sulfate radical anion by reaction with sulfur dioxide in the gas phase**

N. T. Tsona<sup>1</sup>, N. Bork<sup>1,2</sup> and H. Vehkamäki<sup>1</sup>

<sup>1</sup>Division of Atmospheric Sciences and Geophysics, Department of Physics, University of Helsinki, P.O. Box 64, 00014 University of Helsinki, Finland

<sup>2</sup>Department of Chemistry, University of Copenhagen, 2100, Copenhagen, Denmark

Atmos. Chem. Phys. Discuss., 14, 12863–12886, 2014

In this document, we present our replies to the new referee comments which we believe to have answered fully and clearly. We sincerely apologize for the shortcomings and inaccuracies in our original reply and corresponding manuscript changes, and we have carefully ensured that the revised manuscript and supporting information contains all necessary information.

On behalf of all authors,



Narcisse T. Tsona

Doctoral Student  
Division of Atmospheric Sciences  
Department of Physics  
University of Helsinki

narcisse.tsonatchinda@helsinki.fi

**New comment by A. Nadykto:**

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.

**Original comment by A. Nadykto:**

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.

**Original reply by Tsona et al :**

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 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  $\text{SO}_3\text{SO}_3^-$  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."

**New comment by A. Nadykto:**

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.

**New reply by Tsona et al :**

This has been clarified, although we note that PW91 is not superior to the coupled cluster corrected methods for the clustering of  $\text{SO}_4^-$  and  $\text{H}_2\text{O}$ :

New text (page 12865): “On average, it is seen that the performance of PW91 for the two clustering reactions is superior to both CAM-B3LYP and B3LYP, whether or not these are single point coupled cluster corrected.”

**New comment by A. Nadykto :**

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.

**New reply by Tsona et al :**

This statement is a result of comparing the available experimental data to the predictions of the PW91 functional which is central to the ab initio selection procedure. In the revised manuscript, our reasoning is clarified in greater detail, substituting the previous formulation:

New text (page 12866): “For the height of the energy barrier, no direct experimental evidence exists. However, the experimental value of the thermodynamics of the clustering reaction of  $\text{SO}_2$  and  $\text{SO}_4^-$  was found to  $-6.7 \text{ kcal mol}^{-1}$  with a maximum uncertainty of  $\pm 0.4 \text{ kcal mol}^{-1}$  (Fehsendeld and Ferguson, 1974). Due to the inherent limitations of mass spectrometry, the structure of the product cluster could not be determined, wherefore the obtained value may, in principle, either correspond to



However, ab initio calculations clearly indicate that the measured thermodynamics correspond to the former of these reactions, e.g. PW91/aVDZ predicting  $-6.6 \text{ kcal mol}^{-1}$  for the former while  $-9.0 \text{ kcal mol}^{-1}$  for the latter. We may therefore conclude that the conversion of  $\text{SO}_2\text{SO}_4^-$  to  $\text{SO}_3\text{SO}_3^-$  is rather slow, since, otherwise, the oxygen transfer reaction would have taken place in the experimental apparatus and a much higher binding energy, corresponding to reaction (2), would have been measured.

From Table 1 it can be seen that PW91 predicts a transition state located  $3.8 \text{ kcal/mol}$  below the separated reactants, predicting immediate conversion of  $\text{SO}_2\text{SO}_4^-$  to  $\text{SO}_3\text{SO}_3^-$ . According to the above considerations, this is inconsistent with the experimental data. It is therefore likely that PW91 underestimates the height of the energy barrier although no quantification can be made.

On the other hand, B3LYP and CAM-B3LYP predict barriers of  $7.8$  and  $9.3 \text{ kcal mol}^{-1}$ , respectively. In order to obtain a conservative estimate of the atmospheric importance of the  $\text{SO}_2+\text{SO}_4^- \rightarrow \text{SO}_3\text{SO}_3^-$  reaction rather than an upper limit, we choose the CAM-B3LYP functional for our calculations. However, since the CAM-B3LYP functional, according to Table 1, has a tendency of underbinding it should be noted that CAM-B3LYP is likely to overpredict cluster re-evaporation and hence underpredict the rates of reactions (R1) and (R2).”

New caption to Table 2: "Bimolecular rate constant ( $k_{\text{ox, bimol}}$ ) of the  $\text{SO}_2 + \text{SO}_4^-(\text{H}_2\text{O})_n \rightarrow \text{SO}_3\text{SO}_3^-(\text{H}_2\text{O})_n$  reaction. The computational benchmarking (Table 1) suggests that these values are more likely to be underestimated than overestimated."

New text (page 12875): "Discrepancies within the available ab initio data (Table 1) suggest that the reaction rate constants could, in fact, be significantly higher."

**New comment by A. Nadykto:**

In the response, the authors state that: However, PW91 also predicts a very low energy barrier of the  $\text{SO}_2\text{SO}_4^-$  to  $\text{SO}_3\text{SO}_3^-$  conversion, just 2.8 kcal/mol above the  $\text{SO}_2\text{SO}_4^-$  ion complex, i.e. submerged by 3.8 kcal/mol compared to the  $\text{SO}_2 + \text{SO}_4^-$  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.

**New reply by Tsona et al:**

We did not intend to imply that CAM-B3LYP or B3LYP are used as reference methods (neither did we use them as such), but we recognize that the above wording is vague and somewhat misleading. The new manuscript text concerning the performance of the ab initio methods has been carefully checked and should contain no further ambiguity.

**Original reply by Tsona et al :**

If the PW91 prediction is correct, this suggests immediate conversion of the  $\text{SO}_2\text{SO}_4^-$  cluster ion into the  $\text{SO}_3\text{SO}_3^-$  ion and the experimental reference energy would, in fact, not be of the  $\text{SO}_2 + \text{SO}_4^- \rightarrow \text{SO}_2\text{SO}_4^-$  reaction, but of the  $\text{SO}_2 + \text{SO}_4^- \rightarrow \text{SO}_3\text{SO}_3^-$  reaction (unknowing to the experimentalists since the experiments are conducted using mass spectrometry wherein the  $\text{SO}_2\text{SO}_4^-$  and  $\text{SO}_3\text{SO}_3^-$  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  $\text{SO}_2 + \text{SO}_4^- \rightarrow \text{SO}_2\text{SO}_4^-$  (6.6 kcal/mol at PW91/aVDZ). This is a strong argument that a significant energy barrier does separate the conversion of  $\text{SO}_2\text{SO}_4^-$  to  $\text{SO}_3\text{SO}_3^-$ .

**New comment by A. Nadykto :**

According to the authors, the experimental reaction products are pretty much unknown (" $\text{SO}_2\text{SO}_4^-$  and  $\text{SO}_3\text{SO}_3^-$  are indistinguishable"). Is there any possibility that measured properties represent those of a mixture of various ( $\text{SO}_n(-a)\text{SO}_k(-b)$ ), where  $a+b=-1$  and  $n+k=6$ ? Also, please, briefly comment on the experimental uncertainties.

**New comment by N. Tsona et al :**

It is very likely that the  $S_2O_6$  signal in the mass spectrometer represents a mixture of  $SO_2SO_4$  and  $SO_3SO_3$ . However, from comparisons with the ab initio calculations, as discussed above, it appears that the vast majority of the signal is  $SO_2SO_4$ . The experimental uncertainties are not well explained in the article by Fehsenfeld and Ferguson (*J. Chem. Phys.*, 61, 8, 1974), but uncertainties of 0.4 kcal/mol on the Gibbs free binding energies are mentioned as upper limits. This range is mentioned in the revised manuscript as described above.

**Original comment by A. Nadykto :**

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.

**Original comment by Tsona et al :**

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."

**New comment by A. Nadykto :**

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.

**New reply by Tsona et al :**

For the clustering of  $SO_4^-$  with  $H_2O$ , both CCSD(T) and CCSD(T)-F12 calculations do improve the DFT result whereas for the clustering of  $SO_4^-$  and  $SO_2$ , only the CCSD(T)/aVDZ single point correction leads to an improved result compared to the CAM-B3LYP result. We have deleted the changes from the first reply "It is well known that ..." and replaced this with the following:

New text (page 12867): "From Table 1 it is apparent that no systematic improvement of the DFT results is obtained at increasing quality of the coupled cluster single point calculations."

**Original reply by A. Nadykto :**

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.

**Original reply by Tsona et al :**

It is correct that  $\text{SO}_4^-$  can bind up to five water molecules under typical atmospheric conditions, but after clustering with  $\text{SO}_2$  several of these water molecules will evaporate and at  $T = 298.15 \text{ K}$  and 50 % relative humidity, the  $\text{SO}_2\text{SO}_4^-$  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 was 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  $\text{SO}_4^-$  will evaporate after collision with  $\text{SO}_2$ , leaving the  $\text{SO}_2\text{SO}_4^-$  cluster ion mostly dehydrated as will be discussed in Section 3.3.”

**New comment by A. Nadykto :**

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 that  $\text{SO}_2\text{SO}_4^-$  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.

**New comment by Tsona et al:**

We have performed a more thorough analysis of the hydration of the  $\text{SO}_2\text{SO}_4^-$  ion including up to four water molecules using PW91, CAM-B3LYP and B3LYP. Both RI-MP2 and MP2 were tested using Turbomole and Gaussian, respectively, but severe convergence problems for several cluster prevented us from obtaining RI-MP2 or MP2 based hydration energies.

Concerning  $\text{SO}_2\text{SO}_4^-$ , the results are summarized in Figure S2 shown below. The results consistently indicate that the water affinity of  $\text{SO}_2\text{SO}_4^-$  decreases after addition of the second water molecule and that  $\text{SO}_2\text{SO}_4^-$ , most likely, is dehydrated at ambient conditions. Also, the results give no indication that larger hydrates should predominate for either of the  $\text{SO}_4^-$  or  $\text{SO}_3\text{SO}_3^-$  clusters (figures shown in supplement).

Also, we have performed a sensitivity analysis of the hydration patterns on inaccuracies on the Gibbs free hydration energies. These show that, besides minor variations, the conclusions drawn from the original Figure 5, are fairly insensitive to variation on the order of  $\pm 1 \text{ kcal/mol}$ .

The following text has been modified or added to include these findings:

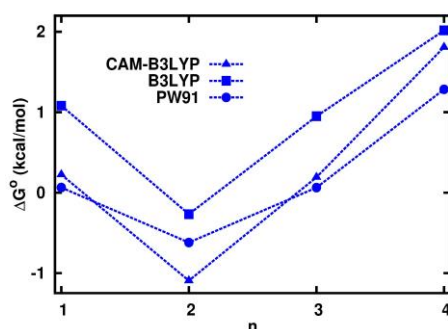


Figure S2 (in supplement): Gibbs free energies of hydration (in kcal mol<sup>-1</sup>) of the SO<sub>2</sub>SO<sub>4</sub><sup>-</sup> (H<sub>2</sub>O)<sub>n-1</sub> anion from DFT using the aug-cc-pVDZ basis set, calculated at 1 atm and 298.15 K. Different functionals are used for comparison. Color coding similar to Fig. 4 in the main article.

Page 12868: “In this work we limit the hydration range to two since several of the water molecules initially bound to SO<sub>4</sub><sup>-</sup> will evaporate after collision with SO<sub>2</sub>, leaving the SO<sub>2</sub>SO<sub>4</sub><sup>-</sup> cluster ion mostly dehydrated as will be discussed in Section 3.3. See also Figures 4 and S2.”

Page 12873: “The binding energies of larger hydrates were investigated using the B3LYP, CAM-B3LYP and PW91 functionals, although not single point corrected according to Eq. (1) due to computational expense. These data are shown in Figures S2, S3 and S4 and indicate that the sulfur anions considered here are unlikely to bind more than a few water molecules. One possible exception to this is the SO<sub>3</sub>SO<sub>3</sub><sup>-</sup> cluster which is seen to form a somewhat stable tetrahydrate (e.g. ΔG<sub>R6,n=3</sub> = -2.1 kcal/mol for PW91/aVDZ) which may be present in noticeable concentrations.”

Page 12874: “Similar figures assuming either a general underbinding or overbinding of 1 kcal mol<sup>-1</sup> are shown in Figures S6 and S7, respectively. These reveal that the general hydration patterns of the SO<sub>4</sub><sup>-</sup>, SO<sub>2</sub>SO<sub>4</sub><sup>-</sup> and SO<sub>3</sub>SO<sub>3</sub><sup>-</sup> anions are quite insensitive to variations in binding energy of this magnitude.”