Response to the comments of Reviewer 3

Thanks to reviewer 3 for his or her valuable comments, we have made significant improvements on the manuscript.

Comments:

General:

a) The main concern is the treatment of heterogeneous chemistry in the kinetic model and its description in the manuscript. Experiments were carried out at about 20-30% relative humidity and the chamber aerosol most probably consisted of liquid droplets, i.e. highly concentrated solutions of H_2SO_4 and MSA in water. Partitioning of DMS oxidation products to the chamber aerosol is then best described as reactive uptake, i.e. mass transfer to the droplet (gas phase diffusion and mass accommodation) followed by reaction on the surface or in the bulk of the droplet. In cases where surface and/or bulk reactions are dominating the uptake, the total uptake coefficient and the reactive uptake coefficient will be identical. Thus reactions (R1)-(R9) could be greatly simplified since only one parameter (the total uptake coefficient) needs to be adjusted for each DMS product instead of several parameters (k_{ads}, k_{des}, k_r). Data on mass accommodation and reactive uptake coefficients can be found in JPL publication 10-6 (Sander et al., 2011). In this way, also the reactive uptake of SO_2 could be handled consistently.

b) The abstract and introduction text suggests that heterogeneous reactions were treated as surface reaction. The formulation of reactions (R7)-(R9) does not explicitly refer to surface or bulk process. In the chamber aerosol probably both surface reactions and bulk reactions occurred. It should be clarified whether reactions (R7)-(R9) were treated in the kinetic model as surface reactions (by surface area) or as bulk reactions (by mass or volume). Also partitioning of DMS oxidation products is defined as adsorption / desorption (to surface) and not as sorption / desorption, while reactions (R1)-(R6) are formulated as bulk processes (by aerosol mass). It should be clarified whether reactions (R1)-(R6) were treated as surface partitioning (by surface area) or as bulk partitioning (by mass or volume).

Response:

a) Thanks for pointing out the method of using mass accommodation and reactive uptake coefficients. However, the solver that we use can process only

gas phase kinetics and has some limitations in expression of the detailed processes such as gas diffusion to a certain particle diameter. We have analyzed the characteristic time of each process before adding the absorption and desorption of a compound into the kinetic mechanisms (see the response to question #2 of reviewer 1) with the appropriate value.

b) In the supplementary material, we have added the following description to rationalize the use of absorptive model.

> "In order to confirm the nature (surface reaction vs. bulk phase reaction) of the reaction of DMSO, DMSO$_2$, and MSIA, the diffuso-reactive parameter, q is characterized using the following equation:
>
> $$q = a\sqrt{\frac{k_r}{D_l}}$$
>
> eq. S3
>
> where a is the particle radius (here assuming 50 nm), k_r is the aqueous phase reaction rate constant and D_l is diffusion coefficient. In general, a high q value indicates that the reaction occurs on the surface. For all three compounds, q is smaller than 0.003 suggesting that their reactions are slow compared to diffusion so that reactions take place throughout the entire volume of the aerosol. The characterization of q value also implies that the gas-particle partitioning can be approached by the absorptive mode."

Point 1

To better understand the impact of heterogeneous chemistry, the average percentage increase of MSA and H$_2$SO$_4$ concentrations in the DMS and DMSO experiments compared to a simulation with only gas phase chemistry should be provided in the abstract.

Response:

We have modified the abstract by inserting this sentence

> "The model predicted concentrations of MSA increase by 200% to 400% and those of sulfuric acid, by 50% to 200% within 120-minute simulation due to heterogeneous chemistry."

The whole abstract has been rewritten. Please see the response to question #1 of reviewer 2.

Point 2

The reference to the 1995 report of IPCC is too old and science on climate change has made great advances since then. What does the most recent IPCC report conclude about the climate relevance of DMS?

Response:
Please see the response to question #2 of reviewer 2.

Point 3
a) A further important complication when comparing results from kinetic models on DMS products with ambient measurements is the propagation of uncertainties of gas-phase reaction rate constants into the computed particle phase concentrations of H_2SO_4 and MSA (Karl et al., 2007). Karl, M., Gross, A., Leck, C., Pirjola, L., Intercomparison of dimethylsulfide oxidation mechanisms for the marine boundary layer: Gaseous and particulate sulfur constituents. J. Geophys. Res., 112, D15304, doi:10.1029/2006JD007914,2007.
b) The reaction of DMS with halogen atoms and halogen oxides should also be mentioned. The review by Barnes et al. (2006) also provides an excellent overview of these.
c) With respect to liquid phase reactions of DMS, the model study by Campolongo et al. (1999) should be cited. Campolongo, F., Saltelli, A., Jensen, N. R., Wilson, J., Hjorth, J., The role of multiphase chemistry in the oxidation of dimethylsulphide (DMS). A latitude dependent analysis. J. Atmos. Chem., 32, 327-356, 1999.
d) A literature survey of observed isoprene concentration over oceans should be made and the observed concentration range should be added when discussing the impact of isoprene on DMS chemistry. While the co-existence of DMS and isoprene is probably relevant over the remote oceans (low NO_x levels); it should be elaborated in which environments with high NO_x levels it could be relevant.

Response:
a) We agree with the reviewer for the possible uncertainties of the particle phase reactions due to the uncertainties in the gas phase reactions. We have included the following sentence in the beginning of description of the aerosol-phase reactions of DMSO in the introduction section.

> "Although different gas mechanims can cause different amount of predicted MSA and H_2SO_4 (Karl et al., 2007), the large discrepancy between observation and model results cannot be explained solely by the uncertainties in gas phase chemistry."

b) We have included the following sentence in the end of the introduction section.

> "Although halogen compounds are known to react fast with DMS (Barnes et al., 2006), in the coastal watersheds with human activities, OH radical

reactions with DMS and its products will be dominant, so in this study, reactions between halogen compounds and DMS are not included."

c) We have included the following sentence in the description of the importance of aerosol-phase reactions of DMS photooxidation products in the introduction section.
> "Campolongo et al. (1999) have found a better match between the measured MSA and the model prediction when the aqueous phase reactions of the DMS oxidaiton products are considered."

d) Please see the response to question #3b of reviewer 1.

Point 4
In section 2.1.1, does the chamber allow to control temperature and relative humidity in the experiments? More details on the chamber operation should be provided (temperature control, ventilation, replenishment of air, etc.)
Response:
Please find the responses to question #7a of reviewer 1.

Point 5
It is stated that the nucleation of MSA and H_2SO_4 produces an initial aerosol mass. The nucleation potential of MSA (binary homogenous nucleation with water molecules, ternary homogenous nucleation with H_2SO_4 and water) is less known and there exist only a few studies in literature. Please provide appropriate citation. Was a detailed model for nucleation of MSA and H_2SO_4 used?
Response:
Our model approach has focused on kinetic reaction mechanisms. The chemical solver used in our study cannot handle the nucleation of MSA and H_2SO_4. In this study, the infinite Henry constants have been assumed for both MSA and sulfuric acid (e.g. see works of von Glasow et al, Atmos. Chem. Phys., 4, 589--608, 2004). Thus, we assume all the MSA and sulfuric acid stay in the aerosol phase once formed.

Point 6

The concept of adsorption / desorption is used for partitioning of DMS products to aerosol particles. The partitioning coefficient Kp is defined according to Kamens et al. (1999). However, the concept of partitioning by Kamens et al. refers to absorption (expressed as forward process) and desorption (expressed as backward process) into (an organic) bulk phase. Later "Aerosol" is defined as the mass of MSA and H_2SO_4, which indicates that the kinetic model handled uptake as bulk phase partitioning. The definition of partitioning as adsorption /

desorption process makes only sense for partitioning to surfaces of e.g. soot particles or mineral dust particles, but not for liquid droplets. If it was intended to use only surface partitioning (physical adsorption and desorption), Kamens et al. (1999) is not the proper citation. Was the uptake of MSA and H_2SO_4 also treated as (reversible) partitioning to the aerosol?

Response:

We have made corresponding changes to the text. We treat the uptake of DMSO by aerosol as an absorption process. Please also refer to the Response to question #2b.

Both MSA and H_2SO_4 are treated as nonvolatile compounds.

Point 7

The rate coefficients k_{ad} and k_{des} were probably very specific to the chamber aerosol and the conditions in the chamber. How were the rate values estimated?

Response:

Please refer to the response to question #2 of reviewer 1.

Point 8

Are reactions (R7)-(R9) considered to be surface reactions or volume reactions? Oxidant (OH, O3 or other gas) is missing on the educt side of the reactions; consequently the reactions would also be gas-phase loss term of oxidants.

Response:

Based on our analysis of characterization time (see the response to question #2 or reviewer 1), the chemistry in the particle phase can be approached by the volume reactions. The production of OH radicals in the particle phase is complex due to photolysis of various products (ROOH, H_2O_2, HONO, and the gas-particle partitioning of OH radicals). In this study, we assume that the concentration of the particle phase OH radical is proportional to light intensity.

To respond to the reviewer, we have added the following paragraph:

> "The major oxidants in the aerosol phase reaction of DMSO, $DMSO_2$ and MSIA are OH radicals (Bardouki et al., 2002). The production of OH radicals in the particle phase is complex due to the photolysis of various OH radical precursors (ROOH, H_2O_2, and HONO) and the partitioning of gas phase OH radicals on the particle. Hence the production of OH radicals in the aerosol depends on light intensity. In this study, we assume that the concentration of the particle phase OH radical is proportional to light intensity. The rate constants ($^i k_r$) of the compounds in the particle phase reaction were empirically determined based on the estimated concentration of the compounds of interest (R7-R9) and experimentally observed concentrations of MSA and sulfuric acid. Based on the analysis

of the chemical flux using the integrated reaction rates in the model, the consumption of OH radicals through mechanisms R7~R9 are less than 3% of the total OH radicals in the system suggesting that consumption of OH radicals through aerosol-phase reactions is insignificant."

Point 9
Section 3.2.3:
 a) according to the kinetic model, which reaction of the DMS scheme was most relevant in terms of ozone production?
b) Note the discrepancies for the thermal decomposition of CH_3SO_3 in literature. A brief discussion of the published rate constant values should be added.
c) Thermal decomposition of CH_3SO_3 opens an additional pathway for producing H_2SO_4 via $SO_3 + H_2O$. According to the kinetic model, how much more H_2SO_4 was produced compared to the SO_2+OH reaction?
Response:
a) The main ozone production goes through the reaction of O_2 with $O(^3P)$ that originates from photolysis of NO_2. NO_2 comes from the reaction between NO and RO_2. Thus, the ozone reaction is the most related to the reaction between NO and sulfur-containing RO_2. As shown in the reactions below, the reaction between the CH_3-S-CH_2-OO. radical with NO is the most important reaction for ozone formation.

Reaction	Integrated reaction rate (IRR)
$CH_3(O)S(O)OO.+NO---->CH_3-SO_3.+NO_2$	0.77
$CH_3-S-CH_2-OO.+NO---->CH_3-S-CH_2O.+NO_2$	135.52
$CH_3-SOO.+NO---->CH_3-SO.+NO_2$	1.06
$CH_3-S(O)OO.+NO---->CH_3(O)S(O).+NO_2$	1.83

b) We have added the following sentence in section 3.2.3 (DMS photooxidation): "The reported reaction rate constant of the decomposition of the CH_3-SO_3. radical (reaction No. 46 in Table S1) spans between 0.004 and 51 s^{-1} (Campolongo, et al., 1999)."
c) We have compared the integrated reaction rates (IRR) of SO_2+OH and CH_3SO_3 decomposition reactions for several DMS photooxidation experiments. It was found that the SO_2+OH route is 0.2-0.4 of the CH_3SO_3 decomposition route indicating that both two routes are important under our chamber experiment conditions.

Point 10
Section 3.3.2: The increased formation of MSA (assuming particulate phase MSA) may be caused by the greater aerosol mass when SOA from isoprene oxidation is present. Was the mass concentration of isoprene-related SOA added to the

concentration of "Aerosol" (i.e. [Aerosol]) in the kinetic model? It should at least be tested with the model if increased MSA concentration can be explained by partitioning of MSA (produced by the gas phase chemistry) to an increased aerosol mass.

Response:

Isoprene SOA is not included in the kinetic model because there is no good model for the formation of isoprene SOA in the presence of acids yet. In our model, we assume that all the MSA produced by the pathway in the gas phase partitions to the aerosol. We have tested the gas-particle partitioning of MSA in the presence of inorganic seed. Our study showed that MSA is predominantly present in the aerosol.

Point 11

The contribution of the chamber experiments to the understanding of DMS gas phase chemistry in the atmosphere has not been pointed out in the conclusion. It is not clear whether the good match of the measurements of H_2SO_4 and MSA could also be achieved by adjustment of gas phase reaction rate constants, not considering heterogeneous reactions.

Response:

To respond to this comment, we have added the following sentences to the conclusion section:

"As shown in DMSO-1 in Figure 2 and DMSO-5 in Figure S3, the gap between the observed MSA concentrations and the predicted MSA concentrations using the gas phase kinetic mechanisms (without heterogeneous reactions) become larger as the MSA concentration increases. This observation evinces that the production of MSA depends on the available aerosol mass, which directly influences heterogeneous chemistry of both DMSO and its oxidation products such as $DMSO_2$ and MSIA. In addition to observations in DMSO experiments, the model using the kinetic mechanisms including heterogeneous chemistry on acidic aerosol comprising MSA and sulfuric acid, underpredicts MSA concentrations in the DMS-isoprene system. The underprediction of MSA appears to be greater when isoprene concentrations are higher. Such deviation is likely caused by the lack of the heterogeneous chemistry of DMS oxidation products on isoprene SOA, suggesting that gas-phase mechanisms alone cannot correctly predict the MSA concentrations produced from the DMS oxidation."

Point 12
a) The reaction of DMS with $O(^3P)$ is probably not relevant in the atmosphere.
b) If this is the main reaction that catalyzes the formation of MSA and H_2SO_4, how relevant is the effect of VOCs on DMS chemistry in the atmosphere?
Response:

a) We agree that this reaction is not so important in the ambient relevant conditions. Please see the Response to the response to question #15 of reviewer 1.

b) The effect of VOC on DMS chemistry in the ambient relevant concentration has been tested using the model in the revised manuscript.

> "Figure S9 illustrates the impact of the isoprene concentration on the yields of MSA and H_2SO_4 in the presence of 0.5 ppb of initial DMS. In the early stage, isoprene has a similar impact on the yields of MSA and H_2SO_4 as observed in high concentration experiments. As reactions progress, the yields of MSA and H_2SO_4 tend to decrease with the increase of initial isoprene concentration. Because isoprene competes with its oxidation products for atmospheric oxidants such as OH and NO_3 radicals, the reactions of $CH_3(O)S(O)\cdot$ with atmsoperhic oxidants become less important and the decomposition of $CH_3(O)S(O)\cdot$ (reaction No. 27) to SO_2 is more important. SO_2 yield has been confirmed thorugh the model simulation showing the significant increase with increasing isoprene concentrations. Since the reactions of $CH_3(O)S(O)\cdot$ with atmospheric oxidants are the main sources of MSA and H_2SO_4, the yields of both MSA and H_2SO_4 decreases in the later stage of experiments with the high concentration of isoprene."

Point 13
The potential formation of organosulfates from isoprene SOA should be discussed (e.g. Surratt et al., 2007a; b). If organosulfates would form by reaction of isoprene oxidation products in the sulfate aerosol, a higher fraction of MSA and H_2SO_4 would partition to the aerosol. As in point 7, the apparently higher yields of MSA and H2SO4 would be due to increased partitioning to the aerosol and not due to accelerated DMS photo-oxidation.
Surratt, J. D., Kroll, J. H., Kleindienst, T. E., Edney, E. O., Claeys, M., Sorooshian, A., Ng, N. L., Offenberg, J. H., Lewandowski, M., Jaoui, M., Flagan, R. C., and Seinfeld, J. H.: Evidence for organosulfates in secondary organic aerosol, Environ. Sci. Technol., 41, 517–527, 2007a.
Surratt, J. D., Lewandowski, M., Offenberg, J. H., Jaoui, M., Kleindienst, T. E., Edney, E. O., and Seinfeld, J. H.: Effect of acidity on secondary organic aerosol formation from isoprene, Environ. Sci. Technol., 41, 5363–5369, 2007b.
Response:
The finding of organosulfate is important but not relevant to the study here. Both MSA and sulfuric acid are predominantly present in the aerosol phase, so the partitioning process of these acids does not affect the production of MSA and sulfuric acid.

Point 14

Did the kinetic model consider any cross-reactions between the isoprene and DMS chemistry mechanisms? Recently, stabilized Criegee Intermediates such as $CH_2OO\cdot$ were found to oxidize SO_2 rapidly (Jiang et al., 2010).

Jiang, L., Xu, Y., and Ding, A.: Reaction of Stabilized Criegee Intermediates from Ozonolysis of Limonene with Sulfur Dioxide: Ab Initio and DFT Study J. Phys. Chem., A 114, 12452-12461, 2010.
Response:
Please refer to the response to question 4 of reviewer 1.

Comments on text and tables
1. **P.14670, abstract and P.14671, line 8**
   Replace "predictability" by "predictive capability".
   Response:
   This has been replaced.

2. **P.14671, line 25**
   Replace "missing aerosol-phase reactions" by "missing heterogeneous reactions".
   Response:
   Done.

3. **P.14672, line 11**
   The statement "However, kinetic studies of the impact of coexisting VOCs and DMS chemistry are inadequate" needs to be explained better and a reference should be added.
   Response:
   There is no more reference on this statement.
   We have changed the sentence and it reads now:
   > "However, no further kinetic studies of the impact of coexisting VOCs on DMS chemistry has been conducted."

4. **P.14671, P. 14674**
   Full names of compounds should be given at first appearance in the text: DMSO, H_2SO_4, $DMSO_2$.
   Response:
   This has been fixed.

5. **P.14676, line 5**
   Define "Aerosol" by using an equation of the form: [Aerosol] = [MSA] +[H2SO4] + …
   Where squared brackets denote concentration.
   Response:
   Done.

6. **P.14672, line 15**
   Replace "surface of aerosol" by "surface of aerosol particles".
   Response:
   The definition of aerosol is the particles that suspend in the air, so it is not necessary to add "particles" after "aerosol".

7. **P.14672, line 22**
   A table listing the DMS related reactions for which adjustments were done based on the experimental observations (described in section 3.2.3) should be added to the manuscript.
   Response:
   The reactions adjusted in this study have been marked in Table S2.

8. **P.14674, line 7**
   Replace "Acetonitrile" by "acetonitrile".
   Response:
   Done.

9. **P.14678, line 21**
   Replace "DMS model" by "DMS chemistry scheme".
   Response:
   This has been replaced.

10. **P. 14681, line 11**
    A mathematical equation expressing the integrated reaction rate should be provided here, together with appropriate reference.
    Response:
    IRR value is numerically calculated.   It has been used in different models, e.g., CMAQ.

11. **P.14681, line 28**
    The sentence "The MSA and H2SO4 produced…" is not clear. Please rephrase.
    Response:
    This sentence has been changed and it now reads.

    > "MSA and H_2SO_4 produced through the gas phase mechanisms provide additional aerosol mass and consequently increase the MSA formation in the aerosol phase through the heterogeneous reactions of DMS oxidation products."

12. **P. 14688, table 1 and P. 14689, table 2**
    Provide standard deviations of temperature and relative humidity.
    Response:
    "Accuracy of RH: ±2%; accuracy of temperature: ±0.5°C."

13. **P.14692, figure 2**
    Add in figure capture whether MSA and H_2SO_4 is gas-phase, particulate phase, or total concentration. The same should be done in figure captures of figures 3-5.
    Response:
    Please see the response to point 5.

14. **Supplement, table S1**
    The rate constant for reaction 1 (1.50E+07) is wrong, certainly a typo. The rate constant of $CH_3S(O)CH_3 + O^3P$ is 8.8E-12 at 298 K, according to JPL publication 10-6 (Sander et al., 2011).
    Response:
    This is a typo and has been fixed.