SO₂ photolysis as a source for sulfur mass-independent isotope signatures in stratospheric aerosols

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Abstract

Signatures of sulfur isotope mass-independent fractionation (S-MIF) have been observed in stratospheric sulfate aerosols deposited in polar ice. The S-MIF signatures are 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 to 220 nm region and photoexcitation in the 250 to 350 nm region. The SO$_2$ photolysis (SO$_2$ + hν → 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, including high $^{34}$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 for stratospheric sulfate aerosols. SO$_2$ photoexcitation 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$_2$ produced SO$_3$ with S-MIF signals, suggesting the transfer of the MIF signals of SO to SO$_3$ by the SO + O$_2$ + M → SO$_3$ + M reaction. This is supported with energy calculations of stationary points on the SO$_3$ potential energy surfaces, which indicate that this reaction occurs slowly on a single adiabatic surface, but that it can occur more rapidly through intersystem crossing. The results from our experiments constrain the termolecular reaction rate to between $1.0 \times 10^{-37}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ and $1.0 \times 10^{-36}$ cm$^6$ molecule$^{-2}$ s$^{-1}$. This rate can explain the preservation of mass independent isotope signatures in stratospheric sulfate aerosols and provides a 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 and an SO$_2$ plume reaching an altitude of 25 km and higher.
1 Introduction

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:

\[
\text{SO}_2 + \text{OH} + \text{M} \rightarrow \text{HOSO}_2 + \text{M} \quad \text{(R1)}
\]

This reaction is followed by:

\[
\text{HOSO}_2 + \text{O}_2 \rightarrow \text{SO}_3 + \text{HO}_2 \quad \text{(R2)}
\]

In the presence of H$_2$O, SO$_3$ readily forms sulfuric acid (H$_2$SO$_4$) via:

\[
\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \quad \text{(R3)}
\]

Ab-initio transition state theory calculations of the isotope effect for OH 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 an inverse 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 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). The experimentally measured isotope effect is insufficient to explain the roughly 2 % enrichment in H$_2^{34}$SO$_4$.
relative to H$_2$SO$_4$ following the major Mt. Agung (1963) eruption (Castleman et al., 1974). 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, 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 to 350 nm absorption region (Savarino et al., 2003; Hattori et al., 2013), SO$_2$ photolysis in the 190 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 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 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 25 km in the wavelength region of 190 to 220 nm, which lies in the spectral window between the Schumann–Runge absorption edge of
oxygen (O₂) and the Hartley bands of ozone (O₃). SO₂ photolysis produces sulfur monoxide (SO) and O(³P) via the following reaction:

\[ \text{SO}_2 + h\nu \rightarrow \text{SO} + \text{O}(³\text{P}) \]  (R4)

It is generally accepted that this reaction is followed by rapid oxidation of SO to SO₂ via (Black et al., 1982; Savarino et al., 2003; Pavlov et al., 2005):

\[ \text{SO} + \text{O}_2 \rightarrow \text{SO}_2 + \text{O}(³\text{P}) \]  (R5)

Reactions (R4) and (R5) combine to form a null cycle for sulfur, but catalyze the formation of odd oxygen (Bekki, 1995). If SO is completely oxidized to SO₂, no isotopic signature from SO₂ photolysis can be preserved (Pavlov et al., 2005).

We propose an additional channel where SO is oxidized directly to SO₃ via the termolecular reaction:

\[ \text{SO} + \text{O}_2 + \text{M} \rightarrow \text{SO}_3 + \text{M} \]  (R6)

A previous study by Black et al. (1982) showed that the maximum termolecular rate constant for Reaction (R6) is 10⁻³⁶ cm⁶ 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 SO₂ 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 SO₂ photolysis (190 to 220 nm) and SO₂ photoexcitation (250 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 present a simple steady state
photochemical model to show that the 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 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\textsubscript{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\textsubscript{2} was flowed through the cell at a rate of 3.33 cm\textsuperscript{3} s\textsuperscript{-1} (200 sccm, standard cubic centimeter per minute). Thermocouples placed at the front and rear of the cell gave consistent measurements to within 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 Fig. 1.

2.2 Temperature effect on SO\textsubscript{2} photolysis (190 to 220 nm) and photoexcitation (250 to 350 nm)

The temperature effect on SO\textsubscript{2} photolysis (190 to 220 nm) was measured using the temperature-controlled reaction cell described in Sect. 2.1. Experiments were performed in a nitrogen-flushed glove box to prevent the spectral interference from the Schumann–Runge band of oxygen (O\textsubscript{2}). A 200 W deuterium (D\textsubscript{2}) arc lamp (D 200 F, Heraeus Noblelight) 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\textsubscript{2} (in N\textsubscript{2}) was flowed through the cell at a rate of 3.33 cm\textsuperscript{3} s\textsuperscript{-1} (200 sccm) for all experiments, and pressure within the cell was held constant at 101.3 kPa, giving an SO\textsubscript{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. Elemental sulfur was recrystallized from DCM 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 Sect. 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 (C₂H₂) was used to trap triplet excited-state SO₂ (³SO₂). During experiments, 5 % SO₂ (in N₂), pure C₂H₂ (Atomic Absorption Grade), and pure N₂ (Ultra High Purity grade) were flowed through the cell continuously at a rate of 0.67 cm³ s⁻¹ (40 sccm), 0.03 cm³ s⁻¹ (2 sccm), and 2.63 cm³ s⁻¹ (158 sccm), respectively. Pressure in the cell was held constant at 101.3 kPa, giving a total flow rate of 3.33 cm³ s⁻¹, an SO₂ partial pressure of 1.01 kPa, and a C₂H₂ 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 Sect. 2.4.

### 2.3 SO₂ photochemistry in the presence of O₂

The photochemistry of SO₂ + O₂ with ultraviolet radiation was studied using a reaction cell at room temperature. The 150 W Xe arc lamp (described in Sect. 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 SO₂, but most experiments were performed with the Xe lamp and no filters.

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 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 sulfate was converted to silver sulfide using the method of Forrest and Newman (1977). Multiple sulfur isotope ratios were measured as described in Sect. 2.4.

### 2.4 Isotope analysis of photochemical products

Photochemical products were converted to silver sulfide (Ag$_2$S). Ag$_2$S was rinsed well three to four times with deionized water and then dried completely at 353 K. Dried Ag$_2$S was weighed for total yield and about 8 µmol of Ag$_2$S 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 h 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 1.6 µmol of Ag$_2$S 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 $\text{SO} + \text{O}_2 \rightarrow \text{SO}_3 \rightarrow \text{SO}_2 + \text{O}$ 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 ($^1\text{A}_1^\prime$), but does not dissociate to the ground state products SO$_2(^1\text{A}_1) + \text{O}(^3\text{P})$ but to SO$_2(^1\text{A}_1) + \text{O}(^1\text{D})$. 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. 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 perturbative triple excitations method (UCCSD(T)-F12a; Knizia et al., 2009).

In addition, complete active space self consistent field (CASSCF) calculations were performed (Knowles and Werner, 1985, 1988). Multi-reference Rayleigh Schrodinger 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 2$s$ orbital for O and the 3$s$ orbital for S were closed, resulting in an active space of 16 electrons in 12 orbitals (16,12). 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.

\[ \delta^xS = \frac{xR_{\text{product}}}{xR_{\text{reference}}} - 1 \]  

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 \( \text{SO}_2 \). 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:

\[ \Delta^{33}S = \frac{(\delta^{33}S + 1)}{(\delta^{34}S + 1)^{0.515}} - 1 \]  

and

\[ \Delta^{36}S = \frac{(\delta^{36}S + 1)}{(\delta^{34}S + 1)^{1.90}} - 1 \]

Almost all physical, chemical, and biological processes fractionate isotopes mass-dependently (i.e. \( \Delta^{33}S = 0 \) and \( \Delta^{36}S = 0 \)). \( \text{SO}_2 \) photochemistry, as well as the photochemistry of other sulfur gases such as \( \text{CS}_2 \), are some of the few exceptions that 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$_2$ photoexcitation are given in Tables 2 and 3, whereas results from SO$_2$ + O$_2$ experiments are presented in Tables 4 and 5. Tables 6–8 give the results from energy calculations on the potential energy surfaces of SO$_3$.

3.1 Temperature experiments

Results from the temperature experiments (Sect. 2.2) are shown in Fig. 2. The SO$_2$ photolysis (190 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 δ$^{34}$S, Δ$^{33}$S, and Δ$^{36}$S, respectively. The relationship between isotopes (i.e. Δ$^{33}$S vs. δ$^{34}$S and Δ$^{36}$S vs. Δ$^{33}$S) did not change significantly as temperature was decreased (0.04 to 0.05 for Δ$^{33}$S/δ$^{34}$S and −3.9 to −4.6 for Δ$^{36}$S/Δ$^{33}$S). SO$_2$ photoexcitation (250 to 350 nm) show decreasing magnitude Δ$^{33}$S and Δ$^{36}$S values at lower temperatures (22.8‰ to 19.0‰ and 52.5‰ to 46.0‰ for Δ$^{33}$S and Δ$^{36}$S, respectively; Table 3). Even at lower temperatures, the product from SO$_2$ photoexcitation experiments show positive Δ$^{33}$S and Δ$^{36}$S values, as shown previously in room-temperature experiments (Whitehill and Ono, 2012; Whitehill et al., 2013).

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 Fig. 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., 2010...
2013) suggest an SO2 photolysis source for the isotope effects during broadband SO2 irradiation with the Xe lamp light source.

Experiments focusing on the photoexcitation band of SO2 using the 250 nm longpass filter (250 LP) and 280 nm longpass filter (280 LP) display a different isotope signature, characterized by positive $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values, whereas sulfate from SO2 photolysis has positive $\Delta^{33}\text{S}$ and negative $\Delta^{36}\text{S}$ 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.

### 3.3 Potential energy surfaces of SO3

Asymptotic energies of SO + O2 on each potential energy surface were compared with the energies obtained by separate calculations of each species with a certain spin (Table 6). CASSCF results correctly produced degenerate energies for the SO+O2 asymptote on the singlet and triplet states, which exactly match the sum of the energies on the SO($^3\Sigma^\text{−}$) and O2($^3\Sigma^\text{−}_g$) calculated separately. CASPT2 results also show the correct degenerate behavior but the energies shift slightly from those calculated separately, which presumably arises from the perturbation. On the other hand, UCCSD(T)-F12a and B3LYP results both attribute SO+O2 on the singlet state to SO($^1\Delta$) + O2($^1\Delta_g$), and B3LYP even gives a qualitatively incorrect energy for SO + O2 on the triplet state, while UCCSD(T)-F12a attributes this one to SO($^1\Delta$) + O2($^3\Sigma^\text{−}_g$). An important conclusion from these data is that one has to use a multi-reference method if an accurate global adiabatic potential energy surface is desired 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 methods can accurately describe the PES away from the SO + O2 region; they are capable of describing several SO3 isomers and the SO2 + O product channel reasonably well.
Energies for the stationary points computed using multi-reference approaches are reported relative to that of the SO(3Σ−) + O2(3Σg−) asymptote. However, the active space used in our CASSCF calculations is not sufficient to provide quantitatively accurate results, but a larger 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(3Σ−) + O2(3Σg−) asymptote, we have used the UCCSD(T) energy sum of the two reactants with the correct spins calculated separately, which has been shown 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 Tables 7 and 8, and the reaction pathways on both PESs are shown graphically in Fig. 4, 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(3Σ−) + O2(3Σg−) → SO3(1A′) reaction (−411.29 kJ mole−1), the SO(3Σ−) + O2(3Σg−) → SO2(1A1) + O(3P) reaction (−54.56 kJ mole−1) and the SO(3Σ−) + O2(3Σg−) → SO2(1A1) + 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 SO2 photochemistry

Isotopologue-specific absorption cross sections are expected to correctly predict the isotope effects from SO2 photolysis (in the 190 to 220 nm region) but fail to reproduce the isotope effects from SO2 photoexcitation (in the 250 to 350 nm region). This is due to the differences in the photophysics and photochemistry between the two absorption regions, which result in different mechanisms for MIF formation (Whitehill and Ono, 2012; Ono et al., 2013; Whitehill et al., 2013).
In the 165 to 235 nm wavelength region, SO$_2$ photolysis 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 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 $^{33}\text{SO}_2$ has a longer excited-state lifetime prior to dissociation than the other isotopologues.

$\text{SO}_2$ photoexcitation in the 250 to 350 nm absorption region produces isotope effects by a completely different mechanism. $\text{SO}_2$ photoexcitation in the 250 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 $\text{SO}_2$ 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 of the isotope effects in photochemical products following $\text{SO}_2$ photoexcitation in the 250 to 350 nm absorption region.

Photoexcitation of $\text{SO}_2$ in the presence of $\text{O}_2$ produces sulfate with both positive $\Delta^{33}\text{S}$ and positive $\Delta^{36}\text{S}$ 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 photophysics of excited-state $\text{SO}_2$ rather than the photochemistry 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 to 320 nm region (Whitehill et al., 2013). This is expected if isotope selective intersystem crossing is overprinting the isotope signals produced by cross section differences.
4.2 Temperature effects on SO$_2$ photolysis

Lyons (2007, 2008) presented isotopologue-specific absorption cross-sections for SO$_2$ in the 190 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 $\sim 2$ 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 Fig. 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 (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 $^{33}\text{SO}_2$. 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 $\Delta^{33}\text{S}$ 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 $\Delta^{33}\text{S}$ values decrease in the presence of high bath gas pressures. This pressure quenching effect is most noticeable for $\Delta^{33}\text{S}$ and does not affect $\delta^{34}\text{S}$ or $\Delta^{36}\text{S}$ values as strongly.

We conclude that the Lyons (2007, 2008) cross sections can 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 $\delta^{34}\text{S}$ 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 and R2, if water is present), O$_2$ oxidation of SO from SO$_2$ photolysis (Reactions R4 and R6), and O oxidation of SO$_2$ via

$$\text{SO}_2 + \text{O} + \text{M} \rightarrow \text{SO}_3 + \text{M} \quad (R7)$$

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 Reaction (R6) will trap the isotopic composition of SO as SO$_3$ and carry the mass-independent sulfur isotope signature from SO$_2$ photolysis (Reaction 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 0.127 kPa (Table 4; Fig. 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$^0$) and SO$_3$ aerosols were formed, with the elemental sulfur (S and related species) formed from SO via:

$$\text{SO} + \text{SO} \rightarrow \text{SO}_2 + \text{S}$$  \hspace{1cm} (R8)

SO photolysis is expected to be a minor source of S compared to Reaction (R8). In the absence of oxygen, SO$_3$ is formed primarily via O oxidation of SO$_2$ (Reaction 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 Reactions R5 or R6) competes with SO disproportionation (Reaction 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 Reaction (R6). In particular,

$$f_{R6} = \frac{\Delta^{33}S_{\text{sulfate, with O}_2}}{\Delta^{33}S_{S^0, \text{no O}_2}}$$  \hspace{1cm} (4)

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

$$\text{rate } R6 = k_{R6}[SO][O_2][M]$$

(5)

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 Eq. (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:

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

(6)

where $J_{SO_2}$ is the photolysis rate constant for reaction (R4). This photolysis rate constant was calculated assuming a spectral irradiance for our 150 W Xe arc lamp of:

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

(7)

where $F_0$ is the spectral irradiance of the xenon lamp at wavelength $\lambda$ (Ono et al., 2013). The spectral irradiance 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 0.127 kPa, this provided a photolysis rate constant of $J_{SO_2} = 5.2 \times 10^{-3}$ s$^{-1}$. The rate constant for reaction R5 is $k_{R5} = 8.0 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Sander et al., 2011) at room temperature (298 K). Using these values and Eqs. (6) and (7), the rate constant for Reaction (R6) ($k_{R6}$) was calculated iteratively. Calculated rate constants ranged from
k_{R6} = 7.3 \times 10^{-38} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \text{ to } k_{R6} = 1.4 \times 10^{-37} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}, with an average value of \( k_{R6} = 1.1 \times 10^{-37} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \) (Table 4). This rate estimate is consistent with the upper bound on \( k_{R6} \leq 1 \times 10^{-36} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \) by Black et al. (1982).

The 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 to 220 nm) is likely to decrease over the course of the lamp’s lifetime, this makes the calculated SO₂ photolysis rate (and resulting SO number density) an upper bound. Reducing the SO₂ photolysis rate increases the effective rate constant. A second source of error is the assumption that we trapped 100% of the SO₃ formed as sulfate. It is possible that some fraction of the SO₃ 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.

4.4 Constraining the rate of the SO + O₂ + M reaction using a kinetic model

To further constrain the rate of Reaction (R6) (the SO + O₂ + M \rightarrow SO₃ + M reaction), we constructed a kinetic model of the chemistry occurring within the cell. We used the same data and conditions as Sect. 4.3, but explicitly modeled the chemistry occurring within the system. SO₂ photolysis rates were calculated as discussed in Sect. 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$_3$. O($^1$D) formed from O$_3$ photolysis was assumed to be instantaneously quenched by N$_2$ and O$_2$ to O($^3$P) and not significantly affect the chemistry of the system.

Reactions considered, rate constants for those reactions, and the sources for the rate constants are given in Table 9. When possible, effective second-order rate constants (calculated assuming $T = 298$ K and $[M] = 2.5 \times 10^{19}$ 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 (Eq. 5) as well as total product (SO$_3$) formation rates. Simulations performed with values of $k_{R6}$ between $1.0 \times 10^{-37}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ and $1.0 \times 10^{-36}$ cm$^6$ molecule$^{-2}$ s$^{-1}$. The observed $f_{R6}$ value (Eq. 5) is best fit by the $k_{R6}$ between $2 \times 10^{-37}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ and $10 \times 10^{-37}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ (Fig. 7, left). The yield of SO$_3$ indicates a lower rate constant of less than $1 \times 10^{-37}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ to $3 \times 10^{-37}$ cm$^6$ molecule$^{-2}$ s$^{-1}$, potentially reflecting low recovery of SO$_3$ in our experiments (Fig. 7, right). Nonetheless, this range of results is consistent with the rate estimate obtained in Sect. 4.3. Thus, our best estimate for the rate of reaction R6 is somewhere between $1.0 \times 10^{-37}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ and $1.0 \times 10^{-36}$ cm$^6$ molecule$^{-2}$ s$^{-1}$. As discussed in Sect. 4.3, the model is sensitive to the SO$_2$ 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$_2$($^3\Sigma_g^-$) → SO$_3$($^1\Delta_1'$) reaction (Fig. 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
is the global minimum, followed by the cyclic-OSOO. There are two shallow wells, denoted as trans-OSOO and cis-OSOO, at the CASPT2 and UCCSD(T)-F12a levels, but they seem 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(\(^3\Sigma_g^-\)) → SO_3(\(^1\Pi\)) 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 298 K of 2.7 \(\times\) 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 \(\times\) 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 \(\times\) 10\(^{-18}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), calculated assuming \(k_{R6} = 1.0 \times 10^{-37}\) cm\(^6\) molecule\(^{-1}\) s\(^{-1}\) and [M] = 2.5 \(\times\) 10\(^{19}\)). We thus conclude that the SO(\(^3\Sigma^-\)) + O_2(\(^3\Sigma_g^-\)) → SO_3(\(^1\Pi\)) + O(\(^3\Pi\)) 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 (Fig. 4; Table 8). The global minimum moves to the cyclic-OSOO, which has a similar geometry to the singlet (ground) state counterpart but with different bond lengths. On the other hand, SO_3(\(^3\Pi\)) becomes highly unfavorable; for example, it is 75.14 kJ mole\(^{-1}\) higher than the SO + O_2 reactant 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\(^3\Sigma_g^-\)) → SO\(_2\(^1\text{A}_1\)) + O\(^3\text{P}\) reaction on the triplet PES has a rate constant of \(2.7 \times 10^{-25}\) 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 Fig. 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 due to the fact that the cyclic-OSOO isomer on both PESs has nearly the same energy. A possible non-adiabatic reaction pathway is depicted in Fig. 4 by the green solid lines connecting every two stationary points. Specifically, for the SO\((^3\Sigma^-) + O_2\(^3\Sigma_g^-\)) → SO\(_3\(^1\text{A}_1\)) 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\(^3\Sigma_g^-\)) → SO\(_2\(^1\text{A}_1\)) + O\(^3\text{P}\) 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 introduce the intersystem crossing have been proposed by other authors for the SO\(_3\) → SO\(_2\) + O reactions (Davis, 1974; Westenberg and Dehaas, 1975; Astholz et al., 1979), thanks to the relatively large spin-orbit coupling. The barrier associated with the intersystem crossing pathway seems to be consistent with the fast rate of Reaction (R5), and supports the facile formation of SO\(_3\).

Unfortunately, rate constants involving the intersystem crossing cannot be readily determined without global PESs for both spin states and the coupling between them. Such a goal can only be achieved by a multi-reference method or configuration interaction method, which is infeasible at the current level.
4.6 Contribution of the SO + O₂ + 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 Reaction (R6) to that formed via OH oxidation of SO₂ (Reaction R1) and O oxidation of SO₂ (Reaction R7) under a select set of atmospheric conditions. We assumed an atmospheric temperature and pressure profile of the US Standard Atmosphere 1976 (COESA, 1976) and noon-time O, OH, and O₃ concentrations given by DeMore et al. (1997). Spectral photon flux in the 180 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 O₂, O₃, and CO₂ being the dominant absorbers. Absorption cross-sections of O₂ (Yoshino et al., 1988, 1992), O₃ (Molina and Molina, 1986), and CO₂ (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 to 220 nm absorption region at different altitudes. SO₂ photolysis rate constants (J_SO₂) were calculated as a function of altitude using the calculated spectral photon fluxes and the SO₂ absorption cross-sections of Manatt and Lane (1993).

The lifetime of SO with respect to oxidation by O₂ (i.e. R5 and R6) is relatively short (on the order of seconds), so SO and SO₂ were assumed to be in photochemical steady state, i.e.

\[
\frac{[\text{SO}]}{[\text{SO}_2]} = \frac{J_{\text{SO}_2}}{k_{\text{R5}[\text{O}_2]} + k_{\text{R6}[\text{O}_2][M]}}
\]

(8)

The rate constant \( k_{\text{R5}} \) was calculated as a function of altitude (i.e. temperature) based on the recommendations of Sander et al. (2011). \( k_{\text{R6}} \) was varied between \( 1.0 \times 10^{-37} \) cm\(^6\) molecule\(^{-2}\) s\(^{-1}\) and \( 1.0 \times 10^{-36} \) cm\(^6\) molecule\(^{-2}\) s\(^{-1}\) to encompass our range of rate estimates from Sect. 4.3. SO oxidation by other oxidants (O₃, O, NO₃, etc.) was assumed to be minor compared to oxidation by O₂ given the minor concentration of most of these species compared with that of O₂. Using the [SO] to [SO₂] ratio,
the rates of Reactions (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:

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

(9)

The rate constants $k_{SO_2+OH}$ and $k_{SO_2+O}$ 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 Fig. 8. Given that SO, OH, and O($^3P$) 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 Fig. 8, the lower-bound estimate for $k_{R6}$ ($1.0 \times 10^{-37}$ cm$^6$ molecule$^{-2}$ s$^{-1}$) gives 4% to 10% of sulfate from Reaction (R6) between 25 km and 50 km altitude. A faster estimate for $k_{R6}$ of $2.0 \times 10^{-37}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ gives 8% to 18% of sulfate from Reaction (R6) between 25 km and 50 km altitude. The upper bound estimate for the rate ($k_{R6} = 1.0 \times 10^{-36}$ cm$^6$ molecule$^{-2}$ s$^{-1}$, from Black et al., 1982) suggests that over 45% of sulfate could be coming from Reaction (R6) between 31 km and 34 km altitude and is probably unrealistic. The contribution from Reaction (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 Reaction (R6) decreases at higher altitude as total number density decrease. The maximum $f_{SO}$ value, thus, is between 30 and 35 km (Fig. 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\textsubscript{2} decay following the Mt. Pinatubo eruption, considering Reaction (R1) as the only sink of SO\textsubscript{2} in the stratosphere. Their modeled decay times for SO\textsubscript{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\textsubscript{2} photolysis followed by Reaction (R6). Inclusion of the SO\textsubscript{2} photolysis sink would decrease the lifetimes for SO\textsubscript{2} above 25 km. The presence of this reaction would also suggest that OH concentrations estimated by Read et al. (1993) based on SO\textsubscript{2} lifetimes might overestimate OH concentrations above 25 km altitude.

SO\textsubscript{2} photolysis is self-limiting, as SO\textsubscript{2} photolysis near the top of the volcanic SO\textsubscript{2} plume absorbs ultraviolet radiation in the range that SO\textsubscript{2} photolysis occurs. As a result, SO\textsubscript{2} photolysis lower in the eruption cloud is reduced and depends upon the overlying SO\textsubscript{2} column density. This would potentially reduce the significance of R6 under heavy SO\textsubscript{2} loading.

Optical shielding effects increase the magnitude of the isotope effect from SO\textsubscript{2} photolysis under high SO\textsubscript{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 vs. 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\textsubscript{2} photolysis, over 100 ‰ and 10 ‰ for \(\delta^{34}\text{S}\) and \(\Delta^{33}\text{S}\) 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\textsubscript{2} photolysis (Fig. 3), it is likely that SO\textsubscript{2} photolysis plays an
important role in the sulfur isotope budget of stratospheric sulfate aerosols. The initial sulfate formed from \( \text{SO}_2 \) photolysis (followed by R6) will contain positive \( \delta^{34}\text{S} \) and \( \Delta^{33}\text{S} \) values and negative \( \Delta^{36}\text{S} \) values. Over time, due to mass balance, the residual \( \text{SO}_2 \) will obtain negative \( \delta^{34}\text{S} \) and \( \Delta^{33}\text{S} \) values and positive \( \Delta^{36}\text{S} \) values. This explains the temporal evolution of the isotopic signatures observed in aerosol samples (for \( \delta^{34}\text{S} \), Castleman et al., 1974) and ice cores (Baroni et al., 2007), which goes from positive \( \delta^{34}\text{S} \) and \( \Delta^{33}\text{S} \) values shortly after an eruption to negative values as time progresses.

4.7 Insignificance of excited-state photochemistry of \( \text{SO}_2 \) in the stratosphere

It has been suggested previously (Savarino et al., 2003; Hattori et al., 2013) that excited-state photochemistry of \( \text{SO}_2 \) in the 250 to 350 nm absorption region (i.e. the \( \tilde{A}(1\text{A}_2)/\tilde{B}(1\text{B}_1) \) states) might be important to the sulfur isotope ratios in stratospheric sulfate aerosols. Previous results (Whitehill and Ono, 2012; Whitehill et al., 2013) have demonstrated that \( \text{SO}_2 \) photoexcitation in this region produces mass-independent sulfur isotope signatures with positive \( \Delta^{36}\text{S}/\Delta^{33}\text{S} \) ratios, as opposed to the negative \( \Delta^{36}\text{S}/\Delta^{33}\text{S} \) ratios measured for stratospheric sulfate aerosols. This study further demonstrates that \( \text{SO}_2 \) photoexcitation in the 250 to 350 nm absorption region produces positive \( \Delta^{36}\text{S}/\Delta^{33}\text{S} \) 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 \( \text{C}_2\text{H}_2 \) to trap triplet-state \( \text{SO}_2 \)). In the present study, we tested \( \text{SO}_2 \) photoexcitation with two different longpass filters (250 nm longpass filter and 280 nm longpass filter) in a \( \text{N}_2/\text{O}_2 \) bath gas. In all cases, we produced sulfate products with positive \( \Delta^{36}\text{S}/\Delta^{33}\text{S} \) ratios. Therefore, our experiments do not provide support for \( \text{SO}_2 \) photoexcitation as a source of the isotope anomalies in modern atmospheric samples.
4.8 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\textsubscript{2} into the stratosphere. Both direct injection into higher altitudes (i.e. above 25 km) or stratospheric transport of the SO\textsubscript{2} plume can bring SO\textsubscript{2} to a sufficient altitude for SO\textsubscript{2} photolysis to occur. The process of SO\textsubscript{2} photolysis produces large mass-independent sulfur isotope signatures in the SO products, particularly when there is high SO\textsubscript{2} loading (and thus optical screening effects). Reaction of SO with O\textsubscript{2} to produce SO\textsubscript{3} (via Reaction R6) provides a pathway for the isotopic signature of SO to be preserved as SO\textsubscript{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 Fig. 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\textsubscript{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\textsubscript{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.

In contrast with this are major low-latitude eruptions such as Pinatubo (1991). 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 \( \text{SO}_2 \) photolysis to play a role in the oxidation to sulfate. The largest mass-independent sulfur isotope signatures (with \( \Delta^{33}\text{S} > 1 \)‰) 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, \( \text{SO}_2 \) photolysis would become a dominant process, and could explain why the signature from this eruption is significantly larger that the other eruptions. Thus, \( \text{SO}_2 \) photolysis, followed by SO oxidation to \( \text{SO}_3 \) (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 to investigate the production of mass-independent sulfur isotope effects under stratospheric conditions. For \( \text{SO}_2 \) photolysis in the 190 to 220 nm region, the magnitude of the mass-independent isotope signature increases with decreasing temperature. The isotope systematics, in particular \( \delta^{34}\text{S} \) and \( \Delta^{36}\text{S} \) values, show excellent agreement with an optical self-screening model based on synthetic absorption cross sections (Lyons, 2007). \( \text{SO}_2 \) photoexcitation experiments show similar signatures to previous experimental studies (Whitehill and Ono, 2012; Whitehill et al., 2013), with positive \( \Delta^{33}\text{S} \) and \( \Delta^{36}\text{S} \) values, but that differ significantly from expectations based on absorption cross sections (Danielache et al., 2012).
The SO\textsubscript{3} (recovered as sulfate) products from SO\textsubscript{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\textsubscript{3}. We hypothesize the SO + O\textsubscript{2} + M → SO\textsubscript{3} + M reaction (R6) and estimate the termolecular rate constant of the reaction to be on the order of 10\textsuperscript{-37} cm\textsuperscript{6} molecule s\textsuperscript{-2} s\textsuperscript{-1}. 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\textsubscript{3} that are associated with the SO(\textsuperscript{3}Σ\textsuperscript{−}) + O\textsubscript{2}(\textsuperscript{3}Σ\textsuperscript{−}) 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\textsubscript{2} + → SO\textsubscript{2} + O reaction (R5) also requires intersystem crossing between the singlet and triplet surfaces.

Depending on the rate of Reaction (R6), we predict that on the order of 10% of sulfate above 25 km altitude could be derived from the SO + O\textsubscript{2} + M channel. Given the large isotope fractionations produced during SO\textsubscript{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. Our model explains the temporal evolution of δ\textsuperscript{34}S and Δ\textsuperscript{33}S values following major volcanic eruptions, and constrains the maximum altitude of the plume to 25 km and above when non-zero Δ\textsuperscript{33}S values are observed.

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References


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Table 1. Summary of experiments performed.

<table>
<thead>
<tr>
<th>Experiment</th>
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<th>Filter</th>
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<th>Bath Gas</th>
<th>Presented in</th>
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<td>photolysis (temp.)</td>
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<td>N₂</td>
<td>Figs. 2 and 5; Table 2</td>
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<td>Fig. 2; Table 3</td>
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<td>N₂/O₂</td>
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Table 2. Isotope ratios of elemental sulfur products from the SO$_2$ photolysis temperature experiments (Sect. 2.2).

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<th>$\delta^{34}\text{S}/%$</th>
<th>$\delta^{36}\text{S}/%$</th>
<th>$\Delta^{33}\text{S}/%$</th>
<th>$\Delta^{36}\text{S}/%$</th>
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<td>129.04</td>
<td>227.26</td>
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Table 3. Isotope ratios of organosulfur products from the SO$_2$ photoexcitation temperature experiments (Sect. 2.2).

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<tr>
<th>$T$/K</th>
<th>$\delta^{33}$S/%</th>
<th>$\delta^{34}$S/%</th>
<th>$\delta^{36}$S/%</th>
<th>$\Delta^{33}$S/%</th>
<th>$\Delta^{36}$S/%</th>
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<td>61.27</td>
<td>22.84</td>
<td>51.6</td>
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Table 4. Results from experiments of SO\textsubscript{2} photolysis in the presence of varying amounts of O\textsubscript{2} (Sect. 2.3) used to estimate \(k_{R6}\) (Sects. 4.3 and 4.4).

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<th>(pO_2/\text{kPa})</th>
<th>Time/ ks</th>
<th>Yield/ (\mu\text{mol S})</th>
<th>(\delta^{33}\text{S}/%)</th>
<th>(\delta^{34}\text{S}/%)</th>
<th>(\delta^{36}\text{S}/%)</th>
<th>(\Delta^{33}\text{S}/%)</th>
<th>(\Delta^{36}\text{S}/%)</th>
<th>calculated (k_{R6}/\text{cm}^6\text{ molecule}^{-2}\text{ s}^{-1})</th>
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<tr>
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\(^\ast S^0 - 1\) 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 \(\text{SO}_2\) photolysis in the presence of \(\text{O}_2\) (Sect. 2.3). All results are from sulfate (\(\text{SO}_3\)) 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.

<table>
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<tr>
<th>Filter</th>
<th>(p\text{SO}_2/) Pa</th>
<th>(p\text{O}_2/) kPa</th>
<th>Flow/ (\text{cm}^3) s(^{-1})</th>
<th>Time/ ks</th>
<th>Yield/ (\mu\text{mol S})</th>
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<th>(\delta^{34}\text{S}/) ‰</th>
<th>(\delta^{36}\text{S}/) ‰</th>
<th>(\Delta^{33}\text{S}/) ‰</th>
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* Experiment performed at 7.7 kPa total pressure to test low pressure limit.
### Table 6.

Comparison of asymptotic energies of SO + O₂ obtained on the singlet and triplet potential energy surfaces for SO₃ and those obtained by the sum of two separated species. All energies are in kJ mole⁻¹ and are relative to the SO(³Σ⁻) + O₂(³Σ₉) calculated separately in each ab-initio method.

<table>
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<th>B3LYP</th>
<th>CASSCF</th>
<th>CASPT2//CASSCF</th>
<th>UCCSD(T)F12a//B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO(³Σ⁻) + O₂(³Σ₉)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(separated)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO(¹Δ) + O₂(³Σ₉)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(separated)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO(³Σ⁻) + O₂(¹Δ₉)</td>
<td>118.78</td>
<td>64.60</td>
<td>136.36</td>
<td>94.98</td>
</tr>
<tr>
<td>(separated)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO(¹Δ) + O₂(¹Δ₉)</td>
<td>160.83</td>
<td>86.57</td>
<td>98.28</td>
<td>121.55</td>
</tr>
<tr>
<td>(separated)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO + O₂ (singlet)</td>
<td>279.57</td>
<td>0.00</td>
<td>-6.86</td>
<td>217.19</td>
</tr>
<tr>
<td>SO + O₂ (triplet)</td>
<td>27.61</td>
<td>0.00</td>
<td>-6.61</td>
<td>122.59</td>
</tr>
</tbody>
</table>

**SO₂ photolysis as a source for sulfur mass-independent isotope signatures**

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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$^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>B3LYP</th>
<th>CASSCF</th>
<th>CASPT2/CASSCF</th>
<th>UCCSD(T)F12a/B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_3$</td>
<td>-287.73</td>
<td>-262.92</td>
<td>-348.69</td>
<td>-411.58</td>
</tr>
<tr>
<td>cyclic-OSOO</td>
<td>-60.17</td>
<td>-50.21</td>
<td>-101.75</td>
<td>-142.72</td>
</tr>
<tr>
<td>trans-OSOO</td>
<td>42.09</td>
<td>53.72</td>
<td>-18.87</td>
<td>-17.66</td>
</tr>
<tr>
<td>cis-OSOO</td>
<td>19.33</td>
<td>35.82</td>
<td>-31.42</td>
<td>-39.08</td>
</tr>
<tr>
<td>TS1: trans-to-cis</td>
<td>108.95</td>
<td>135.14</td>
<td>66.32</td>
<td>42.76</td>
</tr>
<tr>
<td>TS2: trans-to-cyclic</td>
<td>62.51</td>
<td>69.71</td>
<td>3.10</td>
<td>0.17</td>
</tr>
<tr>
<td>TS3: cis-to-cyclic</td>
<td>108.95</td>
<td>114.18</td>
<td>50.42</td>
<td>43.26</td>
</tr>
<tr>
<td>TS4: cyclic-to-SO$_3$</td>
<td>82.42</td>
<td>69.25</td>
<td>56.61</td>
<td>70.33</td>
</tr>
<tr>
<td>SO($^3\Sigma^-$) + O$_2$($^3\Sigma_g^-$)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>SO$_2$($^1\text{A}_1$) + O($^1\text{D}$)</td>
<td>292.04</td>
<td>159.28</td>
<td>206.27</td>
<td>152.84</td>
</tr>
</tbody>
</table>
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\(^{-1}\).

<table>
<thead>
<tr>
<th></th>
<th>B3LYP</th>
<th>CASSCF</th>
<th>CASPT2/CASSCF</th>
<th>UCCSD(T)F12a/B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO(_3)</td>
<td>136.02</td>
<td>293.21</td>
<td>115.90</td>
<td>75.14</td>
</tr>
<tr>
<td>cyclic-OSOO</td>
<td>−70.67</td>
<td>12.18</td>
<td>−105.06</td>
<td>−137.07</td>
</tr>
<tr>
<td>trans-OSOO</td>
<td>26.40</td>
<td>85.81</td>
<td>8.70</td>
<td>16.53</td>
</tr>
<tr>
<td>cis-OSOO</td>
<td>28.58</td>
<td>82.09</td>
<td>16.82</td>
<td>18.49</td>
</tr>
<tr>
<td>TS1: trans-to-cis</td>
<td>30.42</td>
<td>92.72</td>
<td>10.79</td>
<td>25.44</td>
</tr>
<tr>
<td>TS2: OSOO-to-cyclic</td>
<td>96.40</td>
<td>125.35</td>
<td>67.28</td>
<td>67.86</td>
</tr>
<tr>
<td>SO(_2) . . . O</td>
<td>23.35</td>
<td>−71.34</td>
<td>−31.55</td>
<td>−58.28</td>
</tr>
<tr>
<td>TS3: cyclic-to-SO(_2) . . . O</td>
<td>25.44</td>
<td>−62.93</td>
<td>−24.81</td>
<td>−54.06</td>
</tr>
<tr>
<td>SO(3\Sigma^-) + O(_2)(3\Sigma_g^-)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>SO(_2)(1\A_1) + O(3\P)</td>
<td>26.69</td>
<td>−55.44</td>
<td>13.64</td>
<td>−52.93</td>
</tr>
</tbody>
</table>
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), and cm$^6$ molecule$^{-2}$ s$^{-1}$ for third order reactions.

<table>
<thead>
<tr>
<th>Reaction Number</th>
<th>Reaction</th>
<th>Rate constant</th>
<th>Reaction Order</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photochemical Reactions</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R4</td>
<td>SO$_2$ + hν → SO + O</td>
<td>5.2 x 10$^{-3}$</td>
<td>1</td>
<td>Manatt and Lane (1993)</td>
</tr>
<tr>
<td>R9</td>
<td>O$_2$ + hν → O + O</td>
<td>1.7 x 10$^{-6}$</td>
<td>1</td>
<td>Yoshino et al. (1988, 1992)</td>
</tr>
<tr>
<td>R10</td>
<td>O$_3$ + hν → O + O$_2$</td>
<td>1.1 x 10$^{-1}$</td>
<td>1</td>
<td>Molina and Molina (1986)</td>
</tr>
<tr>
<td>R11</td>
<td>O + O + M → O$_2$ + M</td>
<td>1.0 x 10$^{-33}$</td>
<td>3</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>R12</td>
<td>O + O$_2$ + M → O$_3$ + M</td>
<td>6.0 x 10$^{-34}$</td>
<td>3</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>R13</td>
<td>O + O$_3$ → O$_2$ + O$_2$</td>
<td>8.0 x 10$^{-15}$</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>SO$_x$ Chemistry</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R5</td>
<td>SO + O$_2$ → SO$_2$ + O</td>
<td>8.0 x 10$^{-11}$</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>R6</td>
<td>SO + O$_2$ + M → SO$_3$ + M</td>
<td>Varies</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>R7</td>
<td>SO$_2$ + O + M → SO$_3$ + M</td>
<td>1.3 x 10$^{-14}$</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>R8</td>
<td>SO + SO → SO$_2$ + S</td>
<td>8.3 x 10$^{-16}$</td>
<td>2</td>
<td>Chung et al. (1975)</td>
</tr>
<tr>
<td>R14</td>
<td>SO + O + M → SO$_2$ + M</td>
<td>1.3 x 10$^{-11}$</td>
<td>2</td>
<td>Cobos et al. (1985)</td>
</tr>
<tr>
<td>R15</td>
<td>SO + O$_3$ → SO$_2$ + O$_2$</td>
<td>8.4 x 10$^{-14}$</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>R16</td>
<td>S + O$_2$ → SO + O</td>
<td>2.3 x 10$^{-12}$</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>R17</td>
<td>S + O$_3$ → SO + O$_2$</td>
<td>1.2 x 10$^{-11}$</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>Other</td>
<td>k$_{out}$</td>
<td>Exit rate from cell</td>
<td>2.1 x 10$^{-2}$</td>
<td>1</td>
</tr>
</tbody>
</table>

* Effective second order reactions based on falloff curves for [M] = 2.5 x 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 Sect. 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 \( T_{\text{Cell} / ^\circ \text{C}} = 0.8160 \times (T_{\text{Chiller} / ^\circ \text{C}}) + 2.3514 \).
Figure 2. Results of the temperature experiments for SO$_2$ photolysis and SO$_2$ photoexcitation (Sect. 2.2). Results from SO$_2$ photolysis experiments (phot) are shown in filled symbols and SO$_2$ photoexcitation experiments (excit) are in empty symbols.
Figure 3. Isotopic results of the \( \text{SO}_2 + \text{O}_2 \) experiments described in Sect. 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 SO₃ 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 SO³(3Σ⁻) + O₂(3Σ⁻) asymptote. The quintet (black) state is shown qualitatively due to its high energy.
Figure 5. Comparison of SO$_2$ photolysis temperature experiment results with predictions from isotopologue-specific absorption cross-sections (CS).
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 Sect. 4.3 and Table 4.
Figure 7. Results of kinetic model (Sect. 4.4, Table 9) compared to experimental data (circles) for $f_{R6}$ (Eq. 5) vs. fraction of $\text{SO}_3$ formed from R6 in the model (left), as well as total $\text{SO}_3$ 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.
SO$_2$ photolysis as a source for sulfur mass-independent isotope signatures

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**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 25 km is dominantly by OH, which is a mass-dependent process.