Authors reply to reviewers comments concerning research article

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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(Atmos. Chem. Phys. Discuss., 12, 30177-30201, 2012)

We thank both reviewers for insightful and thorough reviews. Since several points are raised by both reviewers, we have gathered all of our replies in this document. Here, we present our replies and descriptions as of how the manuscript may be improved according to the reviewers suggestions. For ease of reading, the reviewers comments are included in italic font.

Attached to this reply is an updated supplement and updated versions of Figures 3, 4, and 5.

On behalf of all authors,

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Replies to Reviewer 1:

1. *It is well accepted that for period-3 atoms such as S, additional functions are necessary. I would then expect the author have used the aug-cc-pV(T+d)Z basis rather than aug-cc- pVTZ.*

We agree that usually, the use of additional d-functions for sulfur is preferable. In this particular study, however, a proper description of the difference in electron affinity between SO_3 and O_3 is essential. Hence, we use this parameter to determine the basis set. The experimental value is ca. 15 kJ mol^{-1} which is best reproduced by using aug-cc-pVTZ, predicting 18 kJ mol^{-1}, while the aug-cc-pV(T+d)Z basis set predicts 35 kJ mol^{-1}. However, we realize that this was not properly described in the present manuscript.

The following should be appended to the computational methods section:
"We note that adding further d-functions, as normally preferable for 3'rd period elements, is not desirable since we found that the otherwise accurate aug-cc-pV(T+d)Z basis set predicted the electron affinity difference to -35 kJ mol^{-1}."

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.*

We agree that the amount of structural and energetic details were insufficient. In the attached updated supplement we have added tables including Cartesian coordinates of all species and harmonic frequencies of all transition states.

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.*

The reactions treated in this paper involves ionic radicals and are thus all electronic doublets. Triplet molecular oxygen is produced but this reaction is, in fact, spin allowed since the spin of the ionic radical product (SO_3^-) may pair with with the oxygen triplet spin and thus remains an overall doublet. However, we agree that this point should be more thoroughly clarified.

The following clarifying sentences should be included:
"We finally stress that all reactants and products are radicals and hence electronic doublets. In all cases, molecular oxygen is treated as an electronic triplet but due to the pairing with the doublet state of the ionic radical, all reactions are spin allowed."

4. *In this work, I find some van der Walls interactions. I cannot accept the van der Walls*

interaction between sulfur atom of O_3SO_2W 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"

Gas phase clusters of ions and dipoles are generally not bound by van der Waals forces and no van der Waals forces are explicitly treated in this paper. As correctly pointed out by the reviewer, between the mentioned S and O atoms in Figure 2, there is no bond. The indicated line and distance was not intended to illustrate a bond, but merely as extra information to give the reader a clearer picture of the atomic configuration. However, this was not properly described in the figure caption which only mentioned bonds. We suggest simply removing this line from the figure. A revised figure is attached to this reply. All remaining lines in this and all other figures are in fact bonds.

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)*

In atmospheric clustering, most often, there is no energy barrier preventing two fragments from forming a molecular cluster. In such cases the energy barrier separating a stable cluster from dissociating into two smaller fragments or molecules, is exactly the thermal energy gained by the clustering itself. We suggest added the following reference which summarizes this point (Ortega et al, From quantum chemical formation free energies to evaporation rates, *Atmos. Chem. Phys.*, 12, 225-235, 2012).

b) *In line 8 page 30185, what is the meaning of question marks?*

This is a formatting error. It should read "when evaluating Reactions (R3a) and (R3b)".

c) *The first paragraph of page 30186, line 2 to 3 "Assuming that the .....540 cm-1." need to references.*

The determination of the 540 cm^{-1} as prefactor is based on a simple functional analysis assuming that the three SO_3^--O_2 stretch frequencies presented in Figure 2 are independent and harmonic. However, since the approach is not standard, we agree that it should be further clarified, e.g. as follows:

"These modes are shown in Figure 2 and are responsible for the nuclear motion leading to charge transfer and cluster decomposition. All modes will be active at all times and their combined magnitudes at time, t, is given by $f(t)=\sum_{\upsilon=(646\ \mathrm{cm\text{-}1},\ 504\ \mathrm{cm\text{-}1},\ 364\ \mathrm{cm\text{-}1})} d_\upsilon \cos(\upsilon t)$, where d_υ is the displacement vector of vibration υ. Assuming that all modes are all in their ground states and that their displacement vectors are of similar magnitudes, we find an effective frequency of 540 cm^{-1} by functional analysis of $f(\upsilon)$."

d) *Are the thermodynamic parameters in standard form? If yes, please add standard symbol, (0), in superscript of thermodynamic parameters. If no, clarify temperature.*

Only standard conditions are considered. We agree that standard symbols should be added.

e) In supplementary data, the authors told “transition state energies are given in table SI-2” but I don’t find them.

The mentioned table contains the correct data, i.e. the relative Gibbs free energies, entropies, and pre-exponentials of all transition states. However, the table caption was misleading and should read "Thermodynamic data of the transition states of the de- and monohydrated reactions (R3a) and (R3b)." It has been corrected in the attached updated supplement.

f) The molecular symmetry of known species is added in the next of molecules.

Besides O_2, O_3, H_2O and other well known molecules, the only species considered containing any symmetry is $SO_3^-O_2$ being C_S. This will be indicated at the first mention of this species. Also, the lack of symmetry in the remaining species will be mentioned.

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.

Basis set superposition error (BSSE) may be important to consider when evaluating weakly bound complexes. However, after determining BSSE of all species, we find that BSSE nowhere contribute by more than 1 kJ/mol and is hence of minor importance. This is mainly due to the fairly large basis set. Still, in our revised manuscript all presented energies will be BSSE corrected.

Replies to Reviewer 2:

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 determining 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.*

Although we agree that a reader would appreciate a benchmark study of the performance of CAM-B3LYP on open shell systems, to the best of our knowledge, no such study has been published. However, after the submission of this manuscript we became aware of another comparison study directly targeting atmospheric sulfur chemistry. Also there it was found that CAM-B3LYP in most parameters outperforms B3LYP. This reference will be included in a revised manuscript (Elm et al, Assessment of Density Functional Theory in Predicting Structures and Free Energies of Reaction of Atmospheric Prenucleation Clusters, *J. Chem. Theory. Comput.* **2012**, 8, 2071−2077).

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 $O_2SO_3^-$ oxidation reaction rate constants ?*

Although the systems are simple, they do not contain any symmetry, besides $SO_3^-O_2$ being C_S. Since the reactant clusters, $SO_3^-O_2(O_3)$ and $SO_3^-O_2(H_2O)(O_3)$, are non-symmetric no symmetry enhancement of the reaction rate constants will be present. As also mentioned to the first reviewer, the general lack of symmetry will be mentioned in a revised manuscript.

We do not explicitly consider other than ground state configurations. We do find several other configurations of the $SO_3^-O_2(H_2O)(O_3)$ clusters close in energy which may contribute to the net reaction rate. However, neither the cluster decomposition reaction, nor the $SO_3^-O_2$ oxidation will be significantly affected much and we argue including more states will add unnecessary complexity to the manuscript.

c) *In the section 3.1 of self-dissociation, the authors correctly point out a discrepancy between the calculated and measure $[SO_3^-]:[O_3SO_3^-]$ ratios. They explain this difference considering that the SO_3^- can be stabilized by more than one water or that the sources and sinks of SO_3^- and $O_2SO_3^-$ 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) .*

We agree that this discrepancy is very interesting. We suggest that the paragraph is re-written as follows:
"These binding energies suggest much lower $[SO_3^-]:[O_2SO_3^-]$ ratios than the observed ratio of 1:10. Although several factors may contribute to this discrepancy it appears most likely that SO_3^- may be stabilized in configurations not considered here, preventing $O_2SO_3^-$ formation. Some of the most obvious candidates include OH, HO_2, other radicals, and/or clusters containing more than one water. It is well known that weakly bound clusters may evaporate inside the spectrometer. In accordance with

this, it seems that the reported field based concentrations of unclustered SO_3^- are overestimated."

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* SO_3 *and* SO_3^-.

See reply to referee 1.

e) *A small misprint in the page 30185 "when evaluating Reaction (??)".*

As also replied to the first reviewer, it should read "when evaluating Reactions (R3a) and (R3b)".

f) The authors reported increment free energy values, although it is not indicated the pres*sure 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 ?*

All data are reported for T=298.15 K and 1 atm.

The influence of ion induced SO_2 oxidation is the primary target of this line of research. Although the present paper represent a significant advance, still, we are lacking some critical information before atmospheric predictions can be made. We have in this manuscript in section "3.4 Overall catalytic turnover " outlined methods for prediction the ion catalyzed contribution of H_2SO_4 fluxes. However, extending this paragraph to include the effects of CO_2, temperature, humidity, and NO_X trace gas composition will be too extensive and is beyond the scope of this study. Currently, we are investigating this line of research but hence argue that it will be more appropriate to publish those results separately.

g) *My major comment is in the section 3.3.1 formation of* $O_3SO_3^-$. *The authors note in the page 310187 "at standard conditions the de- and monohydrated energy barriers are 27.1 and 39.6 kJ mol*$^{-1}$ *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* $O_2SO_3^-$ O_3 *has at least 10 stable configurations within 10 kJ mol*$^{-1}$. *For instance, one of this almost isoenergetic configuration will have the water and ozone molecules in different 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.*

We acknowledge the reviewer for noticing this shortcoming. We determined the transition state described by the reviewer and found that it has both a lower energy barrier (35.1 v.s. 39.6 kJ mol^{-1}), and higher pre-factor (7.4 10^9 s^{-1} v.s. 1.9 10^9 s^{-1}), than the one in the original manuscript. Hence, the "water hindered" pathway is thus somewhat less hindered than initially predicted. However, no conclusions are affected by the discovery of this new transition state.

h) *The authors have considered the possibility of a transition state in the formation of* $SO_5^-O_3$ *and* $SO_5^-WO_3$ *complexes? Which is the binding energy of these complexes ?*

We have not considered any such transition states. Several studies have investigated the collision rates of ion and dipoles and in general find collision limited reactions and large collision cross sections indicating that moderate or strong long range interactions. Further, since no bonds are broken in the initial clustering, the none of the usual per-requisites for the existence of a transition state are present.

The binding energies of the complexes are now available in a table of the PES in the attached updated supplementary material.

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.

We agree, and have included the mentioned table in the attached updated supplement.