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

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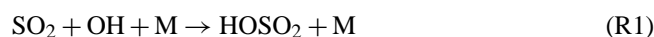
Abstract. Signatures of sulfur isotope mass-independent fractionation (S-MIF) have been observed in stratospheric sulfate aerosols deposited in polar ice. The S-MIF signatures are thought to be associated with stratospheric photochemistry following stratospheric volcanic eruptions, but the exact mechanism 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 O₂ on the S-MIF produced by two absorption band systems of SO₂: photolysis in the 190 to 220 nm region and photoexcitation in the 250 to 350 nm region. The SO₂ photolysis (SO₂ + *hν* → SO + O) experiments showed S-MIF signals with large ³⁴S/³²S fractionations, which increases with decreasing temperature. The overall S-MIF pattern observed for photolysis experiments, including high ³⁴S/³²S fractionations, positive mass-independent anomalies in ³³S, and negative anomalies in ³⁶S, is consistent with a major contribution from optical isotopologue screening effects and data for stratospheric sulfate aerosols. In contrast, SO₂ photoexcitation produced products with positive S-MIF anomalies in both ³³S and ³⁶S, which is different from stratospheric sulfate aerosols. SO₂ photolysis in the presence of O₂ produced SO₃ with S-MIF signals, suggesting the transfer of the S-MIF anomalies from SO to SO₃ by the SO + O₂ + M → SO₃ + M reaction. This is supported with energy calculations of stationary points on the SO₃ 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. Based on our experimental results, we estimate a termolecular rate

constant on the order of 10⁻³⁷ cm⁶ 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 SO₂. The production and preservation of S-MIF signals requires a high SO₂ 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 SO₂ plume must reach an altitude of around 20 to 25 km, where SO₂ photolysis becomes a dominant process. These experiments are the first step towards understanding the origin of the sulfur isotope anomalies in stratospheric sulfate aerosols.

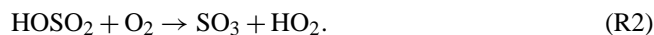
1 Introduction

Explosive volcanic eruptions that inject sulfur dioxide (SO₂) 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 SO₂ 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 SO₂ in the stratosphere:



This reaction is followed by



In the presence of H₂O, SO₃ readily forms sulfuric acid (H₂SO₄) via the following:



Ab initio transition state theory calculations of the isotope effect for OH oxidation Reaction (R1) predict that ³⁴SO₂ is oxidized 0.9 % slower than ³²SO₂ (Tanaka et al., 1994), although calculations with RRKM theory predict an inverse isotope effect, in which ³⁴SO₂ reactions 12 to 15 % faster than ³²SO₂ (Leung et al., 2001). Experimental studies of OH oxidation (R1) showed an inverse isotope effect, but with a smaller magnitude, with ³⁴SO₂ reacting about 1 % faster than ³²SO₂ (Harris et al., 2012). Although the experimentally measured isotope effect might be sufficient to explain the roughly 2 % enrichment in H₂³⁴SO₄ relative to H₂³²SO₄ 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 ³⁴S fractionations.

An additional unexplained observation is the isotope anomalies in ³³S/³²S and ³⁶S/³²S ratios relative to ³⁴S/³²S 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 SO₂ into the stratosphere, stratosphere-derived sulfate can dominate sulfate deposition in ice cores and, when corrected for background levels, can preserve the sulfur isotopic composition of stratospheric sulfate aerosols. Experimental studies demonstrate that OH oxidation of SO₂ (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 SO₂ in the 250 to 350 nm absorption region (Savarino et al., 2003; Hattori et al., 2013), SO₂ photolysis in the 190 to 220 nm absorption region (Ono et al., 2013), and SO₃ photolysis (Pavlov et al., 2005).

We present results of laboratory photochemical experiments that support SO₂ photolysis as the main source for the MIF signatures observed in stratospheric sulfate aerosols following some large (stratospheric) volcanic eruptions. In particular, SO₂ photolysis produces large MIF anomalies, as well as large mass-dependent isotope fractionations (Master-son 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).

Photolysis of SO₂ occurs above around 20 to 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:



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



Reactions (R4) and (R5) combine to form a null cycle for sulfur, but catalyzes 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:



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 Reaction (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 an order of magnitude estimate on the rate of Reaction (R6). 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 path length of 15.3 cm and an inner diameter of 5.2 cm (Ono et al., 2013).

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	Figs. 2 and 5; Table 2
Photoexcitation (temp.)	150 W Xe	250 LP, H ₂ O	225 to 275	N ₂ /C ₂ H ₂	Fig. 2; Table 3
Photolysis (added O ₂)	150 W Xe	None, 200 BP	298	N ₂ /O ₂	Figs. 3 and 6; Tables 4, 5
Photoexcitation (added O ₂)	150 W Xe	250 LP, 280 LP	298	N ₂ /O ₂	Fig. 3; Table 5

Temperature-controlled experiments were performed in a jacketed cell of the same dimensions. The front window of the cell was made of UV-grade SiO₂ (Corning 7980) with greater than 90 % transmittance 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 path length) 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 experiments) or the front of the cell (for other experiments) and exited through an outlet at the opposite end of the cell. An 8 to 10 cm length of glass tubing packed with glass wool was placed immediately after the cell to trap aerosols formed within the cell. Following the aerosol trap, the gas was made to flow 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 set-point pressure, which was usually 101.3 kPa.

Prior to each temperature-controlled experiment, the reaction cell was flushed with nitrogen (N₂) for several hours and the chiller was allowed to reach its set-point temperature and equilibrate for at least an hour. The temperature of the reaction cell was calibrated relative to the chiller set-point temperature on two occasions using a series of K-type thermocouples suspended within the cell. During calibrations, N₂ (without SO₂) was made to flow through the cell at a rate of 3.33 cm³ s⁻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 temperature. No significant differences were observed between the two calibrations. Results for the temperature calibration are shown in Fig. 1.

2.2 Temperature effect on SO₂ photolysis (190 to 220 nm) and photoexcitation (250 to 350 nm)

The temperature effect on SO₂ photolysis (190 to 220 nm) was tested using the temperature-controlled reaction cell described in Sect. 2.1. Experiments were performed in a

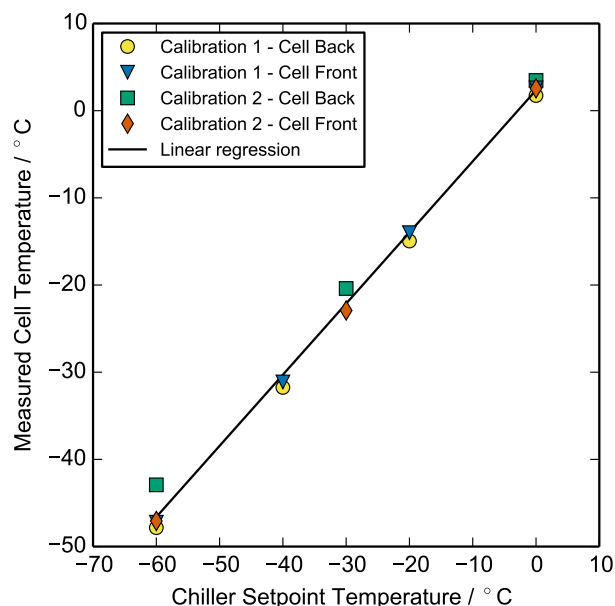


Figure 1. Results of the temperature calibration for the temperature controlled photochemical reactor described in Sect. 2.1. The linear regression shown was used to calibrate the temperature within the cell based on the set-point temperature of the chiller. The regression line is $(T_{\text{Cell}}/^{\circ}\text{C})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

nitrogen-flushed glove box to prevent the spectral interference from the Schumann–Runge band of oxygen (O₂). A 200 W deuterium (D₂) arc lamp (D 200 F, Heraeus Noble-light) 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 SO₂ (in N₂) was made to flow through the cell at a rate of 3.33 cm³ s⁻¹ (200 sccm) for all experiments, and pressure within the cell was held constant at 101.3 kPa, giving an SO₂ 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 to dissolve any elemental sulfur that was formed. The glass wool in the aerosol trap was also collected and rinsed with dichloromethane. Elemental sulfur was recrystallized from 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 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 M Ω) water and a 250 nm long-pass 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 made to flow 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 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 long-pass filter (Asahi Spectra, ZUL0250), or a 280 nm (285 nm cut-on) long-pass filter (Newport Model FSR-WG280) to isolate particular absorption bands of SO₂, but most experiments were performed with the Xe lamp and no filters (Table 1).

Following experiments, the cell was rinsed well first with dichloromethane then with water. Although sulfate was the dominant product, the cell was rinsed well with dichloromethane 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 cm³ of a 1.0 mol dm⁻³ solution of barium chloride (BaCl₂) 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 isotopes were measured as described in Sect. 2.4.

2.4 Isotope analysis of photochemical products

Photochemical products were converted to silver sulfide (Ag₂S). Ag₂S was rinsed well three to four times with deionized water and then dried completely at 353 K. Dried Ag₂S was weighed for total yield and about 8 μmol of Ag₂S 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 (F₂) for at least 8 h at 573 K. The resultant SF₆ was purified cryogenically and by gas chromatography. Isotope ratios of pure SF₆ were measured as SF₅⁺ ions using a Thermo Scientific MAT 253 Isotope Ratio Mass Spectrometer. For sample where less than 1.6 μmol of Ag₂S was recovered, a microvolume (0.4 cm³ volume) cold finger was used to concentrate the sample for analysis.

Replicate analyses (*N* = 28) of the reference material IAEA-S-1 gave 2σ standard deviations of 0.26 ‰ for δ³⁴S, 0.014 ‰ for Δ³³S, and 0.19 ‰ for Δ³⁶S 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 δ³⁴S, 0.08 ‰ for Δ³³S, and 0.8 ‰ for Δ³⁶S. 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 + O₂ → SO₃ → SO₂ + 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 SO₃ PESs. The lowest SO(³Σ⁻) + O₂(³Σ_g⁻) asymptote of the SO₃ PESs involves three degenerate states, namely the singlet, triplet, and quintet states. The singlet state corresponds to the ground state of the SO₃ molecule (¹A₁'), but does not dissociate to the ground state products SO₂(¹A₁) + O(³P) but to SO₂(¹A₁) + O(¹D). The triplet surface corresponds to the ground state products but is adiabatically associated with a higher energy excited-state (triplet) SO₃. The quintet state is much higher in energy than the other two states except at the SO(³Σ⁻) + O₂(³Σ_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 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 perturbative triple excitations (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 Schrödinger

perturbation theory of second order (RSPT2 or CASPT2) calculations (Celani and Werner, 2000) were performed based on the CASSCF wave functions 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.

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

where $x = 33, 34$, or 36 and xR is the ratio of ${}^x\text{S}$ to ${}^{32}\text{S}$ in the substance. For experimental results all isotope ratios will be normalized to the isotope ratios of the initial SO₂. For natural samples (i.e., stratospheric sulfate aerosol samples), the reference is Vienna Canyon Diablo Troilite (V-CDT).

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

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

and

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

Almost all physical, chemical, and biological processes fractionate isotopes mass dependently (i.e., $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ are approximately equal to 0). SO₂ photochemistry, as well as the photochemistry of other sulfur gases such as CS₂, are some of the few exceptions that produce mass-independent fractionation. Therefore, non-zero $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values can be unique tracers of photochemical processes.

3 Results

All experiments performed are summarized in Table 1. Results from temperature experiments on SO₂ photolysis and SO₂ photoexcitation are given in Tables 2 and 3, whereas results from SO₂ + O₂ experiments are presented in Tables 4 and 5. Tables 6, 7, and 8 give the results from energy calculations on the PESs of SO₃.

Table 2. Isotope ratios of elemental sulfur products from the SO₂ photolysis temperature experiments (Sect. 2.2).

T/K	$\delta^{33}\text{S}/\text{‰}$	$\delta^{34}\text{S}/\text{‰}$	$\delta^{36}\text{S}/\text{‰}$	$\Delta^{33}\text{S}/\text{‰}$	$\Delta^{36}\text{S}/\text{‰}$
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 SO₂ photoexcitation temperature experiments (Sect. 2.2).

T/K	$\delta^{33}\text{S}/\text{‰}$	$\delta^{34}\text{S}/\text{‰}$	$\delta^{36}\text{S}/\text{‰}$	$\Delta^{33}\text{S}/\text{‰}$	$\Delta^{36}\text{S}/\text{‰}$
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

3.1 Temperature experiments

Results from the temperature experiments (Sect. 2.2) are shown in Fig. 2. The SO₂ 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 $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$, respectively. The relationship between isotopes (i.e., $\Delta^{33}\text{S}$ vs. $\delta^{34}\text{S}$ and $\Delta^{36}\text{S}$ vs. $\Delta^{33}\text{S}$) did not change significantly as temperature was decreased (0.04 to 0.05 for $\Delta^{33}\text{S}/\delta^{34}\text{S}$ and −3.9 to −4.6 for $\Delta^{36}\text{S}/\Delta^{33}\text{S}$). 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.

SO₂ photoexcitation (250 to 350 nm) experiments show decreasing magnitude $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values at lower temperatures (22.8 to 19.0 ‰ and 52.5 to 46.0 ‰ for $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$, respectively; Table 3). Even at lower temperatures, the product from SO₂ photoexcitation experiments show positive $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ 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

SO₂ photolysis and photoexcitation in the presence of molecular oxygen (O₂) produced mass-independent sulfur isotope

Table 4. Results from experiments of SO₂ photolysis in the presence of varying amounts of O₂ (Sect. 2.3) used to estimate k_{R6} (Sects. 4.3 and 4.4).

Product	pO_2 / kPa	Time/ ks	Yield/ $\mu\text{mol S}$	$\delta^{33}\text{S}/$ ‰	$\delta^{34}\text{S}/$ ‰	$\delta^{36}\text{S}/$ ‰	$\Delta^{33}\text{S}/$ ‰	$\Delta^{36}\text{S}/$ ‰	calculated $k_{R6}/$ $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$
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 ⁰ avg	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}

* S⁰ – 1 and SO₃ – 1 are elemental sulfur and SO₃ from the same experiment. Similarly, S⁰ – 2 and SO₃ – 2 are elemental sulfur and SO₃ from the same experiment.

Table 5. Results from additional experiments of SO₂ photolysis in the presence of O₂ (Sect. 2.3). All results are from sulfate (SO₃) product. Experiments were performed at a constant total pressure of 101.3 kPa unless marked otherwise. Filter types are as follows: 200 BP = 200 nm bandpass filter, 250 LP = 250 nm long-pass filter, 280 LP = 280 nm long-pass filter.

Filter	pSO_2 / Pa	pO_2 / kPa	Flow/ $\text{cm}^3 \text{ s}^{-1}$	Time/ ks	Yield/ $\mu\text{mol S}$	$\delta^{33}\text{S}/$ ‰	$\delta^{34}\text{S}/$ ‰	$\delta^{36}\text{S}/$ ‰	$\Delta^{33}\text{S}/$ ‰	$\Delta^{36}\text{S}/$ ‰
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.

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 Xe lamp data, 200 nm bandpass (200 BP) data, and previous SO₂ photolysis data (Ono et al., 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 long-pass filter (250 LP) and the 280 nm long-pass 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 it demonstrates that MIF in this band region is not produced by chemistry related to acetylene or oxygen. However, the magnitude of the sulfur MIF signatures (i.e., $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values) are considerably smaller than previous experiments using C₂H₂ (Table 3; Whitehill et al., 2013). This suggests that a considerable amount of the sulfate in the system is being produced by a mass-dependent process, such as $^*\text{SO}_2 + \text{SO}_2 \rightarrow \text{SO} + \text{SO}_3$ (Whitehill and Ono, 2012). This

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(³Σ_g⁻) calculated separately in each ab initio method.

	B3LYP	CASSCF	CASPT2// CASSCF	UCCSD(T)F12a// B3LYP
SO(³ Σ ⁻) + O ₂ (³ Σ _g ⁻) (separated)	0	0	0	0
SO(¹ Δ) + O ₂ (³ Σ _g ⁻) (separated)	118.78	64.60	136.36	94.98
SO(³ Σ ⁻) + O ₂ (¹ Δ _g) (separated)	160.83	86.57	98.28	121.55
SO(¹ Δ) + O ₂ (¹ Δ _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(³Σ⁻) + O₂(³Σ_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 Σ ⁻) + O ₂ (³ Σ _g ⁻)	0.00	0.00	0.00	0.00
SO ₂ (¹ A ₁) + O(¹ D)	292.04	159.28	206.27	152.84

would dilute the MIF signature. In addition, there is considerable variability (i.e., a factor of ~ 2) between the two 250 nm long-pass filter experiments, despite identical conditions. The cause of this variability is uncertain but could relate to the amount of water vapor within the system.

3.3 Potential energy surfaces of SO₃

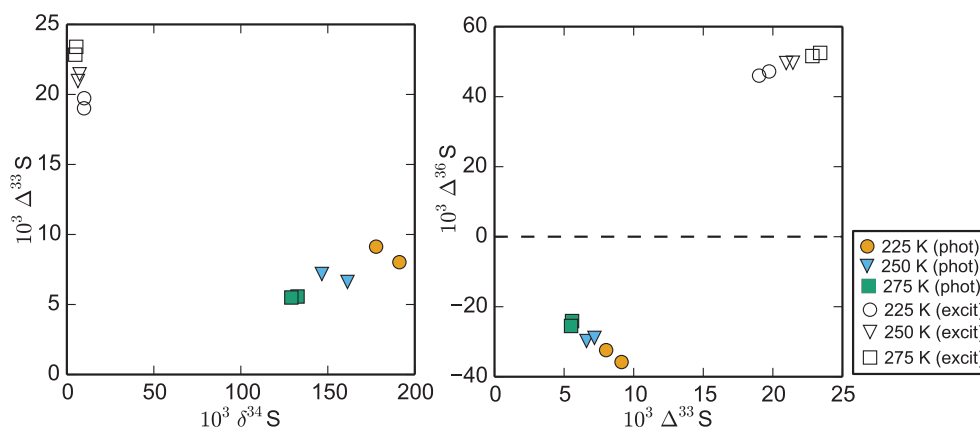
Asymptotic energies of SO + O₂ on each PES were compared with the energies obtained by separate calculations of each species with a certain spin (Table 6). The CASSCF results correctly produced degenerate energies for the SO + O₂ asymptote on the singlet and triplet states, which exactly match the sum of the energies of the SO(³Σ⁻) and O₂(³Σ_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 the other hand, the UCCSD(T)-F12a and B3LYP results both attribute SO + O₂ on the singlet state to SO(¹Δ) + O₂(¹Δ_g), and B3LYP even gives a qualitatively incorrect energy for

SO + O₂ on the triplet state, while UCCSD(T)-F12a attributes the triplet state to SO(^Δ) + O₂(³Σ_g⁻). An important conclusion from these data is that one has to use a multi-reference method if accurate global adiabatic PESs are desired for this system. Otherwise, the asymptotic behavior can be completely wrong. None of the previous studies 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(³Σ_g⁻) asymptote. However, the active space used in our CASSCF calculations is not sufficient to provide quantitatively accurate results, but a larger archive 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

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(³Σ⁻) + O₂(³Σ_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 ...O	23.35	-71.34	-31.55	-58.28
TS3: cyclic-to-SO ₂ ...O	25.44	-62.93	-24.81	-54.06
SO(³ Σ ⁻) + O ₂ (³ Σ _g ⁻)	0.00	0.00	0.00	0.00
SO ₂ (¹ A ₁) + O(³ P)	26.69	-55.44	13.64	-52.93

**Figure 2.** Results of the temperature experiments for SO₂ photolysis and SO₂ photoexcitation (Sect. 2.2). Results from SO₂ photolysis experiments (phot) are shown in filled symbols and SO₂ photoexcitation experiments (excit) are in empty symbols.

the aforementioned problems in the SO(³Σ⁻) + O₂(³Σ_g⁻) asymptote, we have used the UCCSD(T) energy sum of the two reactants with the correct spin calculated 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 the 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 et al., 1986) between the reactants and products for the SO(³Σ⁻) + O₂(³Σ_g⁻) → SO₃(¹A₁) reaction (-411.29 kJ mole⁻¹, the SO(³Σ⁻) + O₂(³Σ_g⁻) → SO₂(¹A₁) + O(³P) reaction (-54.56 kJ mole⁻¹) and the SO(³Σ⁻) + O₂(³Σ_g⁻) → 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

The differences in the photophysics and photochemistry between the photolysis region (190 to 220 nm) and the photoexcitation region (250 to 350 nm) suggest different mechanisms for MIF formation, as discussed previously (Whitehill and Ono, 2012; Ono et al., 2013; Whitehill et al., 2013).

In the 165 to 235 nm wavelength region, SO₂ photolysis occurs through pre-dissociation from the bound \tilde{C} (¹B₂) 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 SO₂ photolysis should be determined entirely by the differences in the absorption cross sections between the different isotopologues of SO₂ (e.g., by isotopologue specific Franck–Condon coupling) (Danielache

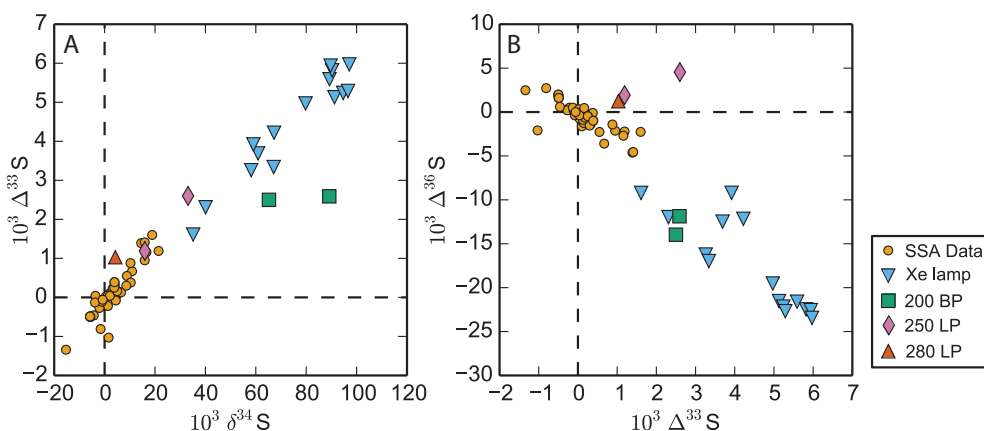


Figure 3. Isotopic results of the SO₂ + O₂ experiments described in Sect. 2.3, compared with stratospheric sulfate aerosol samples (SSA Data) from Savarino et al. (2003), Baroni et al. (2007, 2008), Lanciki (2010), and Lanciki et al. (2012).

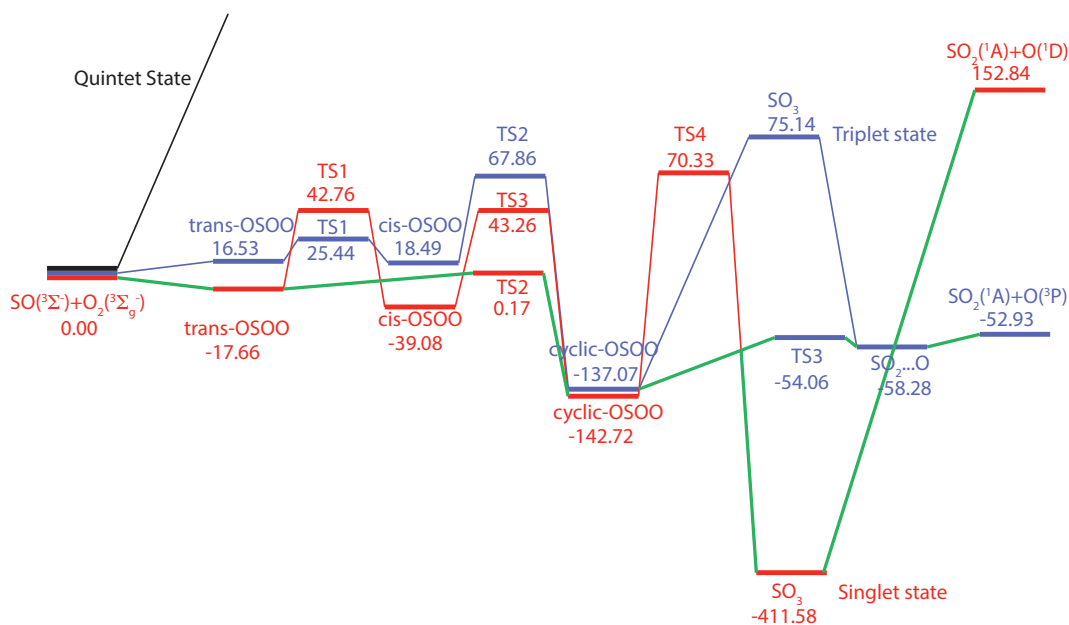


Figure 4. Potential energy profiles on the singlet (red) and triplet (blue) potential energy surfaces for the SO₃ system obtained using B3LYP optimization followed by UCCSD(T)-F12a single point calculation, with the aug-cc-pVTZ basis set. The possible intersystem crossing pathway is depicted by the solid green line. All energies are given in kJ mole⁻¹ relative to the SO(³Σ⁻) + O₂(³Σ_g⁻) asymptote. The quintet (black) state is shown qualitatively due to its high energy.

et al., 2008) and optical screening effects under high SO₂ 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 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 non-adiabatic coupling of the $\tilde{C}(^1B_2)$ and $\tilde{D}(^1A_1)$ states (Tokue and Nanbu, 2010).

For laboratory experiments, the observed isotope effect for SO₂ photolysis is a function not only of differences in the absorption cross sections (Danielache et al., 2008) but also a function of the SO₂ column density. This is because the SO₂ 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 SO₂ column densities (Ono et al., 2013). In addition to the above effects, there appears to be a total (or bath gas) pressure effect on $\Delta^{33}\text{S}$ values. This manifests as reduced $\Delta^{33}\text{S}$ values at higher total (i.e., bath gas) pressures, which is observed with He, SO₂, and N₂ 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 ³³SO₂ has a longer excited-state lifetime prior to dissociation than the other isotopologues.

SO₂ photoexcitation in the 250 to 350 nm absorption region also produces absorption-based isotope effects due to differences in cross sections and optical screening effects. In addition, it produces isotope effects by a completely different mechanism. SO₂ 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; L  v  que et al., 2014). Unlike SO₂ 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 for this isotope selective intersystem crossing as the origin of part of the isotope effects in photochemical products following SO₂ photoexcitation in the 250 to 350 nm absorption region.

Photoexcitation of SO₂ in the presence of O₂ produces sulfate with 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 the previous studies are a result of the photo-physics and photochemistry of excited-state SO₂ rather than the chemistry of the subsequent reactions (i.e., 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 350 nm region (Whitehill et al., 2013). This is expected if isotope selective intersystem crossing is contributing to the isotope signals in addition to cross-section differences and shielding effects.

4.2 Temperature effects on SO₂ photolysis

Lyons (2007, 2008) presented isotopologue-specific absorption cross sections for SO₂ in the 190 to 220 nm absorption region by shifting the measured ³²SO₂ 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 SO₂ 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 $\delta^{34}\text{S}$ 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 $\delta^{34}\text{S}$ is extrapolated back to 213 K. A similar strong agreement is also seen in the $\Delta^{36}\text{S}$ 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 SO₂ photolysis under laboratory conditions (Ono et al., 2013).

Despite the strong agreement for $\delta^{34}\text{S}$ and $\Delta^{36}\text{S}$ values, the Lyons (2007, 2008) cross sections overpredict the magnitude of the mass-independent isotope anomaly in ³³S (i.e., $\Delta^{33}\text{S}$ 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 ³²SO₂ cross sections for ³³SO₂. 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 N₂ bath gas) of the experiments caused a decrease in the $\Delta^{33}\text{S}$ value relative to the 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.

The Lyons (2007, 2008) cross sections are semi-empirical in that they take the measured ³²SO₂ 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, they seem to accurately predict the isotope effects during SO₂ photolysis under low temperature (ca. 213 K) conditions, such as those in the stratosphere.

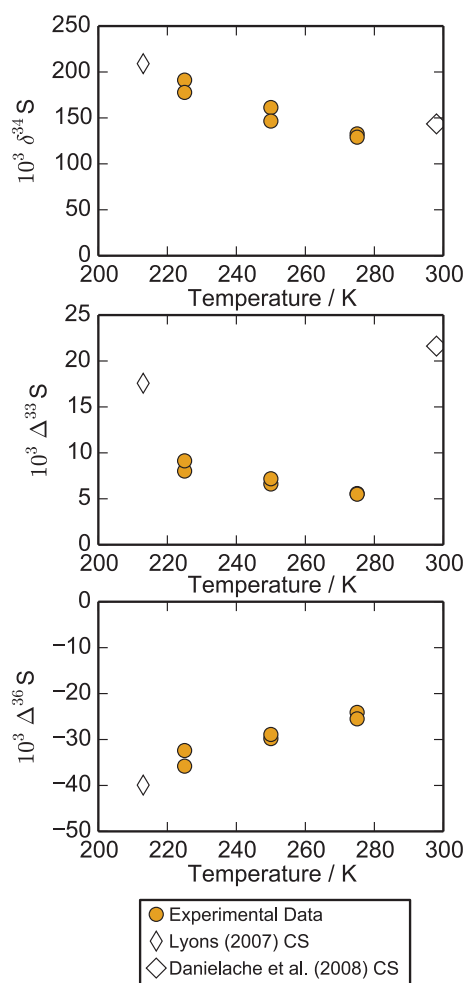


Figure 5. Comparison of SO₂ photolysis temperature experiment results with predictions from isotopologue-specific absorption cross sections (CSs).

4.3 Constraining the rate of the SO + O₂ + M reaction using product formation

Our results demonstrate that photolysis of SO₂ in the presence of molecular oxygen (O₂) produces large amounts of sulfate with considerable mass-independent sulfur isotope anomalies. In our experimental system, there are three dominant pathways for SO₃ formation: OH oxidation of SO₂ (Reactions (R1) and R2, if water is present), O₂ oxidation of SO from SO₂ photolysis (Reactions R4 and R6), and O oxidation of SO₂ via



OH and O oxidation of SO₂ (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 SO₃ and carry the mass-independent isotope signature from SO₂ photolysis (R4).

We performed a series of experiments at a total pressure of 101.3 kPa, a flow rate of 6.67 cm³ s⁻¹ (400 sccm), and an SO₂ 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 % O₂). In all experiments, SO₂ was photolyzed via Reaction (R4). In the experiments with no oxygen, both elemental sulfur (S⁰) and SO₃ aerosols were formed, with the elemental sulfur (S and related species) formed from SO via



SO photolysis is expected to be a minor source of S compared to Reaction (R8). In the absence of oxygen, SO₃ is formed primarily via O oxidation of SO₂ (R7), which is mass dependent (Ono et al., 2013).

At 5.1 kPa O₂ and above, elemental sulfur formation was shut off and SO₃ was the major product. Under these conditions, oxidation of SO (to SO₂ or SO₃ via Reactions (R5) or (R6)) competes with SO disproportionation Reaction (R8).

By comparing the $\Delta^{33}\text{S}$ value of elemental sulfur in the absence of O₂ (0 kPa O₂) with the $\Delta^{33}\text{S}$ value of sulfate in the presence of O₂ (5.1 to 19.8 kPa O₂), it is possible to estimate the fraction of sulfate formed through Reaction (R6). In particular,

$$f_{\text{R6}} = \frac{\Delta^{33}\text{S}_{\text{sulfate, with O}_2}}{\Delta^{33}\text{S}_{\text{S}^0, \text{ no O}_2}}, \quad (4)$$

where f_{R6} is the fraction of total SO₃ 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 cm³), the sulfate formation rate per unit volume per unit time can be calculated. In experiments with 5.1 to 19.8 kPa O₂, 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 Eq. (4), we can estimate the rate of sulfate formation from Reaction (R6) under our experimental conditions. This gave a rate for Reaction (R6) of 3.6×10^{12} molecules cm⁻³ s⁻¹ to 6.6×10^{12} molecules cm⁻³ s⁻¹. Assuming Reaction (R6) is a termolecular reaction, the rate for Reaction (R6) can be written as

$$\text{rate R6} = k_{\text{R6}}[\text{SO}][\text{O}_2][\text{M}], \quad (5)$$

where k_{R6} is the termolecular rate constant for Reaction (R6) and [SO], [O₂], and [M] are the concentrations of SO, O₂, and total third body gases (M = N₂, O₂) in the reaction cell. In Eq. (5), the [O₂] 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

$$[\text{SO}] = \frac{J_{\text{SO}_2}[\text{SO}_2]}{k_{\text{R5}}[\text{O}_2] + k_{\text{R6}}[\text{O}_2][\text{M}]}, \quad (6)$$

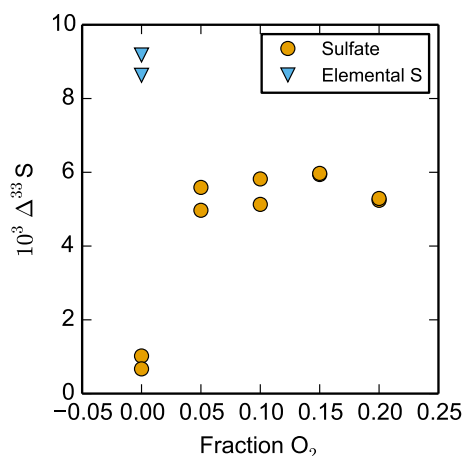


Figure 6. $\Delta^{33}\text{S}$ values of sulfate from the photolysis of SO_2 in the presence of O_2 compared with elemental sulfur and sulfate from SO_2 photolysis in the absence of O_2 . Conditions are described in Sect. 4.3 and Table 4.

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

$$F_0/\text{mW nm}^{-1} = 0.11 \cdot 1.6 \cdot (14 - 9 \cdot \exp(-0.013 \cdot (\lambda/\text{nm} - 200))), \quad (7)$$

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) (Eq. 7) 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 the 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 $J_{\text{SO}_2} = 5.2 \times 10^{-3} \text{ s}^{-1}$. The rate constant for Reaction (R5) is $k_{R5} = 8.0 \times 10^{-37} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Sander et al., 2011) at room temperature (298 K). Using these values and Eqs. (5) and (6), the rate constant for Reaction (R6) was calculated iteratively. Calculated rate constants ranged from $k_{R6} = 7.3 \times 10^{-38} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ 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 calculated rate constant (k_{R6}) appears to decrease at 19.8 kPa O_2 compared with the calculated rate for lower $p\text{O}_2$ 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.

The derived rate constant carries 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 SO_2 photolysis rate (and resulting SO number density) most likely to be 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.

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 the visible formation of sulfate aerosols from SO_3 during the experiments. Unfortunately, we did not have the analytical capability to quantitatively constrain the amount of water vapor in the system during the experiments. The Zero Air and Ultra High Purity Nitrogen used as a source of gas to the cell had maximum of 3 ppm H_2O (by volume), but there could be additional water absorbed onto the surfaces of the system while the cell was 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 $\text{SO} + \text{O}_2 + \text{M}$ reaction using a kinetic model

To further constrain the rate of Reaction (R6) (the $\text{SO} + \text{O}_2 + \text{M} \rightarrow \text{SO}_3 + \text{M}$ reaction), we constructed a kinetic model of the chemistry occurring within the cell. We used the same data and conditions as Sect. 4.3, using the cross sections of Manatt and Lane (1993). Oxygen and ozone photolysis

rates were calculated using the cross sections of Yoshino et al. (1988, 1992) for O₂ and Molina and Molina (1986) for O₃. Quantum yields for O(¹D) vs. O(³P) formation from O₃ photolysis were parameterized based on the recommendation of DeMore et al. (1997). Photolysis rates for HO₂ and H₂O₂ were calculated using the recommended cross sections of Sander et al. (2011). HO₂ photolysis was assumed to produce O(¹D) and OH as products, and H₂O₂ photolysis was assumed to produce 2OH.

The rate constants and their sources are given in Table 9. Effective second-order rate constants (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 f_{R6} values (Eq. 4). Simulations were performed with values of k_{R6} of 1.0×10^{-37} , 1.0×10^{-36} , and 1.0×10^{-35} cm⁶ molecule⁻² s⁻¹. Since the amount of water vapor in the system was not constrained experimentally, three simulations were performed, with H₂O 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 within the system. Although water vapor in the bath gas (N₂ and N₂/O₂) 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 H₂O and 10 ppm H₂O predict rate for Reaction (R6) on the order of 10^{-36} cm⁶ molecule⁻² s⁻¹, with predictions for 100 ppm H₂O being slightly higher.

There is a discrepancy between model predictions and the observed experimental behavior. In particular, lower O₂ 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} cm⁶ 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 (N₂) and oxygen (O₂) are 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 predictions here and those in Sect. 4.3, with those in Sect. 4.3 being an order of magnitude smaller than those in Sect. 4.4. This could be based on the assumption that 100% of the SO₃ was trapped as sulfate in Sect. 4.3, whereas the actual amount might be less than that (implying a higher rate than predicted in Sect. 4.3). However, the model predicts rate constants within an order of magnitude of previous constraints from the literature Black et al. (1982) and within an order of magnitude of predictions from Sect. 4.3. Based on this work, we estimate the termolecular rate constant of Reaction (R6) to be on the order of 10^{-37} to

10^{-36} cm⁶ molecule⁻² s⁻¹. Future work is necessary to better constrain the rate of this reaction.

4.5 Exploring the potential energy surfaces of the SO + O₂ reactions

The experimental evidence presented above suggests the formation of SO₃ via the SO + O₂ reaction. Our theoretical analyses shows that the singlet PES is associated with the ground state of the SO₃ molecule, and thus is the primary surface related to the SO(³Σ⁻) + O₂(³Σ_g⁻) → SO₃(¹A₁) reaction (Fig. 4). As shown in Table 7, four isomers of SO₃ are located on the singlet PES. It is predicted that the D_{3h} SO₃ isomer is the global minimum, followed by cyclic-OSOO. There are two shallower wells, denoted as trans-OSOO and cis-OSOO, at the CASPT2 and UCCSD(T)-F12a levels, but they appear to be energetically higher than the SO(³Σ⁻) + O₂(³Σ_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(³Σ⁻) + O₂(³Σ_g⁻) → SO₃(¹A₁) reaction is the one connecting cyclic-OSOO and SO₃. 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 2.7×10^{-24} cm³ molecule⁻¹ s⁻¹. This is about 8 orders of magnitude lower than the experimental rate constant for Reaction (R5) (8.0×10^{-17} cm³ molecule⁻¹ s⁻¹, Sander et al., 2011), and about 6 orders of magnitude lower than the predicted effective second-order rate constant for Reaction (R6) at 101.3 kPa total pressure (about 2.5×10^{-18} cm³ molecule⁻¹ s⁻¹, calculated assuming $k_{R6} = 1.0 \times 10^{-37}$ cm⁶ molecule⁻² s⁻¹ and $[M] = 2.5 \times 10^{19}$ molecules cm⁻³). We thus conclude that the SO(³Σ⁻) + O₂(³Σ_g⁻) → SO₂(¹A₁) + 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 SO₃ isomer (Fig. 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, SO₃(³A₁) becomes highly unfavorable; for example, it is 75.14 kJ mole⁻¹ higher than the SO + O₂ 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

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, cm³ molecule⁻¹ s⁻¹ for second order reactions (and effective second order reactions, denoted 2*), and cm⁶ molecule⁻² s⁻¹ for third order reactions.

Number	Reaction	Rate constant	Order	Source
Photochemical reactions				
1	O ₂ + hν → O + O	1.0 × 10 ⁻⁵	1	Yoshino et al. (1988, 1992)
2	O ₃ + hν → O + O ₂	5.7 × 10 ⁻³	1	Molina and Molina (1986)
3	O ₃ + hν → O(¹ D) + O ₂	1.0 × 10 ⁻¹	1	Molina and Molina (1986)
4	H ₂ O ₂ + hν → OH + OH	1.7 × 10 ⁻³	1	Sander et al. (2011)
5	HO ₂ + hν → O(¹ D) + OH	1.5 × 10 ⁻²	1	Sander et al. (2011)
6	SO ₂ + hν → SO + O	5.2 × 10 ⁻³	1	Manatt and Lane (1993)
7	SO + hν → S + O	9.7 × 10 ⁻³	1	Phillips (1981)
O _x Chemistry				
8	O + O + M → O ₂ + M	2.5 × 10 ⁻¹⁴	2*	Tsang and Hampson (1986)
9	O + O ₂ + M → O ₃ + M	1.5 × 10 ⁻¹⁴	2*	Sander et al. (2011)
10	O + O ₃ → O ₂ + O ₂	8.0 × 10 ⁻¹⁵	2	Sander et al. (2011)
O(¹ D) Chemistry				
11	O(¹ D) + O ₂ → O + O ₂	4.0 × 10 ⁻¹¹	2	Sander et al. (2011)
12	O(¹ D) + O ₃ → O ₂ + O ₂	1.2 × 10 ⁻¹⁰	2	Sander et al. (2011)
13	O(¹ D) + O ₃ → O + O + O ₂	1.2 × 10 ⁻¹⁰	2	Sander et al. (2011)
14	O(¹ D) + H ₂ → OH + H	1.2 × 10 ⁻¹⁰	2	Sander et al. (2011)
15	O(¹ D) + H ₂ O → OH + OH	2.0 × 10 ⁻¹⁰	2	Sander et al. (2011)
16	O(¹ D) + N ₂ → O + N ₂	3.1 × 10 ⁻¹¹	2	Sander et al. (2011)
17	O(¹ D) + SO ₂ → ?	2.2 × 10 ⁻¹⁰	2	Sander et al. (2011)
HO _x Chemistry				
18	O + OH → O ₂ + H	3.3 × 10 ⁻¹¹	2	Sander et al. (2011)
19	O + HO ₂ → OH + O ₂	5.9 × 10 ⁻¹¹	2	Sander et al. (2011)
20	O + H ₂ O ₂ → OH + HO ₂	1.8 × 10 ⁻¹⁵	2	Sander et al. (2011)
21	H + O ₂ + M → HO ₂ + M	9.7 × 10 ⁻¹³	2*	Sander et al. (2011)
22	H + O ₃ → OH + O ₂	2.9 × 10 ⁻¹¹	2	Sander et al. (2011)
23	H + HO ₂ → OH + OH	7.2 × 10 ⁻¹¹	2	Sander et al. (2011)
24	H + HO ₂ → O + H ₂ O	1.6 × 10 ⁻¹²	2	Sander et al. (2011)
25	H + HO ₂ → H ₂ + O ₂	6.9 × 10 ⁻¹²	2	Sander et al. (2011)
26	OH + O ₃ → HO ₂ + O ₂	7.3 × 10 ⁻¹⁴	2	Sander et al. (2011)
27	OH + H ₂ → H ₂ O + H	6.7 × 10 ⁻¹⁵	2	Sander et al. (2011)
28	OH + OH → H ₂ O + O	1.8 × 10 ⁻¹²	2	Sander et al. (2011)
29	OH + OH + M → H ₂ O ₂ + M	6.4 × 10 ⁻¹²	2*	Sander et al. (2011)
30	OH + HO ₂ → H ₂ O + O ₂	1.1 × 10 ⁻¹⁰	2	Sander et al. (2011)
31	OH + H ₂ O ₂ → H ₂ O + HO ₂	1.8 × 10 ⁻¹²	2	Sander et al. (2011)
32	HO ₂ + O ₃ → OH + O ₂ + O ₂	1.9 × 10 ⁻¹⁵	2	Sander et al. (2011)
33	HO ₂ + HO ₂ (+M) → H ₂ O ₂ + O ₂ + (M)	2.6 × 10 ⁻¹²	2+2*	Sander et al. (2011)
34	O + SO ₂ + M → SO ₃ + M	1.3 × 10 ⁻¹¹	2*	Sander et al. (2011)
35	O ₃ + SO ₂ → SO ₃ + O ₂	2.0 × 10 ⁻²²	2	Sander et al. (2011)
36	OH + S → H + SO	6.6 × 10 ⁻¹¹	2	Sander et al. (2011)
37	OH + SO → H + SO ₂	8.3 × 10 ⁻¹¹	2	Sander et al. (2011)
38	OH + SO ₂ + M → HOSO ₂ + M	9.6 × 10 ⁻¹³	2*	Sander et al. (2011)
39	HO ₂ + SO ₂ → OH + SO ₃	1.0 × 10 ⁻¹⁸	2	Sander et al. (2011)
40	S + O ₂ → SO + O	2.3 × 10 ⁻¹²	2	Sander et al. (2011)

Table 9. Continued.

SO _x Chemistry				
41	S + O ₃ → SO + O ₂	1.2 × 10 ⁻¹¹	2	Sander et al. (2011)
42	SO + O ₂ → SO ₂ + O	8.0 × 10 ⁻¹⁷	2	Sander et al. (2011)
43	SO + O ₂ + M → SO ₃ + M	Varies	2*	
44	SO + O ₃ → SO ₂ + O ₂	8.4 × 10 ⁻¹⁴	2	Sander et al. (2011)
45	HOSO ₂ + O ₂ → HO ₂ + SO ₃	4.3 × 10 ⁻¹³	2	Sander et al. (2011)
46	SO + HO ₂ → SO ₂ + OH	2.8 × 10 ⁻¹¹	2	DeMore et al. (1997)
47	SO + SO → SO ₂ + S	8.3 × 10 ⁻¹⁶	2	Chung et al. (1975)
48	SO + O + M → SO ₂ + M	1.3 × 10 ⁻¹¹	2*	Cobos et al. (1985)
49	SO + SO ₃ → SO ₂ + SO ₂	2.0 × 10 ⁻¹⁵	2	(Chung et al., 1975)
50	S + S + M → S ₂ + M	7.5 × 10 ⁻¹⁴	2*	(Pavlov and Kasting, 2002)
51	SO ₂ + 2H ₂ O → aerosol	2.9 × 10 ⁻³¹	3 (special)	(Sander et al., 2011)
Other				
	Exit rate from cell	2.1 × 10 ⁻²	1	

* Effective second order reactions based on falloff curves for [M] = 2.5 × 10¹⁹ and M = N₂, O₂. See sources for additional information.

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(³Σ⁻) + O₂(³Σ_g⁻) → SO₂(¹A₁) + O(³P) reaction on the triplet PES has a rate constant of 2.7 × 10⁻²⁵ cm³ 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). 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 isomer due to the fact that this isomer on both PESs has nearly the same energy. A possible non-adiabatic reaction pathway is depicted in Fig. 4 by green solid lines connecting every two stationary points. Specifically, for the SO(³Σ⁻) + O₂(³Σ_g⁻) → SO₃(¹A₁') 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 SO₃ product. For the SO(³Σ⁻) + O₂(³Σ_g⁻) → SO₂(¹A₁) + 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 the intersystem crossing have been proposed by other authors for the SO₃ → SO₂ + O reaction (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 Reaction (R5), and supports the facile formation of SO₃.

Unfortunately, rate constants involving the intersystem crossing cannot be readily determined from the current calculations. 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 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 + O₂ + M reaction to sulfate formation in the stratosphere

To determine the significance of 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 U.S. 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°, assuming the spectral photon irradiance of Rottman et al. (2006) to be at the top of the atmosphere and O₂, O₃, and CO₂ to be 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 photoly-

sis rates (J_{SO_2}) 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., Reactions (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.,

$$\frac{[\text{SO}]}{[\text{SO}_2]} = \frac{J_{\text{SO}_2}}{k_{\text{R5}}[\text{O}_2] + k_{\text{R6}}[\text{O}_2][\text{M}]} \quad (8)$$

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} and 1.0×10^{-36} cm⁶ molecule⁻² s⁻¹ to encompass the order of magnitude rate estimates from Sects. 4.3 and 4.4. 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] ratios, the rates of Reactions (R1), (R6), and (R7) can be compared. Assuming these three reactions are the dominant sources of SO₃ (and subsequently sulfate) in the stratosphere, the fraction of sulfate from Reaction (R6) (f_{SO}) can be calculated as

$$f_{\text{SO}} = \frac{\frac{[\text{SO}]}{[\text{SO}_2]} \cdot k_{\text{R6}}[\text{O}_2][\text{M}]}{k_{\text{SO}_2+\text{OH}}[\text{OH}] + k_{\text{SO}_2+\text{O}}[\text{O}] + \frac{[\text{SO}]}{[\text{SO}_2]} \cdot k_{\text{R6}}[\text{O}_2][\text{M}]} \quad (9)$$

The rate constants $k_{\text{SO}_2+\text{OH}}$ and $k_{\text{SO}_2+\text{O}}$ 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 estimate for k_{R6} (1.0×10^{-37} cm⁶ molecule⁻² s⁻¹) gives 4% to 10% of sulfate from Reaction (R6) between 25 and 50 km altitude. A faster estimate for k_{R6} of 2.0×10^{-37} cm⁶ molecule⁻² s⁻¹ gives 8% to 18% of sulfate from Reaction (R6) between 25 and 50 km altitude. The upper bound estimate for the rate ($k_{\text{R6}} = 1.0 \times 10^{-36}$ cm⁶ molecule⁻² s⁻¹, from Black et al., 1982) suggests that over 45% of sulfate could be coming from Reaction (R6) between 31 and 34 km altitude and is probably unrealistic. The contribution from Reaction (R6) depends upon the amount of photons available for SO₂ photolysis, which increases with altitude because of less absorption by the Schumann–Runge band of O₂ and the Hartley bands of O₃. The rate of Reaction (R6) decreases at higher altitude as the total number density decreases. The maximum f_{SO} value, thus, is between around 30 and 35 km (Fig. 8).

Some insight into the rate can be obtained from SO₂ lifetimes in the stratosphere. Following the Mt. Pinatubo (1991) eruption, the Total Ozone Mapping Spectrometer (TOMS)

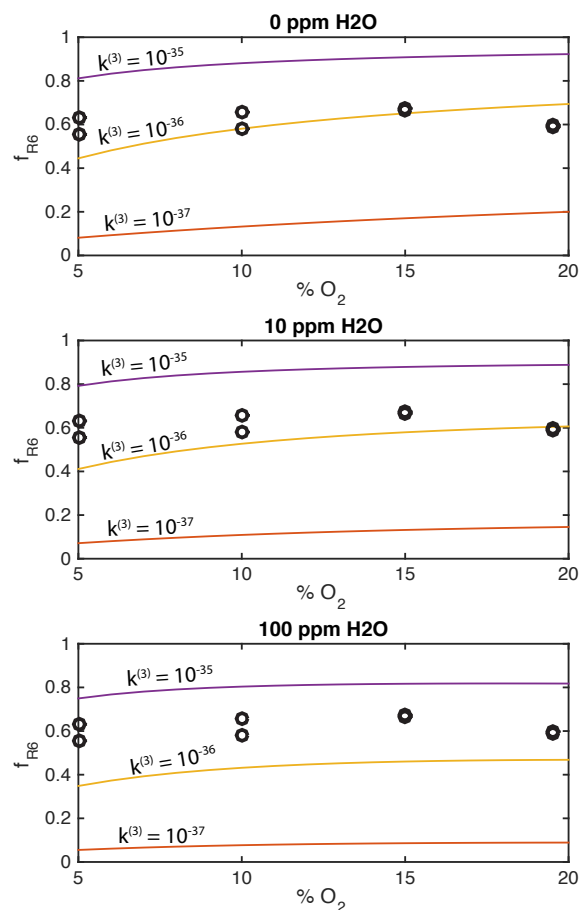


Figure 7. Results of kinetic model (Sect. 4.4, Table 9) compared to experimental data (circles) for f_{R6} (Eq. 4) vs. fraction of SO₃ formed from Reaction R6 in the model. Contours on the plot are labeled with the value of rate constant k_{R6} input into the model for a given run. Experimental data is plotted as black circles. The model was run for three input values of H₂O concentration: 0 ppmv (top), 10 ppmv (middle), and 100 ppmv (bottom).

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 to 35 days for SO₂ 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 SO₂ decay following the Mt. Pinatubo (1991) eruption, considering OH oxidation Reaction (R1) as the only sink of SO₂ in the stratosphere. Their modeled decay times for SO₂ (40 days) are considerably longer than the measured value of 25 days. Bekki and Pyle (1994) attribute this to uncertainties in the OH number densities. The discrepancy, however, could be explained in part by SO₂ photolysis followed by Reaction (R6). Inclusion of the SO₂ photolysis sink would decrease the lifetimes for SO₂ above around 25 km altitude. The presence of this reaction would also suggest that OH concentrations estimated by Read et al. (1993) based on

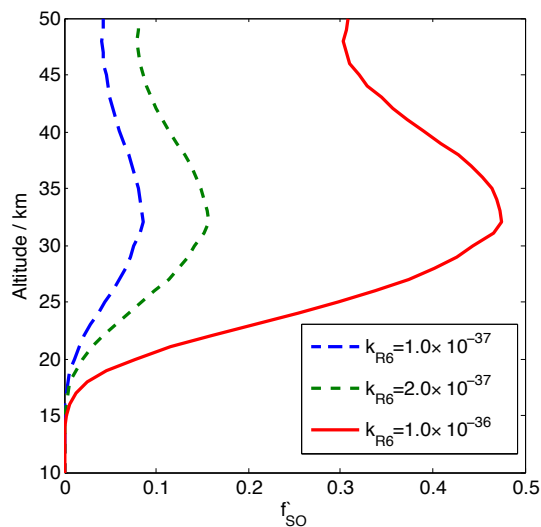


Figure 8. Fraction of sulfate derived from reaction channel R6 (f_{SO}) as a function of altitude for different values of k_{R6} .

SO₂ lifetimes might overestimate OH concentrations above around 25 km altitude.

SO₂ photolysis is self-limiting, as SO₂ photolysis near the top of the volcanic SO₂ plume absorbs ultraviolet radiation in the wavelength range that SO₂ photolysis occurs. As a result, SO₂ photolysis lower in the eruption cloud is reduced and depends upon the overlying SO₂ column density. This would potentially reduce the significance of Reaction (R6) under heavy SO₂ loading.

Optical shielding effects increase the magnitude of the isotope effect from SO₂ photolysis under high SO₂ column densities (Lyons, 2007; Ono et al., 2013). Thus, the isotope fractionation occurring in a volcanic plume 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 estimated using our results and cross sections by Lyons (2007, 2008), the temporal evolution of isotope signatures of sulfate aerosols will require a model that accurately incorporates both the chemistry and the dynamics of the stratosphere.

Given the large isotope signal produced by SO₂ 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 (R6) 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 SO₂ photolysis (Fig. 3), it is likely that SO₂ photolysis plays an important role in the sulfur isotope budget of stratospheric sulfate aerosols. The initial sulfate formed from SO₂ photolysis (followed by Reaction (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 bal-

ance, the residual SO₂ 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 SO₂ in the stratosphere

It has been suggested previously (Savarino et al., 2003; Hattori et al., 2013) that excited-state photochemistry of SO₂ in the 250 to 350 nm absorption region (i.e., the $\tilde{A}(^1A_2)/\tilde{B}(^1B_1)$ states) might be the dominant source of the sulfur isotope ratios in stratospheric sulfate aerosols. Previous results (Whitehill and Ono, 2012; Whitehill et al., 2013) have demonstrated that SO₂ 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 SO₂ 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., addition of C₂H₂ to trap triplet-state SO₂ and the absence of O₂). In the present study, we tested SO₂ photoexcitation with two different long-pass filters (250 nm long-pass filter and 280 nm long-pass filter) in a N₂/O₂ 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 SO₂ photoexcitation as the dominant source of the isotope anomalies in the modern atmosphere.

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 $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios in our photolysis experiments and those in stratospheric sulfate aerosol samples (Fig. 3), the stratospheric sulfate aerosol samples produce a slightly shallower (less negative) $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ slope than the majority of our experimental samples. This could be due in part to the effect of pressure on $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios (Masterson et al., 2011), as the one experiment performed at 7.7 kPa total pressure (Table 5) produced a $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ value 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 $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ signatures from SO₂ photolysis and the positive $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ signature from SO₂ photoexcitation. It is critical that future experiments further explore the isotope effects within these two absorption regions. However, it is also clear that SO₂ photoexcitation alone is not likely to be

responsible for the isotope signatures in stratospheric sulfate aerosols and that SO₂ 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 occurring in the natural environment. One issue is the difference between the spectral photon flux of the Xe and D₂ arc lamps as compared with the solar spectrum. Comparisons of data from different light sources (Xe vs. D₂ lamps) were made previously in static photochemical experiments (Whitehill and Ono, 2012) and showed minor differences depending upon the light source. However, despite the large differences in the spectral photon flux between the Xe and D₂ light sources, the patterns in the isotope fractionation (i.e., $\delta^{34}\text{S}$ vs. $\Delta^{33}\text{S}$ vs. $\Delta^{36}\text{S}$) are similar. Both the Xe and D₂ light sources are broadband, unstructured light sources in the 180 to 220 nm absorption region, where SO₂ photolysis occurs. The solar spectrum, although also broadband, has considerably more fine structure in the spectrum, due to absorption by other gases such as O₂. As demonstrated in early SO₂ 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 from photochemical experiments (Whitehill and Ono, 2012). As shown by Ueno et al. (2009), they predict negative $\Delta^{33}\text{S}$ values from SO₂ photolysis under atmospheric conditions. Photochemical experiments show positive $\Delta^{33}\text{S}$ values under similar conditions. The magnitude of the uncertainties in the cross-section measurements (on the percent level) is too large to be considered quantitative for the permil-level mass-independent fractionations observed in these reactions. Future, higher precision and higher resolution cross-section measurements should resolve some of the discrepancies between measured cross sections and experiments 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 type of isotope fractionations expected under a solar regime.

Another major issue with the experiments that is discussed above (Sect. 4.3) is the poor control in the experiments over the amount of water in the system. Due to the fact that experiments were performed at atmospheric pressure 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 system with nitrogen (< 3 ppb H₂O) prior to each experiment, water could be absorbed onto the surfaces of the system. The presence of water will cause HO_x chemistry to occur and open up an additional (mass-dependent, see Harris et al., 2012) channel for sulfate for-

mation. The amount of water in the system also affects the amount of SO₃ that ends up as sulfate aerosols. This is particularly an issue when attempting to estimate the rate of reactions in the system (Sects. 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 to 350 nm) experiments performed in an identical photochemical system but with the addition of C₂H₂ are not strongly affected by the presence of trace amounts of water in the system, and show considerably better isotopic reproducibility (Whitehill et al., 2013, ; Table 3) than SO₂ photolysis experiments (Ono et al., 2013, ; Tables 2, 4, and 5). This suggests that variability in trace amounts of water present in the system could have a significant effect on the isotopic signatures during SO₂ photolysis, and that water vapor should be carefully controlled in future experiments.

4.9 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 SO₂ into the stratosphere. Both direct injection into higher altitudes (i.e., above around 20 to 25 km) or stratospheric transport of the SO₂ plume can bring SO₂ to a sufficient altitude for SO₂ photolysis to occur. The process of SO₂ photolysis produces large mass-independent sulfur isotope signatures in the SO products, particularly when there is high SO₂ loading (and thus optical screening effects). Reaction of SO with O₂ to produce SO₃ (via Reaction (R6)) provides a pathway for the isotopic signature of SO to be preserved as SO₃, 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 eruption; Savarino et al., 2003) and Laki (1783 eruption; Lanciki et al., 2012). Schmidt et al. (2012) discussed this issue previously and concluded that the Laki aerosols deposited in 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 SO₂ 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 (circa 20 to 20 km or greater) for SO₂ pho-

tolysis to occur. Thus, despite the stratospheric influence of the Laki (1783) eruption, mass-independent sulfur isotope signatures in the preserved aerosols would not be expected. The situation is similar for the Mount Hudson (1991) eruption, which had an injection height of 11 to 16 km (Schoeberl et al., 1993). Again, given the high latitude of the eruption, transport processes are likely insufficient to bring the plume to a sufficient altitude for SO₂ photolysis to become a dominant process.

Low-latitude eruptions such as Pinatubo (1991) might behave differently. Although the initial injection of the Pinatubo (1991) eruption was probably localized below 25 km, the evolution of the plume resulted in its reaching altitudes of 30 km or higher (Gobbi et al., 1992), sufficient altitudes for SO₂ photolysis to become important. The largest mass-independent sulfur isotope signatures from ice core records (with $\Delta^{33}\text{S} > 1\text{‰}$) 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 altitude of 34 km, with a likely estimate being 43 km altitude (Lavigne et al., 2013). At this altitude, SO₂ photolysis would become a dominant process, and could explain why the signature from this eruption is significantly larger than that of other eruptions. Thus, SO₂ photolysis, followed by SO oxidation to SO₃ (via Reaction (R6)), presents a consistent mechanism through which mass-independent sulfur isotope signatures can be produced and preserved in the modern, oxygenated atmosphere.

5 Conclusions

Laboratory photochemical experiments were carried out to investigate the production of mass-independent sulfur isotope effects under stratospheric conditions. For SO₂ 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 the $\delta^{34}\text{S}$ and $\Delta^{36}\text{S}$ values, show excellent agreement with an optical screening model based on synthetic absorption cross sections (Lyons, 2007). SO₂ 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 the signature predicted from absorption cross sections (Danielache et al., 2012).

The SO₃ (recovered as sulfate) products from SO₂ photolysis in the presence of molecular oxygen carry mass-independent sulfur isotope signatures, suggesting a pathway for the direct oxidation of SO to SO₃. We hypothesize the SO + O₂ + M → SO₃ + M (R6) and estimate the termolecular rate constant of this reaction to be on the order of 10⁻³⁷ cm⁶ molecule⁻² s⁻¹ or faster. This is consistent with previous constraints on the maximum rate of this reaction (Black et al., 1982).

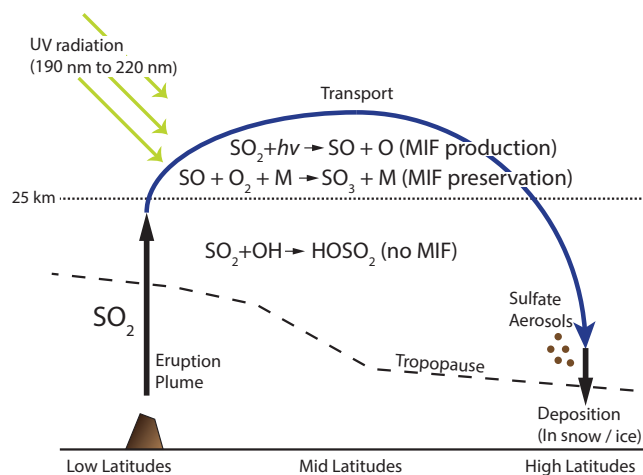


Figure 9. Schematic illustration of the production and preservation of mass-independent fractionation (MIF) in sulfur isotopes following explosive volcanic eruptions. Low latitude eruptions such as Pinatubo (1991) inject large amounts of SO₂ into the stratosphere. Through stratospheric transport, it is brought to altitudes where SO₂ photolysis can occur, producing large MIF signatures. The product of SO₂ photolysis, SO, is preserved via termolecular reaction with O₂. The resulting SO₃ forms sulfate aerosols, which are deposited at high latitudes in polar snow and ice core records. SO₂ oxidation below around 25 km is dominantly by OH, which is a mass-dependent process.

We calculated the energies of stationary points on the singlet and triplet potential energy surfaces of SO₃ that are associated with the SO(³Σ⁻) + O₂(³Σ_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 the SO + O₂ → SO₂ + O Reaction (R5) requires intersystem crossing between the singlet and triplet surfaces to explain the observed rate.

Depending on the rate of Reaction (R6), we predict that on the order of 10% or more of the sulfate above circa 25 km altitude could be derived from the SO + O₂ + M channel. Given the large isotope fractionations produced during SO₂ 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, our model explains the temporal evolution of $\Delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values following major volcanic eruptions, and constrains the maximum altitude of the plume to above circa 20 to 25 km when significant $\Delta^{33}\text{S}$ values are observed.

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