Concerning the research article:

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

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We appreciate the positive comments and constructive suggestions by the referee. Here, we present a point-to-point response to all comments. For clarity, the referee comments are reproduced in blue colored text.

On behalf of all authors,

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Replies to A. Nadykto (Referee)

The manuscript is dedicated to the sulfur cycle relevant to the formation of H$_2$SO$_4$, the key atmospheric nucleation precursor in the Earth’s atmosphere. The topic is important and relevant directly to the atmospheric physics and chemistry. The paper is nicely written, easy to follow, interesting and probably deserves publication. However, there exist a few issues to be addressed prior to publication.

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 SO$_4^-$ + H$_2$O → SO$_4^-$(H$_2$O) and SO$_4^-$ + SO$_2$ → SO$_4^-$(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.

The main difference between the B3LYP and CAM-B3LYP functionals is the amount of exact Hartree-Fock (HF) exchange included. The B3LYP functional includes a constant amount of 20 % HF exchange (and hence 80 % B88 exchange), whereas amount of HF exchange varies from 19 to 85 % in the CAM-B3LYP functional depending on distance (see e.g. Fig. 2 in Yanai et al. (2004)). In particular, the increased amount of exact HF exchange has been shown to be advantageous when treating anions and Rydberg states since the associated diffuse orbitals are ill described by the pure B88 exchange functional. We agree that further clarification will benefit a revised manuscript.

As suggested by the reviewer, we have conducted additional benchmarking of the PW91 and B3LYP functionals (see the revised Table 1, included in this document). As expected from the above considerations, we find that the B3LYP predictions are further from the experimental values than the CAM-B3LYP predictions and as expected by the reviewer, the performance of the PW91 functional on the SO$_2$ + H$_2$O and SO$_4^-$ + SO$_2$ binding energies is superior to the CAM-B3LYP functional. However, PW91 also predicts a very low energy barrier of the SO$_2$SO$_4^-$ to SO$_3$SO$_4^-$ conversion, just 2.8 kcal/mol above the SO$_2$SO$_4^-$ 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. If the PW91 prediction is correct, this suggests immediate conversion of the SO$_2$SO$_4^-$ cluster ion into the SO$_3$SO$_4^-$ ion and the experimental reference energy would, in fact, not be of the SO$_2$ + SO$_4^-$ → SO$_3$SO$_4^-$ reaction, but of the SO$_2$ + SO$_4^-$ → SO$_3$SO$_2^-$ reaction (unknowing to the experimentalists since the experiments are
conducted using mass spectrometry wherein the SO\textsubscript{2}SO\textsubscript{4}\textsuperscript{−} and SO\textsubscript{3}SO\textsubscript{3}\textsuperscript{−} 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\textsubscript{2} + SO\textsubscript{4}\textsuperscript{−} → SO\textsubscript{2}SO\textsubscript{4}\textsuperscript{−} \ (6.6 kcal/mol at PW91/aVDZ). This is a strong argument that a significant energy barrier does separate the conversion of SO\textsubscript{2}SO\textsubscript{4}\textsuperscript{−} to SO\textsubscript{3}SO\textsubscript{3}\textsuperscript{−}.

Hence, although the performance of the PW91 functional is superior when it comes to clustering reactions, PW91 seems to underestimate the energy barrier and we therefore choose the CAM-B3LYP functional to avoid overestimating the atmospheric importance of the SO\textsubscript{2} + SO\textsuperscript{4}\textsuperscript{−} reaction. In the revised manuscript we will, however, stress that the true reaction rates could in fact be significantly higher than the reaction rates based on CAM-B3LYP which therefore are to be considered as lower limits to the true reaction rates.

These considerations and the revised Table 1 will be included in the revised manuscript.

Table 1. Comparison of Gibbs free energy changes at T = 298.15 K of the indicated reactions calculated by different DFT functionals, all using the aug-cc-pVDZ (aVDZ) basis set. Energy units are kcal mol\textsuperscript{−1}.

<table>
<thead>
<tr>
<th>Method</th>
<th>SO\textsubscript{4}\textsuperscript{−}+H\textsubscript{2}O → SO\textsubscript{4}\textsuperscript{−}(H\textsubscript{2}O)</th>
<th>SO\textsubscript{4}\textsuperscript{−}+SO\textsubscript{2} → SO\textsubscript{4}\textsuperscript{−}(SO\textsubscript{2})</th>
<th>SO\textsubscript{4}\textsuperscript{−}(SO\textsubscript{2}) → TS</th>
</tr>
</thead>
<tbody>
<tr>
<td>PW91</td>
<td>-2.7</td>
<td>-6.6</td>
<td>2.8</td>
</tr>
<tr>
<td>B3LYP</td>
<td>-1.5</td>
<td>-4.4</td>
<td>7.8</td>
</tr>
<tr>
<td>CAM-B3LYP</td>
<td>-2.4</td>
<td>-5.0</td>
<td>9.3</td>
</tr>
<tr>
<td>CCSD(T)/aVDZ*</td>
<td>-3.3</td>
<td>-5.6</td>
<td>10.0</td>
</tr>
<tr>
<td>CCSD(T)/aVTZ*</td>
<td>-3.0</td>
<td>-4.2</td>
<td>9.8</td>
</tr>
<tr>
<td>VDZ-F12*</td>
<td>-2.8</td>
<td>-3.5</td>
<td>9.5</td>
</tr>
<tr>
<td>VTZ-F12*</td>
<td>-2.7</td>
<td>-3.6</td>
<td>-</td>
</tr>
<tr>
<td>Experiment**</td>
<td>-5.1</td>
<td>-6.7</td>
<td>-</td>
</tr>
</tbody>
</table>

*Electronic corrections on CAM-B3LYP/aVDZ structures calculated according to Eq. (1) using the indicated coupled cluster methods and basis sets, where VDZ-F12 and VTZ-F12 stand for CCSD(T)-F12/VDZ-F12 and CCSD(T)-F12/VTZ-F12, respectively.

**Fehsenfeld and Ferguson (1974).

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 suggest the following commenting:

“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 electronic energy corrections leads to underestimating the binding energies by this amount.”
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 \(\text{SO}_4^\text{-}\) 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 \(T = 298.15\) K and 50 % relative humidity, the \(\text{SO}_2\text{SO}_4^\text{-}\) 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.

Technical corrections.
Page 12864, last line, "," should be replaced with ",."

This line seems correct.

References in this reply: