Authors' Response to Comments

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Review of: SO2 photolysis as a source for sulfur mass-independent isotope signatures in stratospheric aerosols by Whitehill, Jiang, Guo and Ono

This paper describes a series of experiments into the S-MIF pattern produced by SO2 photochemistry, with emphasis on photolysis. It is asserted that SO2 photolysis is responsible for the S-MIF signal observed in some volcanic sulfate in polar ice cores because some of the SO photoproduct combines with O2 in the atmosphere in a three body reaction to form SO3 which reacts with H2O to produce H2SO4. The rate of this reaction is poorly constrained (the only evidence is one determination in the literature of an upper limit) and an effort is made to estimate it's rate. Stationary points on the SO3 potential energy surface are investigated using quantum chemistry, and a chemical box model is used to interpret the experimental results. The paper describes a well-designed set of experiments and painstaking isotopic analysis. There is a lot of interesting material here that makes it a pleasure to read and a valuable addition to the field. I have a few concerns detailed below that should be addressed prior to publication.

Scientific comments

The Introduction is very well written and gives a readable review of current understanding in the field. In 23501, 23 (page, line) it is stated that the experimentally measured

1% KIE for 34SO2 reaction with OH relative to 32SO2 is incompatible with Castleman's measurement of 1974. First, note that this is a single measurement 40 years ago, good work but it includes some uncertainty. More importantly, the experimental measurement was done in the range of -20 to +40 C and does not include the temperature at which the SO2 + OH oxidation took place high in the atmosphere. One must extrapolate the measured KIEs outside the range of the study without a reason to think the temperature dependence of the KIE would be linear. Overall, given these issues, it is speculative to say the experiment and the field measurement do not agree. Suggest more cautious language - perhaps there is an indication, but nothing as clear cut as the text appears to claim.

Changed to more cautious wording.

There must be some water in the photoreactor, in order to convert SO3 into H2SO4. There is always some water on anything that has been open to the atmosphere, including anything that has not been pumped out under high vacuum for many days. How much water? Was OH produced via water photolysis or O(1D) plus H2O?

Added section discussing water and added HO_x chemistry to photochemical model

23500, 27, why 'requires a high SO2 column density'? Not clearly argued in the text. Please discuss how 'requires' is meant - does this mean a large amount of SO2 between the place where SO2 is photolysed and the sun, in order to ensure self-shielding? Or, simply that there is enough SO2 present in a plume to ensure a signal?

Changed to be more specific

23500, 27, why 'an SO2 plume reaching an altitude of 25 km or higher'? This limit seems somewhat arbitrary. According to Figure 8, 20 km should be sufficient. Including uncertainties, could it not simply say, 'above the tropopause'?

Changed to "around 20 to 25 km". The exact altitude depends on atmospheric conditions and requires modeling beyond the scope of the present paper.

For example at 23514, 12. Isotope selective intersystem crossing due to an accidental near degeneracy is a plausible theory with some evidence to back it up. It is an advance to the field. However, it will act at the same time as other mechanisms including selfshielding and the rate of photoabsorption (isotopologue-dependent cross section), not instead of them. The overall effect will be a combination of the basic mechanisms.

Clarified this section to make it clear that optical isotope effects (i.e. cross-section differences and self-shielding) are also present. Optical isotope effects are definitely important in both absorption regions, but (as shown in Whitehill et al. 2013) cannot explain the entirety of the mass-independent isotope effect in the 250 to 350 nm region.

Section 4.2. The 'Ran-Lyon' model uses isotope-dependent vibrational frequencies to derive shifts, and the isotopologue-dependent absorption cross sections are obtained as shifted versions of the 32SO2 absorption cross section. This approach does not take into account changes in the Franck-Condon factors observed by Danielache et al., or changes in the rotational constants/rotational fine structure. This is important when calculating self-shielding. The agreement with experiment is fine, but keep in mind there is more to the story and the model may have gotten the right answer for the

wrong reasons.

Reworded this section to make it clear that the "Ran-Lyons" model is not accurate. However, it produces reasonable results comparable with experimental data (under some conditions) and thus provide a useful tool until better cross-sections at appropriate temperatures are available.

The model and the discussion do not consider HOx chemistry, and they do not consider photochemistry of the reduced sulfur compounds. Polysulfur product is extracted and analyzed, and so some additional reactions must take place: S + S2 + M –> S3 + M; oxidation of reduced sulfur, photolysis of polysulfur species, etc. Any of them could reasonably give S-MIF in analogy to the oxygen reactions (for example ozone formation, ozone photolysis, etc.).

Added HOx chemistry and polysulfur chemistry (up through S_2) to the kinetic model.

Although we have no constraints on water within the system, HOx chemistry does not cause a major difference in the results at reasonable estimates of water (< 100 ppm). Addition of more water increases the estimated rate constant, so it is consistent with our attempts to find a lower bound on the rate.

Under the conditions tested here (5% - 20% oxygen in nitrogen), the model predicts that S and S_2 will be insignificant species, with steady state concentrations of ~100 molecules cm^3 (for S) and ~10^{-8} molecules cm^3 (for S_2). Therefore, reaction between S and S_2 will not be significant in the presence of oxygen. This is consistent with the lack of elemental sulfur products recovered in all experiments performed in the presence of O_2.

In Figure 6, for the no oxygen case, why don't the sulfate and the elemental sulfur show mass balance of the isotopes, equal and opposite D33S? If SO2 photolysis is the source of both S_n (polysulfur) and sulfate, why don't they have the same D33S?

The mass-balance is satisfied by the residual SO_2, which probably carries a negative D33S value. In these open system experiments, in the absence of oxygen, both S_n and sulfate carry positive D33S values. This is consistent with previous experiments in the literature (e.g. Ono et al. 2013 shows both sulfate and elemental sulfur with positive D33S values). They do not have the same D33S values because, in the absence of O_2, most of the sulfate comes from $SO_2 + O$ or $SO_2 + OH$ reactions rather than SO_2 photolysis, as discussed in Section 4.3.

Is equation (7) for the spectral iradiance of the lamp independent of the distance from the lamp? What is the uncertainty in this empirical equation?

The distance between the cell and the lamp has a minor effect on the spectral irradiance of the lamp due to the absorption of oxygen (and some ozone). A brief section is added acknowledging this. Previous studies (Whitehill and Ono 2012) using a similar lamp tested the effects and found that they are important below about 195 nm, but relatively insignificant (in terms of total SO_2 photolysis rates) at long wavelengths.

Unfortunately, the empirical expression is fit from the manufacturer's data and the uncertainty in the measurement is not available. We guess that it is sufficient to estimate the SO_2 photolysis rate to within an order of magnitude or better, but it is impossible to know without measuring it. Uncertainty in the lamp is discussed in Section 4.3 (although a quantitative estimate is not given).

23522, 7, Tunneling of oxygen and/or sulfur should not have any effect at all on the rates of these reactions. Please omit this throw-away explanation.

We omitted this explanation.

23522, 27, on the fly transition state hopping calculations would ('in theory') be able to derive rate constants without the need for global PESs.

Added a sentence acknowledging the potential of on the fly transition state hopping calculations. Performing such calculations is beyond the scope of this paper.

Section 4.6. First: Three body reactions get faster as temperature decreases. What is the temperature dependence of R6? Second: The discussion in this section ignores the potential role of photoexcitation – the light flux in the photoexcitation range is much larger than in the photodissociation range. Please include and discuss.

The temperature dependence of R6 is beyond the scope of the present work. Added a paragraph in Section 4.7 addressing possible contributions of photoexcitation to the isotope signatures.

23525, 20, Since the Lyons results are do not give accurate high resolution rovibronic structure, how can they give an accurate prediction of self-shielding? The rotational fine structure is very important for self-shielding.

Removed statement that Lyons results predict results accurately.

23526, section 4.7, given the actinic flux spectrum and the SO2 absorption spectrum, it is beyond doubt that photoexcitation will take place. This process very likely has an

isotopic signature. What is there to say that photoexcitation and photodissociation do not occur simultaneously?

Section 4.7 attempts to argue that SO_2photoexcitation alone is not responsible for the anomalous isotope effects and that SO_2 photolysis is important as well. Added a paragraph acknowledging the possible contributions from photoexcitation.

In Table 2, why is there such a large difference between the values obtained in the first and second experiment at each temperature? In each case there is a significant drop in d33S, d34S, d36S. Please discuss. Could S chemistry play a role?

We added a section (Section 4.8 in the revised manuscript) that addresses caveats with the experimental studies and discusses possible sources of variability between duplicate experiments.

Table 3, do the organosulfur product enrichments match the predictions of Danielache et al.?

The results from Table 3 (at lower temperature) cannot be directly compared to the room-temperature measurements of Danielache et al. (2012). Room-temperature experiments under similar conditions are compared to room-temperature cross-sections in a previous publication (Whitehill et al. 2013).

Table 4, it is suspicious that there is a negative trend in k(R6) as the oxygen pressure increases. The model includes O2 pressure and Ox chemistry, so in theory, this trend should not be here. Why is the result so dependent on pO2?

k(R6) results in Table 4 come from the rate estimates in Section 4.3, so they do not explicitly include Ox chemistry. They include only total product formation rate and estimated fraction of product formation from R6 (based on D33S values). In our opinion, the values calculated for pO_2 = 5, 10, 15 kPa are all similar (~1e-37), and it is only at 19.8 kPa that a decrease is observed. This behavior could be due to H_2O limitation on sulfate aerosol formation at higher SO_3 formation rates (i.e. higher O_2 pressures), but this is purely speculative.

Table 5, why are the two runs with each filter (200BP, 250LP) so different in terms of delta values? Please explain.

The two 200BP experiments were performed at very different conditions (300 kPa SO_2 versus 50 kPa SO_2) and that likely explains the discrepancy. The two 250 LP experiments are performed under identical conditions, and yet yields are different by an order of magnitude and isotopic composition is different by a factor of 2. The photoexcitation experiments are challenging and have a very low sulfate formation rate. Additional experiments should be performed to clarify the results from photoexcitation experiments, but is beyond the scope of the present paper.

Table 6. The quantum chemistry results are used to make qualitative arguments and the level of calculations does seem adequate to this task. However, as seen here and in tables 7 and 8, the energies obtained using the different methods are very different. How should we know which one to believe, and is there any way to know that the ultimate method used in this paper is adequate to the task? What are the error bars on the resulting values?

It is true that the energies obtained using different methods are different, implying the difficulties dealing with this challenging system by ab-initio calculations. Among those ab-initio methods used in this work, UCCSD(T) energies should be the most trustworthy based on comparison with asymptotic values and thermodynamic data in Section 3.3.Given the

multi-reference feature and non-adiabatic coupling involved in multiple electronic states of SO_3, however, an ultimately definitive evaluation of the reaction profile would need further higher level treatment which is beyond the scope of this paper.

Table 9, I do not see sulfate formation. How much water is there? What are the concentrations of the HOx radicals?

The model was modified to include HOx chemistry. We found that inclusion of H_2SO_4aerosol formation significantly underestimated total product formation for reasonable values of H_2O, thus suggesting that condensation of SO_3 on the walls of the cell or other aerosol particles might be an important process. Modelling this is beyond the scope of the present paper. Therefore, we focused on the rate of SO_3 formation from different pathways.

Figure 1. Very nice straight line. Does this need to be included, and as Figure 1?

Inclusion of temperature calibration is important for demonstrating that our experiments are robust and that we are testing what we claim to be testing.

Perhaps it could be put in a supplementary infromation file, or better yet, left out. The equation and a short description are all that is needed.

Figure 3, very nice result.

Figure 7, left. The model always predicts increased f_R6 as O2 is increased, yet this is not observed in the experiments. Do you have an explanation? Why should we have believe the model and the resulting rate? The rate is not determined directly, but indirectly, via the model. This introduces many uncertainties (J value, completeness of model), and this difference is yet another indication that the model is not right. (The first, as noted above, was that the value of k varies with the oxygen content).

Our revised model also predicts increased f_R6 values as O_2 is increased, but the effect is smaller than in the original model due to the inclusion of additional chemical reactions. The behavior is quantitatively consistent with our results except for the highest $\%O_2$ value (19.5%). As discussed above, it is unclear why the discrepancy for this value.

Technical comments 23500, 9, add colon: 'the two absorption band systems of SO2: photolysis..andphotoexcitation..'

Changed

23504, 11, better to write 'transmittance at wavelengths longer than 190 nm'. It is not clear if 'above' refers to energy, wavelength, wavenumber, frequency, etc.

Changed

23505, 24, I don't see the need for introducing the nonstandard abbreviation 'DCM' for dichloromethane (by the way, the abbreviation is defined twice in the text). It is used so few times, only on pages 4 and 5, so that if you really must shorten it, why not write CH2Cl2?

Changed to dichloromethane

23509, 19, it is too strict to write '=0'.

There is a range of values that would be considered mass-dependent. Suggest either

'approximately equal' or to give the range.

Changed to "approximately equal". Exact values are subject to controversy.

23512, 22, this sentence does not use a parallel construction as the first have is an expectation and the second half a seeming statement of face. Should the second part rather be, 'but are not expected to reproduce'?

Sentence was removed.

23514, 20, there's not a clear dividing line between chemistry and physics, so it's not clear what is meant here in making a distinction between photochemistry and photophysics. Please rewrite using different terminology.

Changed

23514, 25, it is not clear what is meant by 'overprinting'. See comment above under scientific comments,

Changed to clarify what is meant

23514, 12.
23529, 5, the rate given here does not agree with the range of values given in the abstract, please be consistent.

Changed from rate to order of magnitude estimate and changed manuscript so that it is

consistent throughout.

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This manuscript is a new, important and a convincing piece made by the Ono's group regarding the source and origin of the S-MIF in modern sulfate aerosols. After working on the topic for years, the authors reached an impressive mastering of the SO2 photolysis experiments and their related MIF effects. The paper is really well written exhaustive covering experimental data, molecular dynamic, kinetic chemistry and atmospheric applications. Thus I highly recommend the publication in ACP. This is probably the most accomplished work on the subject, applicable to the present atmosphere. While not yet in direct link with the Archean atmosphere, it is definitely a significant step toward that direction. The present results will certainly help to constrain the structure and composition of the Archean atmosphere, which is currently our main unknown the completely understand the Archean data. Nevertheless, I still want to emphasis that this study should not be considered as the final answer to the issue and more photolysis experiments will be needed to have a complete picture on the topic.

We agree that this study is not the final answer. We hope that this study motivates additional research into this issue.

I have only few minor comments and questions before the paper can be published in acp. Note that molecular dynamic is not my field of expertise and thus I did not critically review this part of the paper and thus unable to judge the quality of the work and the limitation of

the interpretation of the calculations, even if the models used are pretty standard in the field.

1/ recently Gautier et al. showed at Golsdschmidt2014 a new set of ice core data. Reporting the data in a _33S vs_36S plot, the slope obtained is more around -1.9 than -4 as claimed by the author. Can the author comment on that? can the slope of -2 been a mixture of photodissociation and photoexcitation or the result of wavelength dependency effect?

Added a paragraph to Section 4.7 addressing the possible causes of the discrepancy in D36S/D33S and discussing the possibility that photoexcitation might contribute to the isotope signature.

2/Is the data obtained from the full spectra of the Xe lamp (positive _33S negative _36S) consistent with XS and spectral flux of the lamp?

Comparisons of full spectral Xe photolysis data with cross-sections has been performed previously (Whitehill and Ono 2012, Ono et al. 2013). We added a discussion of the cross sections in Section 4.8 of the revised manuscript.

3/ Is there any explanation for the large difference observed between replicated experiments? Large variations are observed for same experimental conditions.

Added a section (Section 4.8) which discusses caveats with the experimental studies. We do not have a satisfactory explanation for the observed differences between replicated experiments except for experimental uncertainties. We hypothesize that it could be due to differences in the trace amounts of water vapor within the system affecting the chemistry in

the cell.

4/ Xe or D2 are significantly different than the solar spectra. How this can impact the obtained results and comparison with ice core data?

Added a section (Section 4.8 in revisedmanuscript)where we discuss differences between Xe and D_2 spectra and the solar spectrum.

5/ Why quenching of O1D is assumed to be instantaneous? Quenching is known for O2 and N2 and should have been easy to implement in the model or to check the validity of the assumption

The model is modified to explicitly model include $O(^1D)$ chemistry, as well as additional reactions.

6/ is it possible than the high barrier encountered for the TS4 on the singlet PES be lowered by heterogeneous chemistry? can this be explored by the molecular dynamic calculation?

Heterogeneous chemistry could be important but is beyond the scope of the present paper.

7/ Why the authors have not used the TUV model for the calculation of photolysis rates in the atmosphere (http://cprm.acd.ucar.edu/Models/TUV/)? This model has became a standard tool in atmospheric photochemistry

Calculations were performed in a very simplified manner using a simple radiative transfer

model. The purpose of the model is a first-order estimate of the importance of the proposed reaction. It is our hope that future modeling studies can

8/ Wording about the SO2 self-limiting effect is ambiguous as it is always the case for any absorbing molecules which by essence limit the radiation for further absorption by the same molecule. I guess they want to say here that taking into account the high concentration of SO2, self-shielding can dominate over shielding by other molecules (eg O3)

It is correct that a self-limiting effect due to shielding is important for all molecules. However, the isotope effect also depends strongly on shielding by SO_2 (and possibly other molecules), as demonstrated by Ono et al. (2013). More modeling is necessary to determine the effect of shielding by ozone and O_2 on the SO_2 absorption in this region.

9/ I'm not convinced that self-shieling will decrease the significance of R6 with respect to OH oxidation pathway as OH will also be impacted by the shielding effect but most importantly by the buffering effect (i.e. titration of OH by SO2)

SO2 oxidation by OH is catalytic, i.e. it does not consume HOx. Models vary as to the significance of SO2 loading on HOx and OH chemistry. It will also depend upon a number of other factors, such as the vertical profile of SO2 and HOx species. Such modeling is beyond the scope of the present paper.

10/The author should add a table displaying the instantaneous fractionation factors. This fundamental for future atmospheric modeling and easy to extract.

Exact fractionation factors will vary with temperature and SO_2 column density, as well as

other atmospheric conditions (i.e. ozone concentrations, altitude, etc.). For this reason, exact fractionation factors are not given and should be derived from more advanced modeling studies. Attempts to provide instantaneous fractionation factors without knowing the exact position in the atmosphere and atmospheric conditions would be misleading.

minor remarks

SO2 and even more O or SO are pretty aggressive compounds. Was there thermocouples protected from oxidation? Can they have reacted with the sulfur compounds?

Thermocouples were only used to calibrate the cell with pure N_2. We assumed the calibration with pure N_2 is similar to the calibration with a small amount of added SO_2. This is discussed in Section 2.1.

Why the setup for photodissociation and phototexcitation are different, in particular the SO2 partial pressure (0.1 kPavs 1 kPa) or quartz window vs a water IR filter, making the comparison between experiments more difficult.

The setup for different experiments are different to maximize product formation and minimize the effect of the light source on the internal temperature of the cell. The D_2 lamp has a higher flux in the 190 – 220 nm region (where SO_2 photolysis occurs) and not much infrared radiation. For SO_2photoexcitation, a Xe lamp is used due to the higher flux at longer wavelengths. Because the Xe lamp has a high infrared radiation flux, a water filter was used to absorb the infrared radiation and prevent it from heating the cell. The water filter was not used for photolysis experiments because the windows of the cell absorb significantly below 220 nm. Different SO_2 partial pressures are used due to the different cross-section amplitudes of the two absorption bands. SO_2photoexcitation is an order of magnitude stronger (i.e. higher absorption cross-section) than SO_2photoexcitation.

Can the spectra of the D2 be given?

The spectral structure of the D_2 lamp is estimated in Whitehill and Ono (2012). The D2 lamp used here should have a similar spectral structure but a stronger irradiance (due to it being 200 W versus 30 W).

Can the shorter wavelengths open another exit channel?

The glass used for the cell windows (Corning 7980) absorbs significantly below around 180 nm to 200 nm, preventing chemistry from the higher energy dissociation band (< 165 nm) of SO_2 from occurring under our experimental conditions. In addition, in experiments performed in room air (versus a nitrogen atmosphere), air absorbs almost all the radiation below around 195 nm. This is discussed in Whitehill and Ono (2012).

Do the author have any idea of the humidity present in the cell/flowing gases and thus have an idea of the lifetime of SO3 to check if their assumption of collecting 100% of SO3 makes sense?

We do not have constraints on the amount of water within the cell. However, the kinetic model of the cell chemistry is modified to include HOx chemistry and an estimate of the amount of water in the cell is made. Attempts to constrain the amount of SO_3 formation based purely on the $SO_3 + 2H_2O$ reaction produce unreasonably small product formation rates, suggesting additional processes (i.e. heterogeneous processes or wall absorption processes) must be trapping SO_3 in the system.

Can the authors give the lamp and filters used in caption tables?

Table 1 summarizes the lamps and filters used in the various experiments for the rest of the

tables.

Many times eq(5) cited in the text actually corresponds to eq(4).

This was an error in the conversion from Word to Latex. This will be corrected in the final version.

Table 4: column 4 yield/umol S, technically this is not a yield but an amount

(Absolute) yield is the amount of product obtained in a chemical reaction (in grams or moles), which is what is reported. Therefore, we believe that yield has been used correctly in this case.

Why in figure 3, the LP experiments show a small MIF when table 3 displays a large effect for the photoexcitation?

In the experiments reported in Table 3, 100% of the product comes from $^3SO_2$, so the isotope signature is not diluted. In the results displayed in Figure 3, most of the SO_3 likely comes from the $^3SO_2+SO_2 \rightarrow SO_3+SO$ reaction, which produces mass-dependent SO_3 (see Whitehill and Ono 2012). A small amount of the SO_3 comes from a mass-dependent channel, such as $^3SO_2 + O_2 \rightarrow SO_3 + O$ (Hattori et al. 2013) or $SO + O_2 + M \rightarrow SO_3 + M$ (with SO from $^3SO_2 + SO_2$ reaction). Therefore, the product sulfate from the photoexcitation experiments in Figure 3 are diluted by a significant amount of mass-dependent sulfate.

SO_2 photolysis as a source for sulfur mass-independent isotope signatures in stratospheric aerosols

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Abstract

Signatures of sulfur isotope mass-independentfractionation(S-MIF) have been observed in stratospheric sulfate aerosols deposited in polar ice. The S-MIF signatures are thought to be associated with stratospheric photochemistry following stratospheric volcanic eruptions, but the exact mechanism responsible for the production and preservation of these signatures is debated.In order to identify the origin and the mechanism of preservation for these signatures, a series of laboratory photochemical experiments were carried out to investigate the effect of temperature and added O_2 on S-MIF produced by the two absorption band systems of SO_2: photolysis in the 190 nm to 220 nm region and photoexcitation in the 250 nm to 350 nm region. The SO_2 photolysis ($SO_2+h\nu \rightarrow SO + O$) experiments showed S-MIF signals with large $^{34}S/^{32}S$ fractionation, which increases with decreasing temperature. The overall S-MIF pattern observed for photolysis experiments, includinghigh $^{34}S/^{32}S$ fractionations,positive mass-independent anomalies in ^{33}S, and negative anomalies in ^{36}S,is consistent with a major contribution from optical isotopologue screening effects and ~~measurements~~ data for stratospheric sulfate aerosols. In contrast, SO_2photoexicitation produced products with positive MIF anomalies in both ^{33}S and ^{36}S that is different from stratospheric aerosols. SO_2 photolysis in the presence of O_2produced SO_3 with S-MIF signals, suggesting the transfer of the MIF signals of SO to SO_3 by the $SO + O_2 + M \rightarrow SO_3 + M$ reaction. This is supported with energy calculations of stationary points on the SO_3 potential energy surfaces,

whichindicate that this reaction occurs slowly on a single adiabatic surface, but that it can occur more rapidly through intersystem crossing. Based on our experimental results, we estimate a termolecular rate constant on the order of 10^{-37} cm^6 $molecule^{-2}$ s^{-1}. ~~The results from our experiments constrain the termolecular reaction rate to between 1.0×10^{-37} cm^6 $molecule^{-2}$ s^{-1} and 1.0×10^{-36} cm^6 $molecule^{-2}$ s^{-1}.~~ This rate can explainthe preservation of mass independent isotope signatures in stratospheric sulfate aerosols and providesa minor, but important, oxidation pathway for stratospheric SO_2~~above about 25 km altitude~~. The production and preservation of S-MIF signals in the stratosphere requires a high SO_2 column density to allow for optical isotopologue screening effects to occur and to generate a large enough signature that it can be preserved. In addition, the ~~andan~~ SO_2 plume must reach an altitude of around 20 to 25 km, where SO_2 photolysis becomes a dominant process~~reaching an altitude of 25 km and higher~~.These experiments are the first step towards understanding the origin of the sulfur isotope anomalies in stratospheric sulfate aerosols.

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1 Introduction

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Explosive volcanic eruptions that inject sulfur dioxide (SO_2) into the stratosphere can cause perturbations to the stratospheric sulfur cycle for years following eruptions. The increase in stratospheric sulfate aerosols associated with injections of SO_2 result in stratospheric warming and tropospheric cooling, and can also trigger changes in atmospheric circulation and increases in ozone depletion (Robock, 2000). Perturbations to the stratospheric sulfur cycle following large volcanic eruptions are recorded as changes in sulfur isotope ratios, as measured in stratospheric sulfate aerosol samples (Castleman et al., 1974), as well as in ice core records (Savarino et al., 2003;Baroni et al., 2007).

The reaction with OH is the dominant oxidation pathway for SO_2 in the stratosphere:

$$SO_2 + OH + M \rightarrow HOSO_2 + M \quad \text{(R1)}$$

This reaction is followed by:

$$HOSO_2 + O_2 \rightarrow SO_3 + HO_2 \quad \text{(R2)}$$

In the presence of H_2O, SO_3 readily forms sulfuric acid (H_2SO_4) via:

$$SO_3 + H_2O \rightarrow H_2SO_4 \quad \text{(R3)}$$

Ab-initio transition state theory calculations of the isotope effect forOH oxidation (R1) predict that $^{34}SO_2$ is oxidized 0.9% slower than $^{32}SO_2$ (Tanaka et al., 1994), although calculations with RRKM theory predicts aninverse isotope effect, in which $^{34}SO_2$ reacts 12% to 15% faster than $^{32}SO_2$ (Leung et al., 2001). Experimental studies of OH oxidation (R1)showed in an inverse isotope effect, but with a smaller magnitude, with$^{34}SO_2$ reacting about 1% faster than $^{32}SO_2$ (Harris et al., 2012). Although the~~The~~ experimentally measured isotope effect ~~is in~~might be sufficient to explain the roughly 2% enrichment in $H_2{}^{34}SO_4$ relative to $H_2{}^{32}SO_4$ following the major Mt. Agung (1963) eruption (Castleman et al., 1974), the large observed isotope effect suggests the possibility of an additional oxidation reaction with larger ^{34}S fractionations.

~~An additional oxidation reaction is necessary to explain the sulfur isotope effects in stratospheric sulfate aerosols following large volcanic eruptions.~~

An additional unexplained observation is the isotope anomalies in $^{33}S/^{32}S$ and $^{36}S/^{32}S$ ratios relative to $^{34}S/^{32}S$ ratios. These signatures of mass-independent fractionation(MIF) have been observed in ice cores associated with large volcanic eruptions (Savarino et al., 2003; Baroni et al., 2007, 2008; Lanciki, 2010; Lanciki et al., 2012). Ice core sulfate peaks are commonly used to reconstruct the impact of past volcanic activity, which is critical to forcing climate models (Robock, 2000). For several years following large injections of SO_2 into the stratosphere, stratosphere-derived sulfate can dominate sulfate deposition in ice cores and, when~~if~~ corrected for background levels, can preserve the sulfur isotopic composition of stratospheric sulfate aerosols. Experimental studies demonstrate that OH oxidation of SO_2 (R1) does not produce mass-independent sulfur isotope anomalies (Harris et al., 2012, 2013), so an additional oxidation mechanism is required to produce the mass-independent sulfur isotope signatures. Three reactions have been proposed to explain these isotope anomalies: excited-state photochemistry of SO_2 in the 250 nm to 350 nm absorption region (Savarino et al., 2003; Hattori et al., 2013), SO_2 photolysis in the 190 nm to 220 nm absorption region (Ono et al., 2013), and SO_3 photolysis (Pavlov et al., 2005).

We present results of laboratory photochemical experiments that support SO_2 photolysis as the main source for the MIF signatures observed in stratospheric sulfate aerosols following some large (stratospheric) volcanic eruptions. In particular, SO_2 photolysis produces large MIF anomalies, as well as large mass-dependent isotope fractionations (Masterson et al., 2011; Whitehill and Ono, 2012; Ono et al., 2013) that are consistent with

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the isotopic signatures observed in stratospheric sulfate aerosols in ice cores (Ono et al., 2013). ~~Even a minor contribution of SO_2 photolysis to the production of sulfate aerosols can have a major influence on the isotope ratios of sulfur.~~

Photolysis of SO_2 occurs above around 20 to 25 km in the wavelength region of 190 nm to 220 nm, which lies in the spectral window between the Schumann-Runge absorption edge of oxygen (O_2) and the Hartley bands of ozone (O_3). SO_2 photolysis produces sulfur monoxide (SO) and $O(^3P)$ via the following reaction:

$$SO_2 + h\nu \rightarrow SO + O(^3P) \quad \text{(R4)}$$

It is generally accepted that this reaction is followed by rapid oxidation of SO to SO_2 via (Black et al., 1982; Savarino et al., 2003; Pavlov et al., 2005):

$$SO + O_2 \rightarrow SO_2 + O(^3P) \quad \text{(R5)}$$

Reactions R4 and R5 combine to form a null cycle for sulfur, but catalyze the formation of odd oxygen (Bekki, 1995). If SOis completely oxidized to SO_2, no isotopic signature from SO_2 photolysis can be preserved (Pavlov et al., 2005).

We propose an additional channel where SO is oxidized directly to SO_3 via the termolecular reaction:

$$SO + O_2 + M \rightarrow SO_3 + M \quad \text{(R6)}$$

A previous study by Black et al. (1982) showed that the maximum termolecular rate constant forreaction R6 is 10^{-36} cm^6 $molecule^{-2}$ s^{-1}. This rate is considered too slow to play an important role for stratospheric chemistry (Black et al., 1982). However, given the large isotope effects produced during SO_2 photolysis, even a minor contribution from R6 will produce a significant signal on the sulfur isotopic composition of stratospheric sulfate aerosols.

We present results from laboratory photochemical experiments that investigate the effect of temperature and molecular oxygen on the isotope effects produced during SO_2 photolysis (190 nm to 220 nm) and SO_2photoexcitation (250 nm to 350 nm). Using the results of the experiments in the presence of molecular oxygen, we calculate a lower bound estimate on the rate of R6. In addition, our proposal is further supported by ab-initio calculations of stationary points along the potential energy surfaces (PESs) for the SO oxidation reactions (R5 and R6). Finally, we presenta simple steady state photochemical model to show that the

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rate constraints on reaction R6 are sufficient for it to make a significant contribution to the isotopic signature of stratospheric sulfate aerosols during volcanically perturbed periods.

2 Methods

2.1 Photochemical reaction set-up

Conditions for all photochemical experiments are listed in Table 1. All experiments were performed in a cylindrical glass photochemical reaction cell with a pathlength of 15.3 cm and an inner diameter of 5.2 cm (Ono et al., 2013). Temperature-controlled experiments were performed in a jacketed cell of the same dimensions. The front window of the cell was made of UV-grade SiO_2 (Corning 7980) with greater than 90% transmittance ~~above~~ at wavelengths longer than 190 nm. The window was sealed to the cell with an o-ring and held in place securely with a plastic clamp. Temperature-controlled experiments also utilized a second pre-cell (5.3 cm pathlength) attached to the front window of the reaction cell and held under vacuum. The purpose of the pre-cell was to thermally insulate the front window and prevent condensation from occurring on the front window during low temperature experiments.

A series of mass-flow controllers controlled the flow rate of gases into the cell. Gas entered the cell through an inlet at the rear of the cell (for temperature cell experiments) or the front of the cell (for other experiments) and exited the cell through an outlet at the opposite end of the cell. An 8 cm to 10 cm length of glass tubing packed with glass wool was placed immediately after the cell exit to trap aerosols formed within the cell. Following the aerosol trap, the gas was flowed through a proportionating valve to a vacuum pump. A capacitance manometer placed before the entrance to the cell monitored the pressure within the cell. The proportionating valve was used to control the pressure within the cell to within 30 Pa of a setpoint pressure, which was usually 101.3 kPa.

Prior to each temperature-controlled experiment, the reaction cell was flushed with nitrogen(N_2) for several hours and the chiller was allowed to reach its setpoint temperature and equilibrate for at least an hour. The temperature of the reaction cell was calibrated relative to the chiller setpoint temperature on two occasions using a series of K-type thermocouples suspended within the cell. During calibrations, N_2(without SO_2) was flowed through the cell at a rate of 3.33 $cm^3\ s^{-1}$ (200 sccm, standard cubic centimeter per minute). Thermocouples placed at the front and rear of the cell gave consistent measurements to within

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5 K, with a higher gradient at lower temperatures. No significant differences were observed between the two calibrations. Results for the temperature calibration are shown in Figure 1.

2.2 Temperature effect on SO_2 photolysis (190 nm to 220 nm) and photoexcitation (250 nm to 350 nm)

The temperature effect on SO_2 photolysis (190 nm to 220 nm) was ~~measured~~ tested using the temperature-controlled reaction cell described in Section 2.1. Experiments were performed in a nitrogen-flushed glove box to prevent the spectral interference from the Schumann-Runge band of oxygen (O_2). A 200 W deuterium (D_2) arc lamp (D 200 F, HeraeusNoblelight) was used as the light source without optical filters. The output from the lamp was collimated using a fused silica plano-convex lens. 1000 ppm SO_2 (in N_2) was flowed through the cell at a rate of 3.33 cm^3 s^{-1} (200 sccm) for all experiments, and pressure within the cell was held constant at 101.3 kPa, giving an SO_2 partial pressure of 0.10 kPa within the cell.

Following photolysis experiments, the cell was removed from the glove box and rinsed well with dichloromethane ~~(DCM)~~ to dissolve any elemental sulfur that was formed. The glass wool in the aerosol trap was also collected and rinsed with ~~DCM~~dichloromethane. Elemental sulfur was recrystallized from ~~DCM~~ dichloromethane and converted to silver sulfide using the reduced chromium chloride method (Whitehill and Ono, 2012; Canfield et al., 1986). Multiple sulfur isotope ratios were measured as described in Section 2.4.

Photoexcitation experiments were performed in a room air atmosphere using a 150 W UV-enhanced xenon (Xe) arc lamp (Newport Model 6254) housed in a lamp housing (Newport Model 67005), which focused and collimated the light to a 3.3 cm diameter beam. The light was passed through a liquid filter (Newport Model 51945) filled with deionized (18.2 MΩ) water and a 250 nm longpass filter (Asahi Spectra, ZUL0250).

Following Whitehill et al. (2013), acetylene (C_2H_2) was used to trap triplet excited-state SO_2 ($^3SO_2$). During experiments, 5% SO_2 (in N_2), pure C_2H_2 (Atomic Absorption Grade), and pure N_2 (Ultra High Purity grade) were flowed through the cell continuously at a rate of 0.67 cm^3 s^{-1} (40 sccm), 0.03 cm^3 s^{-1} (2 sccm), and 2.63 cm^3 s^{-1} (158 sccm), respectively. Pressure in the cell was held constant at 101.3 kPa, giving a total flow rate of 3.33 cm^3 s^{-1}, an SO_2 partial pressure of 1.01 kPa, and a C_2H_2 partial pressure of 1.01 kPa within the cell during the experiments.

Following the experiments, the interior walls of the cell and the window were rinsed with ethanol and water to dissolve any organosulfur products formed. The glass wool in the aerosol trap was also collected. The organosulfur aerosol products were converted to silver sulfide using the Raney nickel hydrodesulfurization method of Oduro et al. (2011). Multiple sulfur isotope ratios were measured as described in Section 2.4.

2.3 SO_2 photochemistry in the presence of O_2

The photochemistry of $SO_2 + O_2$ with ultraviolet radiation was studied using a reaction cell at room temperature. The 150 W Xe arc lamp (described in Section 2.2) was used as the light source without the liquid filter. Several experiments were performed with a 200 ± 35 nm bandpass filter (Model 200-B, Acton Research, Acton, MA), a 250 nm longpass filter (Asahi Spectra, ZUL0250), or a 280 nm (285 nm cut-on)longpass filter (Newport Model FSR-WG280) to isolate particular absorption bands of SO_2, but most experiments were performed with the Xe lamp and no filters (Table 1).

Following experiments, the cell was rinsed well first with dichloromethane ~~(DCM)~~ then with water. Although sulfate was the dominant product, the cell was rinsed well with dichloromethane ~~DCM~~ first to ensure the removal of elemental sulfur. For two experiments performed with no oxygen, elemental sulfur was recovered. After rinsing the cell with water, 5.0 cm^3 of a 1.0 mol dm^{-3} solution of barium chloride ($BaCl_2$) was added to the water used to rinse the cell to precipitate sulfate as barium sulfate. Barium sulfate was rinsed several times with deionized water and dried. The glass wool inside the aerosol trap was combined with the barium sulfate and all sulfatewas converted to silver sulfide using the method of Forrest and Newman (1977). Multiple sulfur isotope ratios were measured as described in Section 2.4.

2.4 Isotope analysis of photochemical products

Photochemical products were converted to silver sulfide (Ag_2S). Ag_2S was rinsed well three to four times with deionized water and then dried completely at 353 K. Dried Ag_2S was weighed for total yield and about 8 μmol of Ag_2S was weighed into an aluminum foil capsule for isotope analysis. Capsules were loaded into nickel reaction chambers and reacted under approximately 7.3 kPa of fluorine gas (F_2) for at least 8 hours at 573 K. The resultant SF_6 was purified cryogenically and by gas chromatography. Isotope ratios of pure SF_6 were measured as SF_5^+ ions using a Thermo Scientific MAT 253 Isotope Ratio Mass Spectrometer.

For samples where less than 1.6μmol of Ag_2S was recovered, a microvolume (0.4 cm^3 volume) coldfinger was used to concentrate the samples for analysis.

Replicate analyses (N = 28) of the reference material IAEA-S-1 gave 2σ standard deviations of 0.26 ‰ for $\delta^{34}S$, 0.014 ‰ for $\Delta^{33}S$, and 0.19 ‰ for $\Delta^{36}S$ for standard isotope ratio mass spectrometry analysis. Microvolume analyses for smaller samples gave 2σ standard deviations for replicate analyses of IAEA-S-1 (N = 14) of 0.9 ‰ for $\delta^{34}S$, 0.08 ‰ for $\Delta^{33}S$, and 0.8 ‰ for $\Delta^{36}S$. Replicate experiments performed under identical conditions had differences larger than the analytical uncertainty, suggesting experimental variability was the dominant source of uncertainty in our measurements.

2.5 Potential energy surfaces of $SO + O_2 \rightarrow SO_3 \rightarrow SO_2 + O$ reactions

To test the feasibility of reaction R6, ab-initio energy calculations at multiple levels of theory were performed to search important stationary points on the SO_3~~potential energy surfaces (~~PESs~~)~~. The lowest$SO(^3\Sigma^-) + O_2(^3\Sigma_g^-)$ asymptote of the SO_3 PESs involves three degenerate states, namely the singlet, triplet, and quintet states. The singlet state corresponds to the ground state of the SO_3 molecule ($^1A_1'$), but does not dissociate to the ground state products $SO_2(^1A_1) + O(^3P)$ but to $SO_2(^1A_1) + O(^1D)$. The triplet surface corresponds to the ground state products but is adiabatically associated with a higher energy excited-state (triplet) SO_3. The quintet state is much higher in energy than the other two states except at the $SO(^3\Sigma^-) + O_2(^3\Sigma_g^-)$ asymptote and will thus not be considered in this study.

The B3LYP density functional (Becke, 1988; Lee et al., 1988) was initially used to optimize each minimum and/or transition state on the singlet and triplet ~~potential energy surfaces~~PESs. Single point calculations at these stationary points were then carried out using an explicitly correlated version of the unrestricted coupled cluster method with single, double and perturbativetriple excitations ~~method~~ (UCCSD(T)-F12a; Knizia et al., 2009).

In addition, complete active space ~~self~~ self-consistent field (CASSCF) calculations were performed (Knowles and Werner, 1985, 1988). Multi-reference Rayleigh Schrö~~ö~~dinger perturbation theory of second order (RSPT2 or CASPT2) calculations (Celani and Werner, 2000) were performed based on the CASSCF wavefunctions in order to account for part of the dynamical correlation.Calculations including the full valence orbitals would involve 24 electrons in 16 orbitals and were not feasible. Instead, the 2s orbital for O and the 3s orbital for S were closed, resulting in an active space of 16 electrons in 12 orbitals (16e,12o).

Dunning's augmented correlation-consistent polarized valence triplet-zeta (aug-cc-pVTZ) basis set was used in all cases (Dunning, 1989). B3LYP calculations were performed with Gaussian09 (Frisch et al., 2009) and the other calculations were performed using MOLPRO(Werner et al., 2012).

2.6 Definitions

Isotopic results will be presented with conventional δ notation, as relative deviations of isotope ratios with respect to reference sulfur.

$$\delta^x S = \frac{{}^x R_{product}}{{}^x R_{reference}} - 1 \quad (1)$$

where x = 33, 34, or 36 and ${}^xR$ is the ratio of ${}^xS$ to ${}^{32}S$ in the substance. For experimental results all isotope ratios will be normalized to the isotope ratios of the initial SO_2. For natural samples (i.e. stratospheric sulfate aerosol samples), the reference is Vienna Canyon Diablo Troilite (V-CDT).

Mass-independent isotope fractionations in ${}^{33}S/{}^{32}S$ and ${}^{36}S/{}^{32}S$ ratios (relative to ${}^{34}S/{}^{32}S$ ratios) will be presented as $\Delta^{33}S$ and $\Delta^{36}S$ values, respectively. These are defined as:

$$\Delta^{33}S = \frac{(\delta^{33}S+1)}{(\delta^{34}S+1)^{0.515}} - 1 \quad (2)$$

and

$$\Delta^{36}S = \frac{(\delta^{36}S+1)}{(\delta^{34}S+1)^{1.90}} - 1 \quad (3)$$

Almost all physical, chemical, and biological processes fractionate isotopes mass-dependently (i.e. $\Delta^{33}S$ and $\Delta^{36}S$ are approximately equal to ~~=~~ 0 ~~0 and $\Delta^{36}S = 0$~~). SO_2photochemistry, as well as the photochemistry of other sulfur gases such as CS_2, are some of the few exceptions that have been shown to produce mass-independent fractionation. Therefore, non-zero $\Delta^{33}S$ and $\Delta^{36}S$ values can be unique tracers of photochemical processes.

3 Results

All experiments performed are summarized in Table 1. Results from temperature experiments on SO_2 photolysis and SO_2photoexcitation are given in Tables 2 and 3, whereas

results from SO_2 + O_2 experiments are presented in Tables 4 and 5. Tables 6, 7, and 8 give the results from energy calculations on the ~~potential energy surfaces~~PESs of SO_3.

3.1 Temperature experiments

Results from the temperature experiments (Section 2.2) are shown in Figure 2. The SO_2 photolysis (190 nm to 220 nm) experiments (Table 2) revealed that the magnitude of the isotope effects increase with decreasing temperatures, from 129‰ to 191‰, 5.5‰ to 9.1‰ and -24.1‰ to -35.8‰, for $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$, respectively. The relationship between isotopes (i.e. $\Delta^{33}S$ versus $\delta^{34}S$ and $\Delta^{36}S$ versus $\Delta^{33}S$) did not change significantly as temperature was decreased (0.04 to 0.05 for $\Delta^{33}S/\delta^{34}S$ and -3.9 to -4.6 for $\Delta^{36}S/\Delta^{33}S$). Variability between duplicate experiments also increased at lower temperatures, highlighting the difficulty of the low temperature experiments and indicating a strong sensitivity to experimental conditions.

SO_2photoexcitation (250 nm to 350 nm) showdecreasing magnitude $\Delta^{33}S$ and $\Delta^{36}S$ values at lower temperatures(22.8‰ to 19.0‰ and 52.5‰ to 46.0‰ for $\Delta^{33}S$ and $\Delta^{36}S$, respectively; Table 3). Even at lower temperatures, the product from SO_2photoexcitation experiments show positive $\Delta^{33}S$ and $\Delta^{36}S$ values, as shown previously in room-temperature experiments (Whitehill and Ono, 2012; Whitehill et al., 2013). As discussed previously (Whitehill et al., 2013), these signatures do not match predictions from isotopologue-specific absorption cross-sections (Danielache et al., 2012), suggesting an additional isotope effect beyond differences in the initial excitation for different isotopologues.

3.2 Oxygen experiments

SO_2 photolysis and photoexcitation in the presence of molecular oxygen (O_2) produced mass-independent sulfur isotope signatures in sulfate products (Tables 4 and 5). Isotope ratios of this product sulfate are shown in Figure 3 and compared with stratospheric sulfate aerosol data from ice cores (Savarino et al., 2003; Baroni et al., 2007, 2008; Lanciki, 2010; Lanciki et al., 2012). Strong agreement between the Xe lamp data, 200 nm bandpass (200 BP) data, and previous SO_2 photolysis data (Ono et al., 2013) suggest an SO_2 photolysis source for the isotope effects during broadband SO_2 irradiation with the Xe lamp light source.

Experiments focusing on the photoexcitation band of SO_2 using the 250 nm longpass filter (250 LP) and 280 nm longpass filter (280 LP) display a different isotope signature,

characterized by positive $\Delta^{33}S$ and $\Delta^{36}S$ values, whereas sulfate from SO_2 photolysis has positive $\Delta^{33}S$ and negative $\Delta^{36}S$ values. This is consistent with previous findings (Whitehill and Ono, 2012; Whitehill et al., 2013), and demonstrates the MIF in this band region is not produced by chemistry related to acetylene nor oxygen. However, the magnitude of the sulfur MIF signatures (i.e. $\Delta^{33}S$ and $\Delta^{36}S$ values) are considerably smaller than previous experiments using C_2H_2 (Table 3, Whitehill et al., 2013). This suggests that a considerable amountof the sulfate in the system is being produced by a mass-dependent process, such as $^*SO_2 + SO_2 \rightarrow SO + SO_3$ (Whitehill and Ono, 2012). This would dilute the MIF signature.In addition, there is considerable variability (i.e. a factor of ~2) was observed between the two 250 nm longpass filter experiments, despite identical experimental conditions. The cause of this variability is uncertain but could relate to the amountof water vapor within the system.

3.3 Potential energy surfaces of SO_3

Asymptotic energies of $SO+O_2$ on each ~~potential energy surface~~PES were compared with the energies obtained by separate calculations of each species with a certain spin (Table 6). The CASSCF results correctly produced degenerate energies for the $SO+O_2$ asymptote on the singlet and triplet states, which exactly match the sum of the energies of~~n~~ the $SO(^3\Sigma^-)$ and $O_2(^3\Sigma_g^-)$species calculated separately. The CASPT2 results also showed the correct degenerate behavior but the energies shift slightly from those calculated separately, which presumably arises from the perturbative treatment in CASPT2~~on~~. On the other hand, the UCCSD(T)-F12a and B3LYP results both attribute $SO+O_2$ on the singlet state to $SO(^1\Delta)+O_2(^1\Delta_g)$, and B3LYP even gives a qualitatively incorrect energy for $SO+O_2$ on the triplet state, while UCCSD(T)-F12a attributes the triplet state ~~this one~~ to $SO(^1\Delta)+O_2(^3\Sigma_g^-)$. An important conclusion from these data is that one has to use a multi-reference method if ~~an~~ accurate global adiabatic ~~potential energy surface~~PES~~i~~s aredesired for this system. Otherwise, the asymptotic behavior can be completely wrong.None of the previous studies has noticed this, and as a result a single-reference method was always selected(Jou et al., 1996; Martin, 1999;Goodarzi et al., 2010; Ahmed, 2013). Fortunately, single reference methodscan accurately describe the PES away from the $SO+O_2$ region; they are capable of describing several SO_3 isomers and the SO_2+O product channel reasonably well.

Energies for the stationary points computed using multi-reference approaches are reported relative to that of the $SO(^3\Sigma^-)+O_2(^3\Sigma_g^-)$asymptote. However, the active space used in our CASSCF calculations is not sufficient to provide quantitatively accurate results, but a larger

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active space is still computationally infeasible. For single-reference calculations, we chose to use the UCCSD(T) energies at optimized B3LYP geometries for the stationary points. To avoid the aforementioned problems in the $SO(^3\Sigma^-)+O_2(^3\Sigma_g^-)$asymptote, we have used the UCCSD(T) energy sum of the two reactants with the correct spinscalculated separately, which has been shown above to be accurate. The sum of these two energies thus provides the reference for other stationary points on both singlet and triplet PESs. All energies of stationary points are listed in Tables7 and 8, and the reaction pathways on both PESs are shown graphically in Figure4, using the energies of the UCCSD(T)//B3LYP calculations.It is seen from Tables 7 and 8 that the experimental derived energy differences (from Chase, 1986) between reactants and products for the $SO(^3\Sigma^-)+O_2(^3\Sigma_g^-)\rightarrow SO_3(^1A_1')$ reaction (-411.29 kJ $mole^{-1}$), the $SO(^3\Sigma^-)+O_2(^3\Sigma_g^-)\rightarrow SO_2(^1A_1)+O(^3P)$ reaction (-54.56 kJ $mole^{-1}$) and the $SO(^3\Sigma^-)+O_2(^3\Sigma_g^-) \rightarrow SO_2(^1A_1)+O(^1D)$ reaction (135.27 kJ $mole^{-1}$) are reproduced well by the UCCSD(T)-F12a//B3LYP calculations, while the other methods contain significant errors.

4 Discussion

4.1 Origin of mass-independent fractionation during SO_2 photochemistry

~~Isotopologue specific absorption cross sections are expected to correctly predict the isotope effects from SO_2 photolysis (in the 190 nm to 220 nm region) but fail to reproduce the isotope effects from SO_2 photoexcitation (in the 250 nm to 350 nm region). This is due to t~~The differences in the photophysics and photochemistry between the photolysis region (190 nm to 220 nm) and the photoexcitation region (250 nm to 350 nm) ~~two absorption regions, whichresult in~~suggest different mechanisms for MIF formation, as discussed previously (Whitehill and Ono, 2012; Ono et al., 2013; Whitehill et al., 2013).

In the 165 nm to 235 nm wavelength region, SO_2photolysis occurs through predissociation from the bound $\tilde{C}(^1B_2)$ state. Near the dissociation threshold of 218.7 nm (Becker et al., 1995), the quantum yield of photolysis is less than unity, although it increases to greater than 0.99 at wavelengths shorter than 215 nm (Katagiri et al., 1997). In the region where the quantum yield is close to unity (i.e. less than 215 nm), the isotope effects due to SO_2 photolysis should be determined entirely by the differences in the absorption cross-sections between the different isotopologues of SO_2 (e.g., by isotopologue specific Franck-Condon coupling; Danielache et al., 2008) and optical screening effects under high SO_2 column

densities (Lyons, 2007, 2008; Ono et al., 2013). In the narrow spectral region from 215 nm to 218.7 nm, where the quantum yield of photodissociation varies, it is possible that quantum yield differences between isotopologues could potentially produce additional isotope effects beyond those predicted from absorption cross-sections. However, in this region, photodissociation occurs primarily via vibronic mixing of the $\tilde{C}(^1B_2)$ state levels with the dissociative continuum of the electronic ground, $\tilde{X}(^1A_1)$ state (Katagiri et al., 1997).Due to the high density of vibronic levels for the $\tilde{X}(^1A_1)$ state, it is unlikely that there will be significant isotope effects in the coupling strength between the $\tilde{C}(^1B_2)$ and $\tilde{X}(^1A_1)$ states.Dissociation occurring through mixing with repulsive singlet and triplet states is expected to be small, as is the nonadiabatic coupling of the $\tilde{C}(^1B_2)$ and $\tilde{D}(^1A_1)$ states (Tokue and Nanbu, 2010).

For laboratory experiments, the observed isotope effects for SO_2 photolysis is a function not only of differences in the absorption cross-sections (Danielache et al., 2008) but also a function of the SO_2 column density. This is because the SO_2 absorption cross-section has significant fine structure, which causes optical screening effects to occur (Lyons, 2007). This optical screening effect produces larger isotope effects at higher SO_2 column densities (Ono et al., 2013). In addition to the above effects, there appears to be a total (or bath gas) pressure effect on $\Delta^{33}S$ values. This manifests as reduced $\Delta^{33}S$ values at higher total (i.e. bath gas) pressures, which is observed with He, SO_2, and N_2 bath gases (Masterson et al., 2011; Whitehill and Ono, 2012; Ono et al., 2013). The mechanism responsible for these pressure effects is still uncertain, but it could suggest that $^{33}SO_2$ has a longer excited-state lifetime prior to dissociation than the other isotopologues.

SO_2photoexcitation in the 250 nm to 350 nm absorption regionalso produces absorption-based isotope effects due to differences in cross-sections and self-shielding. In addition, it produces isotope effects by a completely different mechanism. SO_2photoexcitation in the 250 nm to 350 nm region occurs by initial excitation into a coupled $\tilde{A}(^1A_2)/\tilde{B}(^1B_1)$ singlet excited state that undergoes intersystem crossing to the photochemically active triplet $\tilde{a}(^3B_1)$ state (Xie et al., 2013; Lévêque et al., 2014). Unlike SO_2 photolysis, where the quantum yield of reaction (i.e. photolysis) is near unity, the quantum yield for intersystem crossing between the singlet and triplet states is highly variable and state-dependent. Due to the relatively low density of states in the crossing region ($\tilde{A}\,^1A_2 \rightarrow \tilde{a}\,^3B_1$), the branching between quenching to the ground state and intersystem crossing to the triplet state will be a strong function of isotope substitution. Whitehill et al. (2013) argue that this isotope selective intersystem crossing as

the origin of ~~most~~ part of the isotope effects in photochemical products following SO_2photoexcitation in the 250 nm to 350 nm absorption region.

Photoexcitation of SO_2 in the presence of O_2 produces sulfate with both positive $\Delta^{33}S$ and positive $\Delta^{36}S$ signals, similar to the organic sulfur observed in Whitehill et al. (2013) and the elemental sulfur in Whitehill and Ono (2012). This suggests that the anomalous isotope signatures observed from photoexcitation in previous studies are a result of the photophysicsand photochemistry of excited-state SO_2 rather than the ~~photo~~chemistry of subsequent reactions (i.e., the chemistry with acetylene).Our experimental results show significant discrepancy with isotope effects predicted by isotopologue-specific absorption cross-sections (Danielache et al., 2012; Hattori et al., 2013) for the 250 nm to 320 nm region (Whitehill et al., 2013). This is expected if isotope selective intersystem crossing is ~~overprinting~~ contributing to the isotope signals ~~produced by~~in addition to cross section differences and shielding effects.

4.2 Temperature effects on SO_2 photolysis

Lyons (2007, 2008) presentedisotopologue-specific absorption cross-sections for SO_2 in the 190 nm to 220 nm absorption region by shifting the measured $^{32}SO_2$ absorption cross-sections of Freeman et al.(1984)by an amount based on the calculated isotope shifts of Ran et al. (2007). It has been unclear whether these absorption cross-sections can correctly predict the isotope effects due to SO_2 photolysis (Danielache et al. 2008), as they include only isotope shifts and not other potential differences among isotopologues. Previous comparisons with experimental data showed significant discrepancies (i.e. a factor of ~2 in $\delta^{34}S$ values) between experimental data and that predicted by the Lyons (2007, 2008) cross-sections (Whitehill and Ono, 2012; Ono et al., 2013). Such discrepancies were attributed to the difference in temperature between the Lyons (2007, 2008) cross-sections, which are based on cross-sections measured at 213 K (Freeman et al., 1984) and the temperature of the experiments (298 K). Given the new temperature data in the present study, it is possible to compare calculations based on the Lyons (2007, 2008) cross-sections with temperature-dependent experimental isotope data. Calculations were performed as described in previous papers (Whitehill and Ono, 2012; Ono et al., 2013) and are compared to experimental data in Figure 5.

Excellent agreement with the Lyons (2007,2008) cross-sections can be seen when the observed temperature dependence on $\delta^{34}S$ are extrapolated back to 213 K. A similar strong agreement is also seen in the $\Delta^{36}S$ values. This new data fills in the major gap between predictions based on the Lyons (2007, 2008) cross-sections and the room-temperature experimental data, and provides further support to an optical origin of mass-independent fractionation during SO_2 photolysis under laboratory conditions (Ono et al., 2013).

Despite the strong agreement for $\delta^{34}S$ and $\Delta^{36}S$ values, the Lyons (2007, 2008) cross-sections over-predict the magnitude of the mass-independent isotope anomaly in ^{33}S (i.e. $\Delta^{33}S$ values) when compared with experimental data. There are several possible explanations for this. One reason is that there are significant differences between the actual cross-sections and those predicted by shifting the $^{32}SO_2$ cross-sections for $^{33}SO_2$. Measurements by Danielache et al. (2008) at room temperature suggest that there are some differences between the isotopologue-specific absorption cross-sections aside from just the spectral shifts accounted for by Lyons (2007, 2008). A second possibility is that the high total pressure (101.3 kPa, including the N_2 bath gas) of the experiments caused a decrease in the $\Delta^{33}S$ value relative to values observed at lower total pressures. It has been previously observed (Masterson et al., 2011; Whitehill and Ono, 2012; Ono et al., 2013) that $\Delta^{33}S$ values decrease in the presence of high bath gas pressures. This pressure quenching effect is most noticeable for $\Delta^{33}S$ and does not affect $\delta^{34}S$ or $\Delta^{36}S$ values as strongly.

The Lyons (2007, 2008) cross sections are semi-empirical in that they take the measured $^{32}SO_2$ cross-sections of Freeman et al. (1984) and shift them using theoretical isotope shifts predicted by Ran et al. (2007). Although the Lyons (2007, 2008) cross-sections are not necessarily accurate,

~~We that~~ the Lyons (2007, 2008) cross sections seem to~~an~~ accurately predict the isotope effects during SO_2 photolysis under low temperature (ca. 213 K) conditions, such as those in the stratosphere~~.~~.

~~Conversely, cross sections measured at room temperature (e.g., Danielache et al., 2008) will underestimate $\delta^{34}S$ fractionations when applied to stratospheric conditions.~~

4.3 Constraining the rate of the SO+ O_2 + M reaction using product formation

Our results demonstrate that photolysis of SO_2 in the presence of molecular oxygen (O_2) produces large amounts of sulfate with considerable mass-independent sulfur isotope

anomalies. In our experimental system, there are three dominant pathways for SO_3 formation:OH oxidation of SO_2 (reactions R1 + R2, if water is present), O_2 oxidation of SO from SO_2 photolysis (reactions R4 + R6), and O oxidation of SO_2 via

$$SO_2 + O + M \rightarrow SO_3 + M \quad \text{(R7)}$$

OH and O oxidation of SO_2 (reactions R1 and R7) are mass dependent (Harris et al., 2012; Whitehill and Ono, 2012; Ono et al., 2013). However, oxidation of SO via R6 will trap the isotopic composition of SO as SO_3 and carry the mass-independent sulfur isotope signature from SO_2 photolysis (R4).

We performed a series of experiments at a total pressure of 101.3 kPa, a flow rate of 6.67 cm^3 s^{-1}(400 sccm) and an SO_2 partial pressure of 0.127kPa (Table 4; Figure 6). The partial pressure of molecular oxygen was varied from 0 kPa to 19.8 kPa (0 % to 19.5% O_2). In all experiments, SO_2 was photolyzed via R4. In the experiments with no oxygen, both elemental sulfur (S^o) and SO_3 aerosols were formed, with the elemental sulfur (S and related species) formed from SO via:

$$SO + SO \rightarrow SO_2 + S \quad \text{(R8)}$$

SO photolysis is expected to be a minor source of S compared to R8. In the absence of oxygen, $SO_3$is formed primarily via O oxidation of SO_2 (R7), which is mass dependent (Ono et al., 2013).

At 5.1 kPa O_2 and above, elemental sulfur formation was shut off and SO_3 was the major product. Under these conditions, oxidation of SO (to SO_2 or SO_3 via R5 or R6) competes with SO disproportionation (R8).

By comparing the $\Delta^{33}S$ value of elemental sulfur in the absence of O_2 (0 kPa O_2) with the $\Delta^{33}S$ value of sulfate in the presence of O_2 (5.1 kPa to 19.8 kPa O_2), it is possible to estimate the fraction of sulfate formed through R6. In particular,

$$f_{R6} = \frac{\Delta^{33}S_{\text{sulfate, with } O_2}}{\Delta^{33}S_{S^0, \text{ no } O_2}} \quad (5)$$

~~Where~~where f_{R6} is the fraction of total SO_3 formed that comes from reaction R6. Given the product yields (Table 4), the time each experiment was run, and the volume of the reaction cell (approximately 325 cm^3), the sulfate formation rate per unit volume per unit time can be calculated. In the experiments with 5.1 kPa to 19.8 kPa O_2, the sulfate formation rates were

between 5.3×10^{12} molecules cm^{-3} s^{-1} and 1.2×10^{13} molecules cm^{-3} s^{-1}. Combining this with the f_{R6} values calculated from equation 5, we can estimate for the rate of sulfate formation from reaction R6 under our experimental conditions. This gave a rate for reaction 6 of 3.6×10^{12} molecules cm^{-3} s^{-1} to 6.6×10^{12} molecules cm^{-3} s^{-1}. Assuming R6 is a termolecular reaction, the rate for R6 can be written as:

$$\text{rate R6} = k_{R6}[SO][O_2][M] \quad (6)$$

where k_{R6} is the termolecular rate constant for reaction R6 and [SO], [O_2] and [M] are the concentrations of SO, O_2 and total third body gases (M = N_2, O_2) in the reaction cell. In equation (6), the [O_2] and [M] terms are known from the experimental conditions. The [SO] term is estimated by assuming a photochemical steady state for SO in the cell. SO production via Reaction R4 is balanced by SO destruction via Reactions R5 and R6. This gives us a steady state SO concentration of:

$$[SO] = \frac{J_{SO_2}[SO_2]}{k_{R5}[O_2] + k_{R6}[O_2][M]} \quad (7)$$

where J_{SO2} is the photolysis rate constant for R4. This photolysis rate constant was calculated assuming a spectral irradiance for our 150 W Xe arc lamp of:

$$F_0 / \text{mW nm}^{-1} = 0.11 \cdot 1.6 \cdot (14 - 9 \cdot \exp(-0.013 \cdot (\lambda / \text{nm} - 200))) \quad (8)$$

where F_0 is the spectral irradiance of the xenon lamp at wavelength λ (Ono et al., 2013). This flux might be modified slightly as a function of the distance between the cell and the lamp, due to interferences from the absorption of oxygen. However, sensitivity studies performed here and previously (Whitehill and Ono, 2012) suggest that the effect of the oxygen absorption on the total SO_2 photolysis rate is minor compared to the uncertainty in the lamp photon flux. The lamp photon flux data was determined from the manufacturer's data and uncertainty estimates were not available. Despite this, the function used by Ono et al. (2013) (Equation 8) was used to obtain an estimate for the total SO_2 photolysis rate.

The spectral irradiance of the lamp was used to calculate the photon flux entering the cell, accounting for absorption of the cell windows from measured transmission data. The SO_2 absorption cross-sections of Manatt and Lane (1993) were used to calculate the photolysis rate in the cell, accounting for optical screening effects from SO_2 and O_2 within the cell. With an SO_2 partial pressure of 0.127kPa, this provided a photolysis rate constant of $J_{SO2} = 5.2\times10^{-3}$ s^{-1}. The rate constant for reaction R5 is $k_{R5} = 8.0\times10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} (Sander et al.,

2011) at room temperature (298 K). Using these values and equations (6) and (7), the rate constant for R6 (k_{R6}) was calculated iteratively. Calculated rate constants ranged from k_{R6} = 7.3×10^{-38} cm^6 molecule^{-2} s^{-1} to k_{R6} = 1.4×10^{-37} cm^6 molecule^{-2} s^{-1}, with an average value of k_{R6} = 1.1×10^{-37} cm^6 molecule^{-2} s^{-1} (Table 4).This rate estimate is consistent with the upper bound on $k_{R6} \leq 1\times10^{-36}$ cm^6 molecule^{-2} s^{-1} by Black et al. (1982).

The calculated rate constant (k_{R6}) appears to decrease at 19.8 kPa O_2 compared with the calculated rate for lower pO_2 values. It is unclear why this behavior is observed. The relatively strong agreement for the other conditions strengthens our confidence that the model is robust.

TheThe derived rate constant carries a large amount of uncertainty due to a number of sources of error in the rate calculation. One source of error in the calculation is in the spectral irradiance of the xenon lamp, which was fit from the manufacturer's literature and not directly measured. Because the spectral irradiance is likely to change over the lamp's lifetime, the actual spectral irradiance at the time the experiments were performed might be different than the values calculated here. As the spectral irradiance in the high-energy side of the ultraviolet (190 nm to 220 nm) is likely to decrease over the course of the lamp's lifetime, this makes the calculated SO_2 photolysis rate (and resulting SO number density) an upper bound. Reducing the SO_2 photolysis rate increases the effective rate constant.A second source of error is the assumption that we trapped 100% of the SO_3 formed as sulfate. It is possible that some fraction of the SO_3 remained in the gas phase and did not condense as aerosol particles. A third source of error is the assumption that the reaction R6 behaves as a termolecular reaction despite the high total pressure (101.3 kPa) of the system. It is possible that the reaction is saturated at (or near) this pressure and is thus behaving as an effective bimolecular reaction. In any of these three cases, the estimate of the rate constant for reaction R6 would be a lower bound on the actual termolecular rate constant.

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It is also important to consider the impact of water vapor within the system. Although attempts were made to minimize the amount of water vapor in the system, there was almost certainly some water vapor in the system during our experiments. This is evidenced by thevisible formation of sulfate aerosols from SO_3 during the experiments. Unfortunately, we did not have theanalytical capability to quantitatively constrain the amount of water vapor in the system during the experiments. The Zero Air and Nitrogen used as a source of gas to the cell has a maximum of 3 ppm H_2O (by volume), but there could be additional water absorbed

onto the surfaces of the system while the cell is disassembled. We assume 100% of the SO_3 was trapped as sulfate, giving a lower bound estimate on the rate of reaction R6.

4.4 Constraining the rate of the SO + O_2 + M reaction using a kinetic model

To further constrain the rate of R6 (the SO + O_2 + M → SO_3 + M reaction), we constructed a kinetic model of the chemistry occurring within the cell. We used the same data and conditions as Section 4.3, but explicitly modeled the chemistry occurring within the system. SO_2 photolysis rates were calculated as discussed in Section 4.3, using the cross sections of Manatt and Lane (1993). Oxygen and ozone photolysis rates were calculated using the cross-sections Yoshino et al. (1988, 1992) for O_2 and Molina and Molina(1986) for O_3. Quantum yields for $O(^1D)$ versus $O(^3P)$ formation from O_3 photolysis were parameterized based on the recommendation of DeMore et al. (1997). Photolysis rates for HO_2 and H_2O_2 were calculated using the recommended cross-sections of Sander et al. (2011). HO_2 photolysis was assumed to produce $O(^1D)$ and OH as products, and H_2O_2 photolysis was assumed to produce 2OH. ~~$O(^1D)$ formed from O_3 photolysis was assumed to be instantaneously quenched by N_2 and O_2 to $O(^3P)$ and not significantly affect the chemistry of the system.~~

The rate constants and their sources~~Reactions considered, rate constants for those reactions, and the sources for the rate constants~~ are given in Table 9. ~~When possible, e~~Effective second-order rate constants (calculated assuming T = 298 K and [M] = 2.5×10^{19} molecule cm^{-3}) were used for termolecular reactions. Initial guesses were made for the concentration of species within the system. The system was assumed to be in photochemical steady state and solved iteratively until convergence. Comparisons were made between the data and the calculations for ~~both~~ f_{R6} values (Equation 5) ~~as well as total product (SO_3) formation rates~~.Simulations were performed with values of k_{R6} ~~between~~ of 1.0×10^{-37} cm^6 $molecule^{-2}$ s^{-1}, ~~and~~ 1.0×10^{-36} cm^6 $molecule^{-2}$ s^{-1}, and 1.0×10^{-35} cm^6 $molecule^{-2}$ s^{-1}. Since the amount of water vapor in the system was not constrained experimentally, three simulations were performed, with H_2O concentrations of 0 ppm (by volume), 10 ppm (by volume), and 100 ppm (by volume), which spans a range of reasonable estimates for water vapor concentration in the system. Although water vapor in the bath gas (N_2 and N_2/O_2) are less than 3 ppm (by volume), additional water could be absorbed onto the inner surfaces of the cell and released during the experiment.Results for 0 ppm H_2O and 10 ppm H_2O predict rates for reaction R6 on the order of 10^{-36} cm^6 $molecule^{-2}$ s^{-1}, with predictions for 100 ppm H_2O being slightly higher.

There is a discrepancy between model predictions and the observed experimental behavior. In particular, lower O_2 fractions produce higher estimated rates and vice versa.In addition, the model predicts rates mostly higher than the previous upper bound on the rate calculated by Black et al. (1982) of 10^{-36} cm^6 $molecule^{-2}$ s^{-1}. Helium was used as a bath gas for the Black et al. (1982) experiments, as compared with nitrogen or nitrogen / oxygen used as the bath gas here. Nitrogen (N_2) and oxygen (O_2) are a more efficient third body quenchers than helium. Thus, the rate of the termolecular reaction with nitrogen (or nitrogen/oxygen) as a bath gas could be higher than the maximum constraint suggested by Black et al. (1982). There is also an order of magnitude discrepancy between the predictions here and those in Section 4.3, with those in Section 4.3 being an order of magnitude smaller than those in Section 4.4.This could be based on the assumption that 100% of the SO_3 was trapped as sulfate in Section 4.3, whereas the actual amount might be less than that (implying a higher rate than predicted in Section 4.3). However, the model predicts rate constants within an order of magnitude of previous constraints from the literature (Black et al., 1982) and Section 4.3.Based on this work, we estimate the rate of this reaction to be on the order of 10^{-37} cm^6 $molecule^{-2}$ s^{-1} to 10^{-36} cm^6 $moelcule^{-2}$ s^{-1}. Future work is necessary to better constrain the rate of this reaction.

~~The observed fR6 value (equation 5) is best fit by the kR6 between 2×10 37 cm6 molecule 2 s 1 and 10×10 37 cm6 molecule 2 s 1 (Figure 7, left). The yield of SO3 indicates a lower rate constant of less than 1×10 37 cm6 molecule 2 s 1 to 3×10 37 cm6 molecule 2 s 1, potentially reflecting low recovery of SO3 in our experiments (Figure 7, right).Nonetheless, this range of results is consistent with the rate estimate obtained in Section 4.3. Thus, our best estimate for the rate of reaction R6 is somewhere between 1.0×10^-37 cm^6 molecule^-2 s^-1 and 1.0×10^-36 cm^6 molecule^-2 s^-1. As discussed in Section 4.3, the model is sensitive to the SO2 photolysis rate, which depends upon the lamp spectrum.~~

4.5 Exploring the potential energy surfaces of the SO + O_2 reactions

The experimental evidence presented above suggests the formation of SO_3 via the SO+O_2 reaction. Our theoretical analysis shows that the singlet PES is associated with the ground state of the SO_3 molecule, and thus is the primary surface related to the $SO(^3\Sigma^-) + O_2(^3\Sigma_g^-) \rightarrow SO_3(^1A_1')$ reaction (Figure 4). As shown in Table 7, four isomers of SO_3 are located in the singlet PES. It is predicted that the $D_{3h}SO_3$~~molecule~~ isomer is the global minimum, followed by ~~the~~ cyclic-OSOO. There are two shallower wells, denoted as trans-OSOO and cis-OSOO,

at the CASPT2 and UCCSD(T)-F12a levels, but they ~~seem~~ appear to be energetically higher than the $SO(^3\Sigma^-) + O_2(^3\Sigma_g^-)$ asymptote at the B3LYP and CASSCF levels. No barrier was found for the formation of either trans-OSOO or cis-OSOO, but there is a barrier for the isomerization and the barrier height depends upon the level of the ab-initio calculation. The rate-determining barrier for the $SO(^3\Sigma^-) + O_2(^3\Sigma_g^-) \rightarrow SO_3(^1A_1')$ reaction is the one connecting ~~the~~ cyclic-OSOO and SO_3. The lowest barrier height for this reaction (given by CASPT2) is 56.6 kJ $mole^{-1}$. Using the partition function at the B3LYP level, a conventional transition-state theory rate calculation predicts a pressure-saturated (i.e. effective bimolecular) thermal rate constant for reaction R6 at 298K of 2.7×10^{-24} cm^3 $molecule^{-1}$ s^{-1}. This is about eight orders of magnitude lower than the experimental rate constant for reaction R5 (8.0×10^{-17} cm^3 $molecule^{-1}$ s^{-1}, Sander et al., 2011), and about six orders of magnitude lower than the minimum effective second-order rate constant for reaction R6 at 101.3 kPa total pressure (about $2.5\times10^{-18}cm^3$ $molecule^{-1}$ s^{-1}, calculated assuming $k_{R6} = 1.0\times10^{-37}$ cm^6 $molecule^{-1}$ s^{-1} and $[M] = 2.5\times10^{19}$).We thus conclude that the$SO(^3\Sigma^-) + O_2(^3\Sigma_g^-) \rightarrow SO_2(^1A_1) + O(^3P)$ reaction cannot occur on the singlet surface without invoking the spin-forbidden intersystem crossing between the singlet and triplet surfaces.

The triplet PES is very different from the singlet PES with regard to the energy of each SO_3 isomer (Figure 4; Table 8). The global minimum moves to the cyclic-OSOO isomer, which has a similar geometry to the singlet (ground) state counterpart but with different bond lengths. On the other hand, $SO_3(^3A_1')$ becomes highly unfavorable; for example, it is 75.14 kJ $mole^{-1}$ higher than the $SO + O_2$ reactants at the UCCSD(T)-F12a level. The trans-OSOO complex remains in a planar geometry, in which the O-S-O-O dihedral angle is 180°; however, the cis-OSOO complex was found to be out-of-plane, in which the O-S-O-O dihedral angle is about 74°. We still use "cis-OSOO" to denote this isomer for convenience. Unlike the singlet PES, trans-OSOO and cis-OSOO share the same transition state for the isomerization to cyclic-OSOO. This process represents the rate-limiting step for the reaction on the triplet surface. The barrier height is 67.86 kJ $mole^{-1}$ at the UCCSD(T)-F12a level, which is still high. In the adiabatic picture, the $SO(^3\Sigma^-) + O_2(^3\Sigma_g^-) \rightarrow SO_2(^1A_1) + O(^3P)$ reaction on the triplet PES has a rate constant of 2.7×10^{-25} cm^3 $molecule^{-1}$ s^{-1} at 298 K, estimated using transition-state theory. This is still considerably slower than the experimentally measured rate constant for reaction R5.

It is clear that a single PES is unable to reproduce the experimental data for reactions R5 and R6. ~~The deviation is rather large and cannot be attributed to tunneling effects.~~ In order to explore the possibility of intersystem crossing, two adiabatic minimum energy pathways on both spin states are shown in Figure 4 and the energies are extracted at the UCCSD(T)-F12a//B3LYP level. There are several places that the two PESs cross each other, and a spin flip could happen in the region near the cyclic-OSOO isomer due to the fact that this~~e cyclic-OSOO~~ isomer on both PESs has nearly the same energy. A possible non-adiabatic reaction pathway is depicted in Figure 4 by the green solid lines connecting every two stationary points. Specifically, for the $SO(^3\Sigma^-) + O_2(^3\Sigma_g^-) \rightarrow SO_3(^1A_1')$ reaction, the two reactants first approach each other to form cyclic-OSOO on the singlet PES, and jump to the triplet PES to avoid the high barrier region, followed by back transition to the singlet state to form the SO_3 product. For the $SO(^3\Sigma^-) + O_2(^3\Sigma_g^-) \rightarrow SO_2(^1A_1) + O(^3P)$ reaction, the intermediate cyclic-OSOO may be generated on the singlet PES, followed by intersystem crossing from the singlet to triplet surface and then reach the products without overcoming a high barrier. Indeed, several different mechanisms introducing~~e~~ the intersystem crossing have been proposed by other authors for the $SO_3 \rightarrow SO_2 + O$ reaction~~s~~(Davis, 1974; Westenberg and Dehaas, 1975; Astholz et al., 1979), thanks to the relatively large spin-orbit coupling of the heavy sulfur. The barrier associated with the intersystem crossing pathway seems to be consistent with the fast rate of R5, and supports the facile formation of SO_3.

Unfortunately, rate constants involving the intersystem crossing cannot be readily determined from the current calculations. ~~without g~~Global PESs for both spin states and the coupling between them would be required for a complete calculation. Such a goal can only be achieved by a multi-reference method or configuration interaction method, which is infeasible at the current level. On-the-fly ~~transition state~~surface hopping calculations would present an alternative method to derive rate constants without the need for global potential energy surfaces and should be pursued in future work.

4.6 Contribution of the SO + O_2 + M reaction to sulfate formation in the stratosphere

To determine the significance of the reaction R6 to sulfate formation in the stratosphere, we compared the rate of sulfate formation via R6 to that formed via OH oxidation of SO_2 (reaction R1) and O oxidation of SO_2 (reaction R7) under a select set of atmospheric

conditions.We assumed an atmospheric temperature and pressure profile of the U.S. Standard Atmosphere 1976 (COESA, 1976) and noon-time O, OH, and O_3 concentrations given by DeMore et al. (1997). Spectral photon flux in the 180 nm to 220 nm region was calculated as a function of altitude for a solar zenith angle of 40°by assuming the spectral photon irradiance of Rottman et al. (2006) at the top of the atmosphere and O_2, O_3, and CO_2 being the dominant absorbers. Absorption cross-sections of O_2 (Yoshino et al., 1988, 1992), O_3(Molina and Molina, 1986), and CO_2(Shemansky, 1972) were used with concentration and column density data for the species to calculate the transmission of the atmosphere to radiation in the 180 nm to 220 nm absorption region at different altitudes. SO_2 photolysis rate constants (J_{SO2}) were calculated as a function of altitude using the calculated spectral photon fluxes and the SO_2 absorption cross-sections of Manatt and Lane (1993).

The lifetime of SO with respect to oxidation by O_2 (i.e. R5 and R6) is relatively short (on the order of seconds), so SO and SO_2 were assumed to be in photochemical steady state, i.e.

$$\frac{[SO]}{[SO_2]} = \frac{J_{SO_2}}{k_{R5}[O_2] + k_{R6}[O_2][M]} \quad (9)$$

The rate constant k_{R5} was calculated as a function of altitude (i.e. temperature) based on the recommendations of Sander et al. (2011). k_{R6} was varied between 1.0×10^{-37} cm^6 $molecule^{-2}$ s^{-1} and 1.0×10^{-36} cm^6 $molecule^{-2}$ s^{-1} to encompass ~~our range of~~the order of magnitude rate estimates from Section 4.3 and 4.4. SO oxidation by other oxidants (O_3, O, NO_3, etc.) was assumed to be minor compared to oxidation by O_2 given the minor concentration of most of these species compared with that of O_2. Using the [SO] to [SO_2] ratio, the rates of R1, R7, and R6 can be compared. Assuming these three reactions are the dominant source of SO_3 (and subsequently sulfate) in the stratosphere, the fraction of sulfate from reaction R6 (f_{SO}) can be calculated as:

$$f_{SO} = \frac{\frac{[SO]}{[SO_2]} \cdot k_{R6}[O_2][M]}{k_{SO_2+OH}[OH] + k_{SO_2+O}[O] + \frac{[SO]}{[SO_2]} \cdot k_{R6}[O_2][M]} \quad (10)$$

The rate constants k_{SO2+OH} and k_{SO2+O} are the effective bimolecular rate constants for reactions R1 and R7, as recommended by Sander et al. (2011). f_{SO} values were calculated for a 40° solar zenith angle (local noon at 40°N latitude and a 0° solar declination angle) and are shown in Figure 8. Given that SO, OH, and O(^{3}P) are all formed as a result of photochemistry, they

should have similar daily cycles. As a result, the f_{SO} values calculated for local noon should be similar to daily average f_{SO} values.

As seen in Figure 8, the lower ~~bound~~ estimate for k_{R6} (1.0×10^{-37} cm^6 $molecule^{-2}$ s^{-1}) gives 4% to 10% of sulfate from R6 between 25 km and 50 km altitude. A faster estimate for $k_{R6}$of 2.0×10^{-37} cm^6 $molecule^{-2}$ s^{-1} gives 8% to 18% of sulfate from R6 between 25 km and 50 km altitude. The upper bound estimate for the rate (k_{R6} = 1.0×10^{-36} cm^6 $molecule^{-2}$ s^{-1}, from Black et al., 1982) suggests that over 45% of sulfate could be coming from R6 between 31 km and 34 km altitude and is probably unrealistic.The contribution from R6 depends upon the amount of photons available for SO_2 photolysis, which increases with altitude because of less absorption by Schuman-Runge band of $O_2$and the Hartley bands of O_3. The rate of R6 decreases at higher altitude as total number density decrease. The maximum f_{SO} value, thus, is between 30 and 35 km (Figure 8).

Some insight into the rate can be obtained from SO_2 lifetimes in the stratosphere. Following the Mt. Pinatubo (1991) eruption, the Total Ozone Mapping Spectrometer (TOMS) data (Bluth et al., 1992) and Microwave Limb Sounder (MLS) data (Read et al., 1993) were used to estimate an e-folding time of 33 days to 35 days for SO_2 in the stratosphere. A later reanalysis of the TOMS data and TIROS Optical Vertical Sounder (TOVS) data (Guo et al., 2004) reduced this value to 25 days. Bekki and Pyle (1994) modeled the SO_2 decay following the Mt. Pinatubo eruption, considering R1 as the only sink of SO_2 in the stratosphere. Their modeled decay times for SO_2 (40 days) are considerably longer than the measured value of 25 days.Bekki and Pyle (1994) attributed this to uncertainties in the OH number densities. The discrepancy, however, could be explained in part by SO_2 photolysis followed by R6.Inclusion of the SO_2 photolysis sink would decrease the lifetimes for SO_2 above around 25 km. The presence of this reaction would also suggest that OH concentrations estimated by Read et al. (1993) based on SO_2 lifetimes might overestimate OH concentrations above around 25 km altitude.

SO_2 photolysis is self-limiting, as SO_2 photolysis near the top of the volcanic SO_2 plume absorbs ultraviolet radiation in the range that SO_2 photolysis occurs. As a result, SO_2 photolysis lower in the eruption cloud is reduced and depends upon the overlying SO_2 column density. This would potentially reduce the significance of R6 under heavy SO_2 loading.

Optical shielding effects increase the magnitude of theisotope effectfrom SO_2 photolysis under high SO_2 column densities (Lyons et al., 2007; Ono et al., 2013). Thus, the isotope

fractionation occurring in a volcanic cloud is a tradeoff between larger fractionations but lower photolysis rates at higher column densities versus smaller fractionations but higher photolysis rates at lower column densities. Although the instantaneous fractionation factors can be ~~accurately~~ estimated using our results and cross section by Lyons (2007, 2008), the temporal evolution of isotope signatures of sulfate aerosol will require a model that accurately incorporates both chemistry and dynamics of stratosphere.

Given the large signal produced by SO_2 photolysis, over 100‰ and 10‰ for $\delta^{34}S$ and $\Delta^{33}S$ values, respectively (Whitehill and Ono, 2012; Ono et al., 2013), even a 10% contribution from reaction R5 could make a substantial contribution to the isotope signature of sulfate formed above circa 25 km altitude. Given the strong similarity in the isotopic signature of stratospheric sulfate aerosols from volcanic eruptions and those produced during SO_2 photolysis (Figure 3), it is likely that SO_2 photolysis plays an important role in the sulfur isotope budget of stratospheric sulfate aerosols. The initial sulfate formed from SO_2 photolysis (followed by R6) will contain positive $\delta^{34}S$ and $\Delta^{33}S$ values and negative $\Delta^{36}S$ values. Over time, due to mass balance, the residual SO_2 will obtain negative $\delta^{34}S$ and $\Delta^{33}S$ values and positive $\Delta^{36}S$ values. This explains the temporal evolution of the isotopic signatures observed in aerosol samples (for $\delta^{34}S$,Castleman et al., 1974) and ice cores (Baroni et al., 2007), which goes from positive $\delta^{34}S$ and $\Delta^{33}S$ values shortly after an eruption to negative values as time progresses.

4.7 Insignificance of excited-state photochemistry of SO_2 in the stratosphere

It has been suggested previously (Savarino et al., 2003; Hattori et al., 2013) that excited-state photochemistry of SO_2 in the 250 nm to 350 nm absorption region (i.e. the $\tilde{A}(^1A_2)/\tilde{B}(^1B_1)$ states) might be ~~important~~ the dominant source of~~to~~ the sulfur isotope ratios in stratospheric sulfate aerosols. Previous results (Whitehill and Ono, 2012; Whitehill et al., 2013) have demonstrated that SO_2photoexctiation in this region produces mass-independent sulfur isotope signatures with positive $\Delta^{36}S/\Delta^{33}S$ ratios, as opposed to the negative $\Delta^{36}S/\Delta^{33}S$ ratios measured for stratospheric sulfate aerosols. This study further demonstrates that SO_2photoexcitation in the 250 nm to 350 nm absorption region produces positive $\Delta^{36}S/\Delta^{33}S$ ratios, even at temperatures approaching stratospheric temperatures. Our previous experiments (Whitehill and Ono, 2012; Whitehill et al., 2013) have been questioned as being

inapplicable to the modern atmosphere (Hattori et al., 2013) due to the experimental conditions (i.e. the addition of C_2H_2 to trap triplet-state SO_2). In the present study, we tested SO_2photoexcitation with two different longpass filters (250 nm longpass filter and 280 nm longpass filter) in a N_2/O_2 bath gas. In all cases, we produced sulfate products with positive $\Delta^{36}S/\Delta^{33}S$ ratios. Therefore, our experiments do not provide support for SO_2photoexcitation as ~~a~~ the dominant source of the isotope anomalies in modern atmospheric samples.

However, contribution from both absorption bands to the isotope effects observed in stratospheric sulfate aerosols is possible and should be considered further. Despite the strong correspondence between $\Delta^{36}S/\Delta^{33}S$ ratios in our photolysis experiments and stratospheric sulfate aerosol samples (Figure 3), the stratospheric sulfate aerosol samples produces a slightly shallower (less negative) $\Delta^{36}S/\Delta^{33}S$ slope than the majority of our experimental samples. This could be due in part to the effect of pressure on $\Delta^{36}S/\Delta^{33}S$ ratios (Masterson et al., 2011), as the one experiment performed at 7.7 kPa total pressure (Table 5) produced a $\Delta^{36}S/\Delta^{33}S$ more similar to the stratospheric sulfate aerosol samples than the experiments performed at 101.3 kPa total pressure. It could also be due, however, to mixing between the negative $\Delta^{36}S/\Delta^{33}S$ signatures from SO_2 photolysis and the positive $\Delta^{36}S/\Delta^{33}S$ signatures from SO_2photoexcitation. It is critical that future experiments further explore the isotope effects within these two absorption regions. However, it is also clear that SO_2photoexcitation alone is not likely to be responsible for the isotope signatures and that SO_2 photolysis is necessary as well.

4.8 Caveats for Experimental Studies

There are a number of difficulties with directly applying photochemical results from laboratory studies to processes occurringin the natural environment. One issue is the difference between the spectral photon flux of the Xe and D_2 arc lamps as compared with the solar spectrum. Comparisons of data from different light sources (Xe versus D_2 lamps) were made previously in static photochemical experiments (Whitehill and Ono, 2012) and showed minor differences depending upon the light source. However, despitethe large differences in the spectral photon flux between the Xe and D_2 light sources, the patterns in the isotope fractionation (i.e. $\delta^{34}S$ versus $\Delta^{33}S$ versus $\Delta^{36}S$) are similar. Both the Xe and D_2 light sources are broadband, unstructured light sources in the 180 nm to 220 nm absorption region, where SO_2 photolysis occurs. The solar spectrum, although also broadband, has considerably more fine structure in the spectrum, due to absorption by other gases such as O_2. As demonstrated

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in early SO_2 photolysis experiments (Farquhar et al. 2001), highly structured light sources (such as laser light sources) can cause anomalous isotope effects different from those observed in a broadband regime (Whitehill and Ono, 2012).

Unfortunately, the currently available measured absorption cross-sections (Danielache et al. 2008) do not reproduce the results of photochemical experiments (Whiteihll and Ono, 2012). As shown by Ueno et al. (2009), they predict negative$\Delta^{33}S$ values from SO_2 photolysis under reasonable atmospheric conditions. Photochemical experiments show positive $\Delta^{33}S$ values near zero (except in the self-shielding regime; Ono et al., 2013) under similar conditions. It is also important to note that the magnitude of uncertainties in the cross-section measurements (on the percent level) are too large to be considered quantitative for that of mass-independent fractionation observed in these reactions. Future, higher-precision and higher resolution cross-section measurements should resolve some of these discrepancies and allow for stratospheric fractionations under solar spectral conditions to be modeled. In the absence of this data, however, experiments using solar-like spectra (i.e. Xe arc lamp) can provide a first order constraint on the types of isotope fractionations expected under a solar regime.

Another major issue with the experiments that was discussed above is the poor control in the experiments over the amount of water in the system. Due to the fact that experiments were performed at room temperature rather than at vacuum, it is difficult to put definitive constraints on the amount of water present in the system. Although attempts were made to flush the systems with nitrogen (< 3 ppb H_2O) prior to each experiment, water could be adsorbed onto the surfaces of the system. The presence of water will cause HO_x chemistry to occur and open up an additional (mass-dependent, Harris et al. 2012) channel for sulfate formation. The amount of water in the system also affects the amount of SO_3 that ends up as sulfate aerosols. This is particularly an issue when attempting to estimate the rate of reactions in the system (Section 4.3 and 4.4). Differences in the amount of water within the system during different experiments could explain some of the isotopic variability between replicate experiments (Tables 4 and 5).Photoexcitation (250 nm to 350 nm) experiments performed in an identical photochemical system but with the addition of acetylene (C_2H_2) are not strongly affected by the presence of trace amounts of water in the system, and showed considerably better isotopic reproducibility (Whitehill et al. 2013; Table 3) than SO_2 photolysis experiments (Ono et al., 2013; Tables 2, 4, and 5). This suggests that variabilityin trace

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amounts of water present in the system could have a significant affect on the isotopic signatures during SO_2 photolysis, and that water vapor should be carefully controlled in future experiments.

4.84.9 Production and preservation of mass-independent sulfur isotope signatures in ice cores

The results presented in this paper can explain the production and preservation of mass-independent sulfur isotope signatures in the modern atmosphere. Large volcanic eruptions, such as Pinatubo (1991) and Agung (1963) inject large amounts of SO_2 into the stratosphere. Both direct injection into higher altitudes (i.e. above around 20 to 25 km) or stratospheric transport of the SO_2 plume can bring SO_2 to a sufficient altitude for SO_2 photolysis to occur. The process of SO_2 photolysis produces large mass-independent sulfur isotope signatures in the SO products, particularly when there is high SO_2 loading (and thus optical screening effects). Reaction of SO with O_2 to produce SO_3 (via R6) provides a pathway for the isotopic signature of SO to be preserved as SO_3, which can subsequently form sulfate aerosols. Some portion of the sulfate aerosols containing the mass-independent sulfur isotope signatures are transported to polar regions, where they can be deposited in polar precipitation and preserved in ice core records. A schematic illustration of the process is shown in Figure 9.

Some eruptions, despite their stratospheric influence, produce sulfate peaks in ice core records but do not contain mass-independent sulfur isotope signatures. Such eruptions include Cerro Hudson (1991, Savarino et al., 2003) and Laki (1783, Lanciki et al., 2012). Schmidt et al. (2012) discussed this issue previously and concluded that the Laki aerosols deposited in the Greenland ice cores were predominantly upper tropospheric or lower stratospheric in origin.Estimates for the height of the Laki (1783) eruption plume are only 15 km (Thordarson and Self, 2003), which penetrates the stratosphere but is not sufficiently high for SO_2 photolysis to be a dominant process (Schmidt et al., 2012). Due to the higher latitude of the eruption, transport processes are unlikely to bring the eruption plume to a sufficient altitude (25 km) for SO_2 photolysis to occur. Thus, despite the stratospheric influence of the Laki eruption, mass-independent sulfur isotope signatures in the preserved aerosols would not be expected. The situation is similar for the Cerro Hudson (1991) eruption, which had an injection height of 11 km to 16 km (Schoeberl et al., 1993). Again, given the high latitude of

the eruption, transport processes are likely insufficient to bring the plume ~~above 25 km~~to a sufficient altitude for SO_2 photolysis to becomea dominant process.

~~In contrast with this are major low~~Low-latitude eruptions such as Pinatubo (1991) might behave differently. Although the initial injection of the Pinatubo eruption was probably localized below 25 km, the evolution of the plume resulted in the plume reaching altitudes of 30 km or higher (Gobi et al., 1992), sufficient altitudes for SO_2 photolysis to play a role in the oxidation to sulfate. The largest mass-independent sulfur isotope signatures (with $\Delta^{33}S$ > 1‰) observed to date are from the Samalas (1257, Lavigne et al., 2013) eruption (Lanciki et al., 2012). Evidence suggests the eruption plume from this reaction reached a minimum of 34 km altitude, with a likely estimate being 43 km altitude (Lavigne et al., 2013). At this altitude, SO_2 photolysis would become a dominant process, and could explain why the signature from this eruption is significantly larger that the other eruptions. Thus, SO_2 photolysis, followed by SO oxidation to SO_3 (via R6), presents a consistent mechanism through which mass-independent sulfur isotope signatures can be produced and preserved in the modern, oxygenated stratosphere.

5 Conclusions

Laboratory photochemical experiments were carried out to investigate the production of mass-independent sulfur isotope effects under stratospheric conditions. For SO_2 photolysis in the 190 nm to 220 nm region, the magnitude of the mass-independent isotope signature increases with decreasing temperature. The isotope systematics, in particular $\delta^{34}S$ and $\Delta^{36}S$ values, show excellent agreement with an optical self-screening model basedon synthetic absorption cross sections (Lyons, 2007). SO_2photoexctiation experiments show similar signatures to previous experimental studies (Whitehill and Ono, 2012; Whitehill et al., 2013), with positive $\Delta^{33}S$ and $\Delta^{36}S$ values, but that differ significantly from expectations based on absorption cross sections (Danielache et al., 2012).

The SO_3 (recovered as sulfate) products from SO_2 photolysis in the presence of molecular oxygen carry mass-independent sulfur isotope signatures, suggesting a pathway for the direct oxidation of SO to SO_3. We hypothesize the $SO + O_2 + M \rightarrow SO_3 + M$ reaction (R6) and estimate the termolecular rate constant of the reaction to be on the order of 10^{-37} cm^6

molecules^{-2} s^{-1} or faster. This is consistent with previous constraints on the maximum rate of this reaction (Black et al., 1982).

We calculated the energies of stationary points on the singlet and triplet potential energy surfaces of SO_3 that are associated with the $SO(^3\Sigma^-)+O_2(^3\Sigma_g^-)$ asymptote at several different levels of theory and show that reaction R6 is theoretically possible via intersystem crossing between the singlet and triplet surfaces. We also show that the measured rate for SO + O_2 + $\rightarrow$ SO_2 + O reaction (R5) also requires intersystem crossing between the singlet and triplet surfaces.

Depending on the rate of R6, we predict that on the order of 10% of sulfate above 25 km altitude could be derived from the SO + O_2 + M channel. Given the large isotope fractionations produced during SO_2 photolysis, our model can explain the source and preservation mechanism of mass-independent sulfur isotope signatures measured in stratospheric sulfate aerosols in polar ice samples. Furthermore, o~~O~~ur modelexplains the temporal evolution of $\delta^{34}S$ and $\Delta^{33}S$ values following major volcanic eruptions, andconstrains the maximum altitude of the plume toabove 20 to 25 km~~and above~~ when non-zero $\Delta^{33}S$ values are observed.

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1 Table 1. Summary of experiments performed

Experiment	Lamp	Filter	*T* / K	Bath Gas	Presented in
photolysis (temp.)	200 W D_2	None	225 to 275	N_2	Figures 2, 5; Table 2
photoexcitation (temp.)	150 W Xe	250 LP, H_2O	225 to 275	N_2/C_2H_2	Figure 2; Table 3
photolysis (added O_2)	150 W Xe	None, 200 BP	298	N_2/O_2	Figures 3, 6; Tables 4, 5
photoexcitation (added O_2)	150 W Xe	250 LP, 280 LP	298	N_2/O_2	Figure 3; Table 5

2

Table 2. Isotope ratios of elemental sulfur products from the SO_2 photolysis temperature experiments (Section 2.2)

T / K	$\delta^{33}S$ / ‰	$\delta^{34}S$ / ‰	$\delta^{36}S$ / ‰	$\Delta^{33}S$ / ‰	$\Delta^{36}S$ / ‰
225	103.05	191.16	349.12	8.02	-32.4
225	97.85	177.76	315.71	9.13	-35.8
250	87.19	161.31	288.97	6.61	-29.8
250	80.68	146.58	259.31	7.18	-28.9
275	72.16	132.59	236.37	5.57	-24.1
275	70.35	129.04	227.26	5.50	-25.5

Table 3. Isotope ratios of organosulfur products from the SO_2photoexcitation temperature experiments (Section 2.2)

T / K	$\delta^{33}S$ / ‰	$\delta^{34}S$ / ‰	$\delta^{36}S$ / ‰	$\Delta^{33}S$ / ‰	$\Delta^{36}S$ / ‰
225	24.18	9.88	65.72	19.01	46.0
225	24.94	9.95	67.09	19.73	47.2
250	25.29	7.33	64.39	21.44	49.7
250	24.30	6.37	62.38	20.96	49.6
275	26.24	5.39	63.29	23.4	52.5
275	25.39	4.84	61.27	22.84	51.6

Table 4.Results from experiments of SO_2 photolysis in the presence of varying amounts of O_2 (Section 2.3) used to estimate k_{R6} (Sections 4.3 and 4.4).

Product	pO_2 / kPa	Time / ks	Yield / μmol S	$\delta^{33}S$ / ‰	$\delta^{34}S$ / ‰	$\delta^{36}S$ / ‰	$\Delta^{33}S$ / ‰	$\Delta^{36}S$ / ‰	calculatedk_{R6} / cm^6 $molecule^{-2}$ s^{-1}
*S^0 - 1	0.00	21.6		74.00	129.68	220.54	8.63	-31.9	
*S^0 - 2	0.00	21.6		78.42	137.52	232.90	9.18	-34.8	
S^0avg	0.00						8.91	-33.3	
*SO_3 - 1	0.00	21.6	35.3	14.16	25.64	43.82	1.02	-5.2	
*SO_3 - 2	0.00	21.6	28.9	11.51	21.14	36.21	0.67	-4.2	
SO_3	5.07	7.2	46.0	45.47	79.75	134.34	4.97	-19.5	1.4×10^{-37}
SO_3	5.07	7.2	32.6	50.85	89.24	150.93	5.59	-21.6	1.1×10^{-37}
SO_3	10.13	7.2	37.1	51.60	90.27	151.99	5.82	-22.5	1.3×10^{-37}
SO_3	10.13	7.2	41.3	51.35	91.22	155.00	5.13	-21.5	1.3×10^{-37}
SO_3	15.20	7.2	37.4	51.43	89.67	150.68	5.94	-22.6	1.3×10^{-37}
SO_3	15.20	7.2	20.8	55.14	97.09	164.55	5.97	-23.4	7.3×10^{-38}
SO_3	19.75	10.8	40.4	53.18	94.68	161.22	5.24	-22.2	8.3×10^{-38}
SO_3	19.75	10.8	39.1	54.18	96.59	164.45	5.29	-22.7	8.1×10^{-38}

* S^0 - 1 and SO_3 - 1 are elemental sulfur and SO_3 from the same experiment. Similarly, S^0 - 2 and SO_3 - 2 are elemental sulfur and SO_3 from the same experiment.

Table 5. Results from additional experiments of SO_2 photolysis in the presence of O_2 (Section 2.3). All results are from sulfate (SO_3) product. Experiments were performed at a constant total pressure of 101.3 kPa unless marked otherwise. Filter types are: 200 BP = 200 nm bandpass filter, 250 LP = 250 nm longpass filter, 280 LP = 280 nm longpass filter.

Filter	pSO_2 / Pa	pO_2 / kPa	Flow / $cm^3\ s^{-1}$	Time / ks	Yield / µmol S	$\delta^{33}S$ / ‰	$\delta^{34}S$ / ‰	$\delta^{36}S$ / ‰	$\Delta^{33}S$ / ‰	$\Delta^{36}S$ / ‰
none	314.0	19.00	16.67	1.8	62.3	38.45	67.23	117.84	4.22	-12.2
none	316.6	18.99	6.67	12.8	105.7	34.71	60.89	104.88	3.69	-12.5
none	50.7	20.06	1.67	18.0	70.9	32.91	58.18	95.36	3.26	-16.2
none	50.7	20.06	1.67	10.8	41.8	37.46	67.09	112.12	3.34	-17.0
none	25.2	20.16	1.68	18.0	40.8	22.80	40.08	64.63	2.31	-12.0
none	25.2	20.16	1.68	10.8	19.3	19.59	35.15	58.01	1.61	-9.2
*none	349.9	0.20	0.29	19.8	34.0	34.02	59.04	104.90	3.92	-9.2
200 BP	316.6	18.99	6.67	67.8	86.2	47.67	89.15	162.21	2.59	-11.9
200 BP	50.7	20.06	1.67	36.0	-	35.65	65.22	111.79	2.50	-14.0
250 LP	506.5	18.23	1.67	61.2	14.9	9.40	15.97	32.53	1.19	1.9
250 LP	506.5	18.23	1.67	61.2	1.9	19.56	33.12	68.70	2.60	4.5
280 LP	316.6	18.99	6.67	86.4	6.7	3.22	4.25	9.34	1.03	1.2

* Experiment performed at 7.7 kPa total pressure to test low pressure limit

Table 6. Comparison of asymptotic energies of $SO+O_2$ obtained on the singlet and triplet potential energy surfaces for SO_3 and those obtained by the sum of two separated species. All energies are in kJ mole^{-1} and are relative to the $SO(^3\Sigma^-) + O_2(^3\Sigma_g^-)$ calculated separately in each ab-initio method.

	B3LYP	CASSCF	CASPT2//CASSCF	UCCSD(T)F12a//B3LYP
$SO(^3\Sigma^-) + O_2(^3\Sigma_g^-)$ (separated)	0	0	0	0
$SO(^1\Delta) + O_2(^3\Sigma_g^-)$ (separated)	118.78	64.60	136.36	94.98
$SO(^3\Sigma^-) + O_2(^1\Delta_g)$ (separated)	160.83	86.57	98.28	121.55
$SO(^1\Delta) + O_2(^1\Delta_g)$ (separated)	279.57	151.17	234.64	216.48
$SO+O_2$ (singlet)	279.57	0.00	-6.86	217.19
$SO+O_2$ (triplet)	27.61	0.00	-6.61	122.59

Table 7. Energies for stationary points on the singlet state potential energy surface at various ab-initio levels. The energy is relative to the $SO(^3\Sigma^-) + O_2(^3\Sigma_g^-)$ asymptote and zero point energy is not included. All energies are given in kJ $mole^{-1}$.

	B3LYP	CASSCF	CASPT2//CASSCF	UCCSD(T)F12a//B3LYP
SO_3	-287.73	-262.92	-348.69	-411.58
cyclic-OSOO	-60.17	-50.21	-101.75	-142.72
trans-OSOO	42.09	53.72	-18.87	-17.66
cis-OSOO	19.33	35.82	-31.42	-39.08
TS1: trans-to-cis	108.95	135.14	66.32	42.76
TS2: trans-to-cyclic	62.51	69.71	3.10	0.17
TS3: cis-to-cyclic	108.95	114.18	50.42	43.26
TS4: cyclic-to-SO_3	82.42	69.25	56.61	70.33
$SO(^3\Sigma^-)+O_2(^3\Sigma_g^-)$	0.00	0.00	0.00	0.00
$SO_2(^1A_1)+O(^1D)$	292.04	159.28	206.27	152.84

Table 8. Energies for stationary points on the triplet state potential energy surface at various ab-initio levels. The energy is relative to the $SO(^3\Sigma^-) + O_2(^3\Sigma_g^-)$ asymptote and zero point energy is not included. All energies are given in kJ $mole^{-1}$.

	B3LYP	CASSCF	CASPT2//CASSCF	UCCSD(T)F12a//B3LYP
SO_3	136.02	293.21	115.90	75.14
cyclic-OSOO	-70.67	12.18	-105.06	-137.07
trans-OSOO	26.40	85.81	8.70	16.53
cis-OSOO	28.58	82.09	16.82	18.49
TS1: trans-to-cis	30.42	92.72	10.79	25.44
TS2: OSOO-to-cyclic	96.40	125.35	67.28	67.86
$SO_2 \ldots O$	23.35	-71.34	-31.55	-58.28
TS3: cyclic-to-$SO_2 \ldots O$	25.44	-62.93	-24.81	-54.06
$SO(^3\Sigma^-)+O_2(^3\Sigma_g^-)$	0.00	0.00	0.00	0.00
$SO_2(^1A_1)+O(^3P)$	26.69	-55.44	13.64	-52.93

Table 9. Reactions and rate constants included in the kinetic model of the chemistry occurring within reaction cell. Rate constants have units of s^{-1} for first order reactions, cm^3 $molecule^{-1}$ s^{-1} for second order reactions (and effective second order reactions, denoted *2), and cm^6 $molecule^{-2}$ s^{-1} for third order reactions.

Reaction Number	Reaction	Rate constant	Reaction Order	Source
Photochemical Reactions				
1	$O_2 + h\nu \rightarrow O + O$	1.0×10^{-5}	1	Yoshino et al. (1988, 1992)
2	$O_3 + h\nu \rightarrow O + O_2$	5.7×10^{-3}	1	Molina and Molina (1986)
3	$O_3 + h\nu \rightarrow O(^1D) + O_2$	1.0×10^{-1}	1	Molina and Molina (1986)
4	$H_2O_2 + h\nu \rightarrow OH + OH$	1.7×10^{-3}	1	Sander et al. (2011)
5	$HO_2 + h\nu \rightarrow O(^1D) + OH$	1.5×10^{-2}	1	Sander et al. (2011)
6	$SO_2 + h\nu \rightarrow SO + O$	5.2×10^{-3}	1	Manatt and Lane (1993)
7	$SO + h\nu \rightarrow S + O$	9.7×10^{-3}	1	Phillips (1981)
O_x Chemistry				
8	$O + O + M \rightarrow O_2 + M$	2.5×10^{-14}	*2	Tsang and Hampson (1986)
9	$O + O_2 + M \rightarrow O_3 + M$	1.5×10^{-14}	*2	Sander et al. (2011)
10	$O + O_3 \rightarrow O_2 + O_2$	8.0×10^{-15}	2	Sander et al. (2011)
$O(^1D)$ Chemistry				
11	$O(^1D) + O_2 \rightarrow O + O_2$	4.0×10^{-11}	2	Sander et al. (2011)
12	$O(^1D) + O_3 \rightarrow O_2 + O_2$	1.2×10^{-10}	2	Sander et al. (2011)
13	$O(^1D) + O_3 \rightarrow O + O + O_2$	1.2×10^{-10}	2	Sander et al. (2011)
14	$O(^1D) + H_2 \rightarrow OH + H$	1.2×10^{-10}	2	Sander et al. (2011)
15	$O(^1D) + H_2O \rightarrow OH + OH$	2.0×10^{-10}	2	Sander et al. (2011)
16	$O(^1D) + N_2 \rightarrow O + N_2$	3.1×10^{-11}	2	Sander et al. (2011)
17	$O(^1D) + SO_2 \rightarrow ?$	2.2×10^{-10}	2	Sander et al. (2011)
HO_x Chemistry				
18	$O + OH \rightarrow O_2 + H$	3.3×10^{-11}	2	Sander et al. (2011)

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19	$O + HO_2 \rightarrow OH + O_2$	5.9×10^{-11}	2	Sander et al. (2011)
20	$O + H_2O_2 \rightarrow OH + HO_2$	1.8×10^{-15}	2	Sander et al. (2011)
21	$H + O_2 + M \rightarrow HO_2 + M$	9.7×10^{-13}	*2	Sander et al. (2011)
22	$H + O_3 \rightarrow OH + O_2$	2.9×10^{-11}	2	Sander et al. (2011)
23	$H + HO_2 \rightarrow OH + OH$	7.2×10^{-11}	2	Sander et al. (2011)
24	$H + HO_2 \rightarrow O + H_2O$	1.6×10^{-12}	2	Sander et al. (2011)
25	$H + HO_2 \rightarrow H_2 + O_2$	6.9×10^{-12}	2	Sander et al. (2011)
26	$OH + O_3 \rightarrow HO_2 + O_2$	7.3×10^{-14}	2	Sander et al. (2011)
27	$OH + H_2 \rightarrow H_2O + H$	6.7×10^{-15}	2	Sander et al. (2011)
28	$OH + OH \rightarrow H_2O + O$	1.8×10^{-12}	2	Sander et al. (2011)
29	$OH + OH + M \rightarrow H_2O_2 + M$	6.4×10^{-12}	*2	Sander et al. (2011)
30	$OH + HO_2 \rightarrow H_2O + O_2$	1.1×10^{-10}	2	Sander et al. (2011)
31	$OH + H_2O_2 \rightarrow H_2O + HO_2$	1.8×10^{-12}	2	Sander et al. (2011)
32	$HO_2 + O_3 \rightarrow OH + O_2 + O_2$	1.9×10^{-15}	2	Sander et al. (2011)
33	$HO_2 + HO_2(+M) \rightarrow H_2O_2 + O_2(+M)$	2.6×10^{-12}	2 + *2	Sander et al. (2011)
SO_x Chemistry				
34	$O + SO_2 + M \rightarrow SO_3 + M$	1.3×10^{-11}	*2	Sander et al. (2011)
35	$O_3 + SO_2 \rightarrow SO_3 + O_2$	2.0×10^{-22}	2	Sander et al. (2011)
36	$OH + S \rightarrow H + SO$	6.6×10^{-11}	2	Sander et al. (2011)
37	$OH + SO \rightarrow H + SO_2$	8.3×10^{-11}	2	Sander et al. (2011)
38	$OH + SO_2 + M \rightarrow HOSO_2 + M$	9.6×10^{-13}	*2	Sander et al. (2011)
39	$HO_2 + SO_2 \rightarrow OH + SO_3$	1.0×10^{-18}	2	Sander et al. (2011)
40	$S + O_2 \rightarrow SO + O$	2.3×10^{-12}	2	Sander et al. (2011)
41	$S + O_3 \rightarrow SO + O_2$	1.2×10^{-11}	2	Sander et al. (2011)
42	$SO + O_3 \rightarrow SO_2 + O$	8.0×10^{-17}	2	Sander et al. (2011)
43	$SO + O_2 + M \rightarrow SO_3 + M$	Varies	*2	Sander et al. (2011)

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44	$SO + O_3 \rightarrow SO_2 + O_2$	8.4×10^{-14}	2	Sander et al. (2011)
45	$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$	4.3×10^{-13}	2	Sander et al. (2011)
46	$SO + HO_2 \rightarrow SO_2 + OH$	2.8×10^{-11}	2	DeMore et al. (1997)
47	$SO + SO \rightarrow SO_2 + S$	8.3×10^{-16}	2	Chung et al. (1975)
48	$SO + O + M \rightarrow SO_2 + M$	1.3×10^{-11}	*2	Cobos et al. (1985)
49	$SO + SO_3 \rightarrow SO_2 + SO_2$	2.0×10^{-15}	2	Chung et al. (1975)
50	$S + S + M \rightarrow S_2 + M$	7.5×10^{-14}	*2	Pavlov and Kasting (2002)
51	$SO_2 + 2\ H_2O \rightarrow$ aerosol	2.9×10^{-31}	3 (special)	Sander et al. (2011)
Other				
k_out	Exit rate from cell	2.1×10^{-2}	1	

* Effective second order reactions based on falloff curves for [M] = 2.5×10^{19} and M = N_2, O_2. See sources for additional information.

Reaction Number	Reaction	Rate constant	Reaction Order	Source
Photochemical Reactions				
R4	$SO_2 + h\nu \rightarrow SO + O$	5.2×10^{-3}	1	Manatt and Lane (1993)
R9	$O_2 + h\nu \rightarrow O + O$	1.7×10^{-6}	1	Yoshino et al. (1988, 1992)
R10	$O_3 + h\nu \rightarrow O + O_2$	1.1×10^{-1}	1	Molina and Molina (1986)
O_x Chemistry				
R11	$O + O + M \rightarrow O_2 + M$	1.0×10^{-33}	3	Sander et al. (2011)
R12	$O + O_2 + M \rightarrow O_3 + M$	6.0×10^{-34}	3	Sander et al. (2011)
R13	$O + O_3 \rightarrow O_2 + O_2$	8.0×10^{-15}	2	Sander et al. (2011)
SO_x Chemistry				
R5	$SO + O_2 \rightarrow SO_2 + O$	8.0×10^{-11}	2	Sander et al. (2011)
R6	$SO + O_2 + M \rightarrow SO_3 + M$	Varies	3	
R7	$SO_2 + O + M \rightarrow SO_3 + M$	1.3×10^{-14}	*2	Sander et al. (2011)

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R8	$SO + SO \rightarrow SO_2 + S$	8.3×10^{-16}	2	Chung et al. (1975)
R14	$SO + O + M \rightarrow SO_2 + M$	1.3×10^{-11}	*2	Cobos et al. (1985)
R15	$SO + O_3 \rightarrow SO_2 + O_2$	8.4×10^{-14}	2	Sander et al. (2011)
R16	$S + O_2 \rightarrow SO + O$	2.3×10^{-12}	2	Sander et al. (2011)
R17	$S + O_3 \rightarrow SO + O_2$	1.2×10^{-11}	2	Sander et al. (2011)
Other				
k_out	Exit rate from cell	2.1×10^{-2}	1	

* Effective second order reactions based on falloff curves for [M] = 2.5×10^{19} and M = N_2, O_2. See sources for additional information.

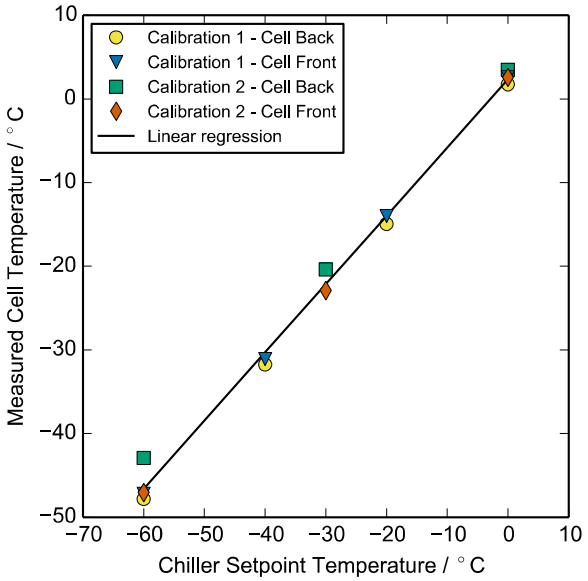


Figure 1.Results of the temperature calibration for the temperature controlled photochemical reactor described in Section 2.1 The linear regression shown was used to calibrate the temperature within the cell based on the setpoint temperature of the chiller. The regression line is $(T_{Cell} / °C) = 0.8160 \times (T_{Chiller} / °C) + 2.3514$.

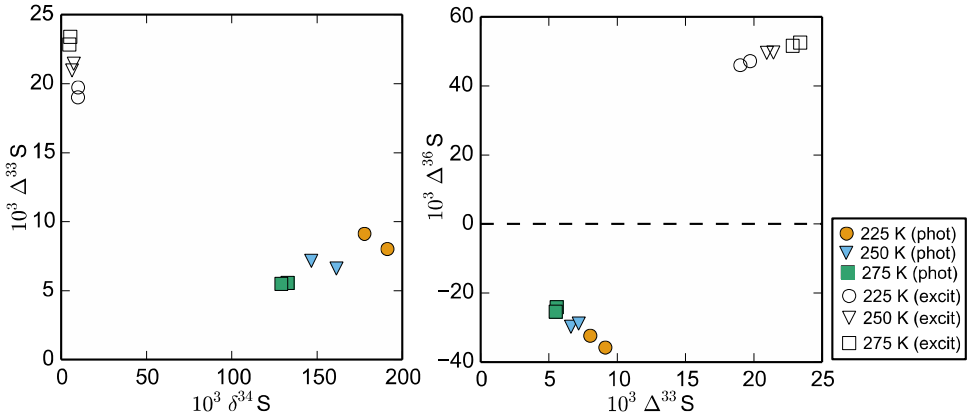


Figure 2.Results of the temperature experiments for SO_2 photolysisand SO_2photoexcitation (Section 2.2). Results from SO_2 photolysis experiments (phot) are shown in filled symbols and SO_2photoexcitation experiments (excit) are in empty symbols.

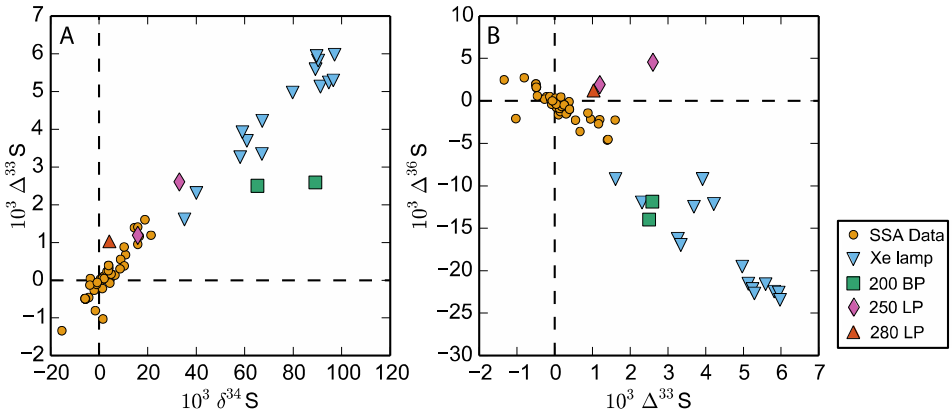


Figure 3.Isotopic results of the $SO_2 + O_2$ experiments described in Section 2.3, compared with stratospheric sulfate aerosol samples (SSA Data) from Savarino et al. (2003), Baroni et al. (2007, 2008), Lanciki (2010), and Lanciki et al. (2012).

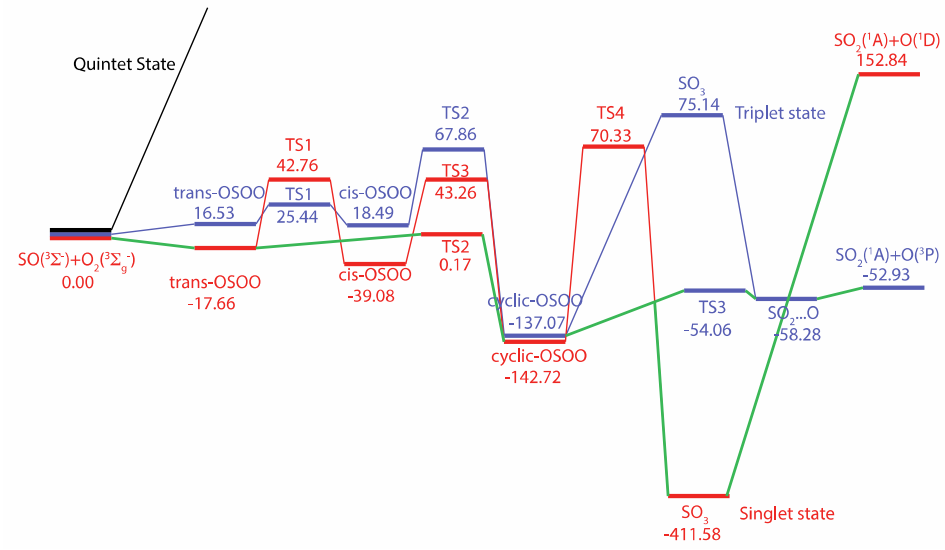
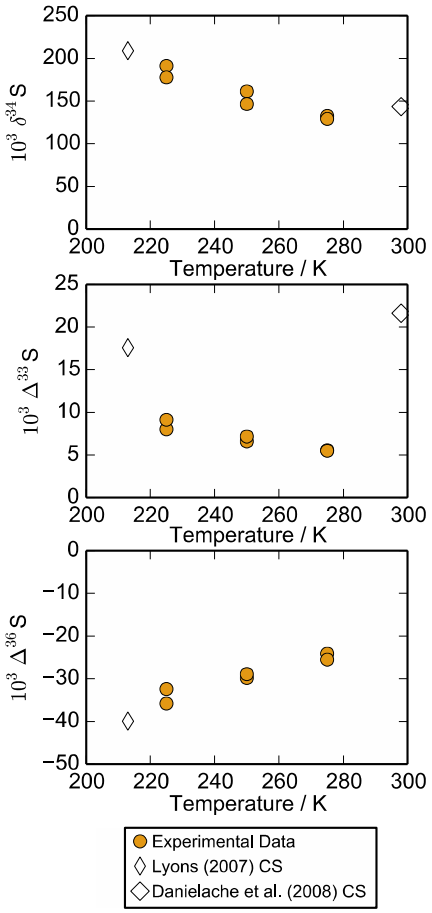


Figure 4.Potential energy profiles on the singlet (red) and triplet (blue) potential energy surfaces for the SO_3 system obtained using B3LYP optimization followed by UCCSD(T)-F12a single point calculation, with the AVTZ basis set. The possible intersystem crossing pathway is depicted by the solid green line. All energies are given in kJ mole^{-1} relative to the $SO(^3\Sigma^-)+O_2(^3\Sigma_g^-)$ asymptote. The quintet (black) state is shown qualitatively due to its high energy.



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2 Figure 5.Comparison of SO_2 photolysis temperature experiment results with predictions from
3 isotopologue-specific absorption cross-sections (CS).

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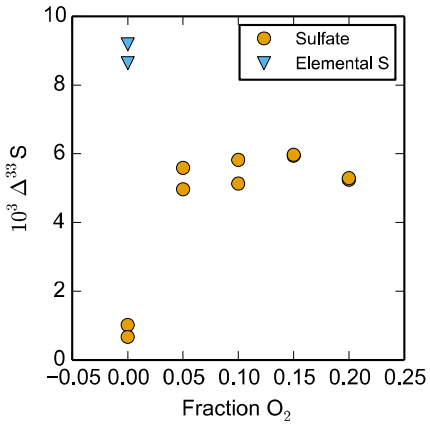

Figure 6.$\Delta^{33}S$ values of sulfate from the photolysis of SO_2 in the presence of O_2 compared with elemental sulfur and sulfate from SO_2 photolysis in the absence of O_2. Conditions are described in Section 4.3 and Table 4.

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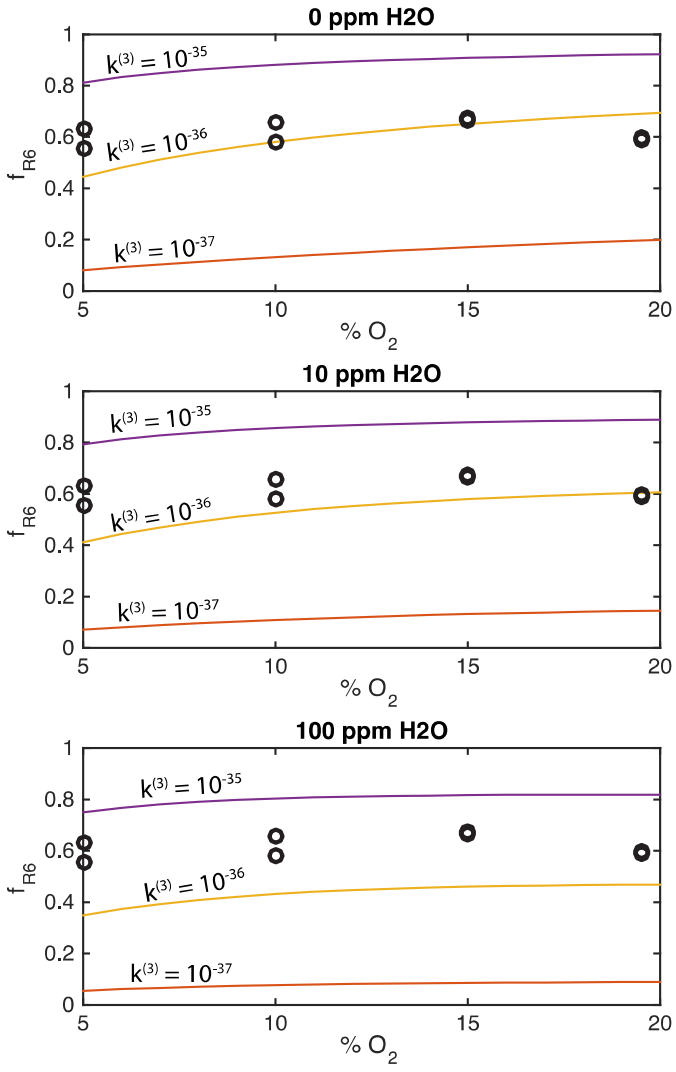

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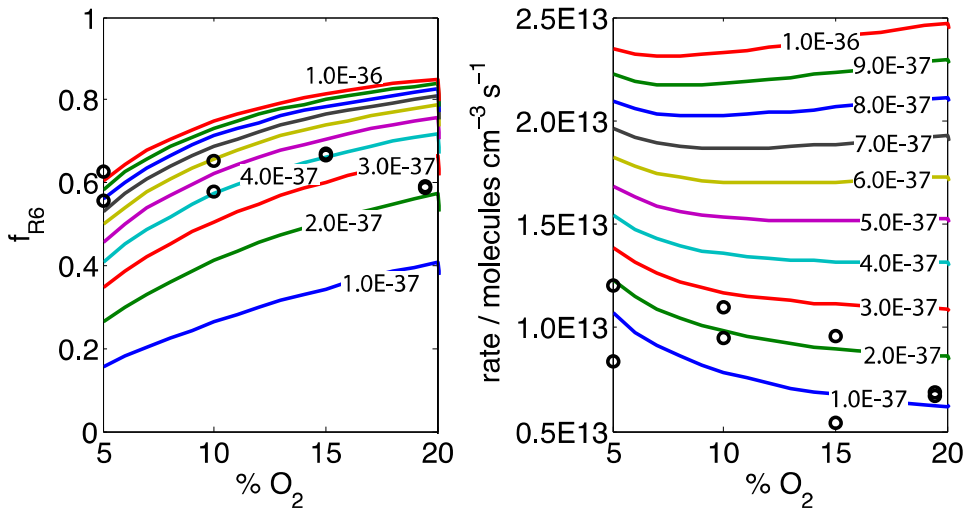

Figure 7. Results of kinetic model (Section 4.4, Table 9) compared to experimental data (circles) for f_{R6} (Equation 5) versus fraction of SO_3 formed from R6 in the model ~~(left), as well as total SO_3 formation rate (right).~~ Contours on the plot are labeled with the value of rate constant k_{R6} input into the model for a given run. Experimental data is plotted as black circles. The model was run for three input values of H_2O concentration: 0 ppmv (top), 10 ppmv (middle), and 100 ppmv (bottom).

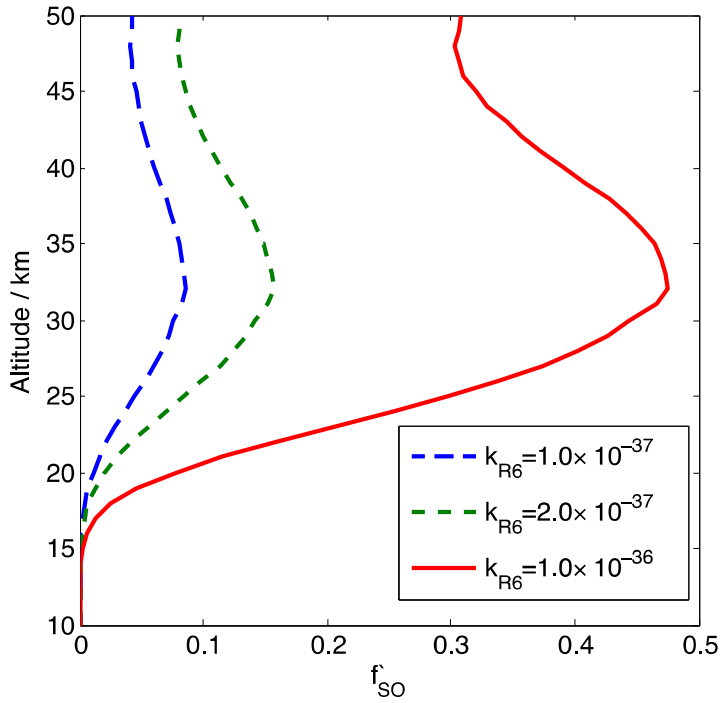

Figure 8.Fraction of sulfate derived from reaction channel R6 (f_{SO}) as a function of altitude for different values of k_{R6}.

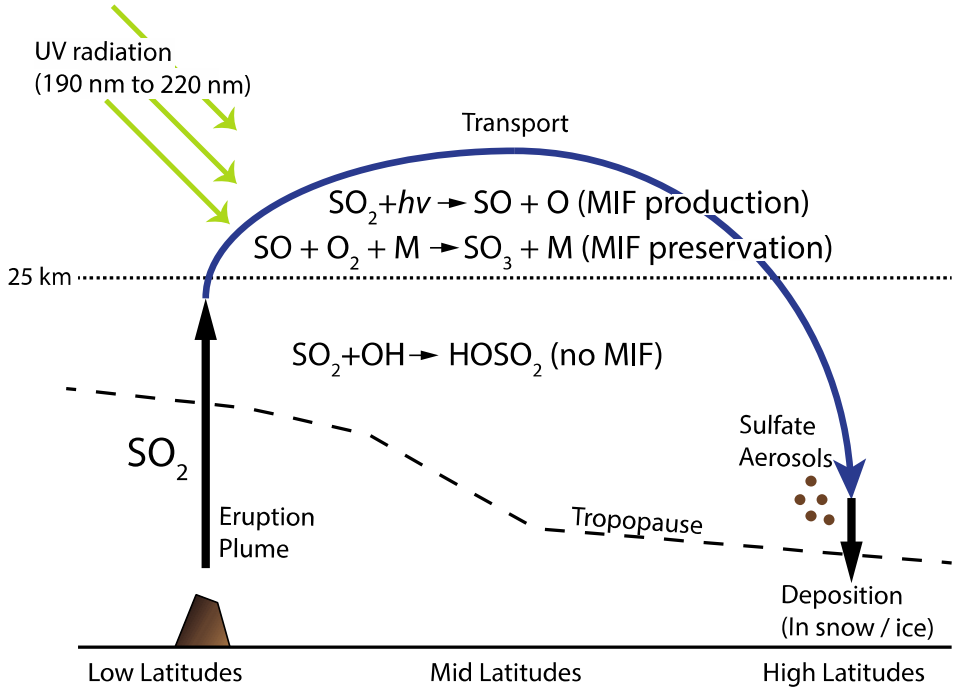

Figure 9.Schematic illustration of the production and preservation of mass-independent fractionation (MIF) in sulfur isotopes following explosive volcanic eruptions. Low latitude eruptions such as Pinatubo (1991) inject large amounts of SO_2 into the stratosphere. Through stratospheric transport, it is brought to altitudes where SO_2 photolysis can occur, producing large MIF signatures. The product of SO_2 photolysis, SO, is preserved via termolecular reaction with O_2. The resulting SO_3 forms sulfate aerosols, which are deposited at high latitudes in polar snow and ice core records. SO_2 oxidation below around 25 km is dominantly by OH, which is a mass-dependent process.

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