High-Resolution UV Absorption Cross-section Measurements of 32S, 33S, 34S, and 36S Sulfur Dioxide for the B ^1 B_1-X ^1 A_1 Absorption Band

Yuanzhe Li¹, Sebastian Oscar Danielache¹, Yoshiaki Endo², shinkoh Nanbu¹, and Yuichiro Ueno²

¹Sophia University ²Tokyo Institute of Technology

March 25, 2024

Abstract

High-resolution and high-precision spectrum data presents a challenging measurement. We report newly measured ultraviolet absorption cross-sections of 32SO2, 33SO2, 34SO2, and 36SO2 for the - band over the wavelength range 240 to 320 nm at a resolution of 0.4 cm-1. The resolution is improved by 20 times compared to a previous study (Danielache et al., 2012). A least absolute deviation linear regression method was applied to calculate the cross-sections and spectral errors from a set of measurements recorded at a wide range of pressure to ensure optimal signal-to-noise ratio at all wavelengths. Based on this analysis, error bars on the measured cross-sections ranged between 3 and 10%. The overall features of measured cross-sections, such as peak positions of isotopologues, are consistent with previous studies. We provide improved spectral data for studying sulfur mass-independent fraction (S-MIF) signatures in SO2 photoexcitation. Our spectral measurements predict that SO2 photoexcitation produces $33E = -0.8\pm0.2$ and 36E = -4.0+-0.4Danielache et al. (2012).

















Hosted file

2023_S02 Measurement_Supporting Infomation-v2.docx available at https://authorea.com/users/ 600989/articles/732208-high-resolution-uv-absorption-cross-section-measurements-of-32s-33s-34s-and-36s-sulfur-dioxide-for-the-b-%CC%B5%CC%83-1-b_1-x-%CC%B5%CC%83-1-a_1absorption-band

1 High-Resolution UV Absorption Cross-section Measurements of ³²S, ³³S,

2 ³⁴S, and ³⁶S Sulfur Dioxide for the \tilde{B}^1B_1 - \tilde{X}^1A_1 Absorption Band

3 Y. Li¹, S. O. Danielache¹, Y. Endo², S. Nanbu¹, Y. Ueno^{2,3,4}

- 4 ¹Department of Materials and Life Science, Faculty of Science and Technology, Sophia
- 5 University, Japan
- 6 ²Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Tokyo, Japan
- ³Earth-Life Science Institute, Tokyo Institute of Technology, Tokyo, Japan
- ⁴Institute for Extra-cutting-edge Science and Technology Avant-garde Research (X-star),
- 9 Super-cutting-edge Grand and Advanced Research (SUGAR) Program, Japan Agency for
- 10 Marine-Earth Science and Technology (JAMSTEC), Yokosuka, Japan
- 11 Corresponding author: Yuanzhe Li (<u>liyuanzhe@eagle.sophia.ac.jp</u>)

12 Key Points:

- We report measured cross-sections of ${}^{32}SO_2$, ${}^{33}SO_2$, ${}^{34}SO_2$, ${}^{36}SO_2$ for the $\tilde{B}^1B_1-\tilde{X}^1A_1$ absorption band over the wavelength range 240 to 320 nm at a resolution of 0.4 cm⁻¹.
- A least absolute deviation linear regression method was applied to calculate the cross-sections, and the error bars on the measured cross-sections ranged between 3 and 10%.
- Reported absorption cross-sections predict relatively small mass-independent fractionation (${}^{33}E = -0.8 \pm 0.2\%$ and ${}^{36}E = -4.0 \pm 0.4\%$) during SO₂ photoexcitation for top of the atmosphere solar spectra.
- 20

21 Abstract

High-resolution and high-precision spectrum data presents a challenging measurement. We
 report newly measured ultraviolet absorption cross-sections of ³²SO₂, ³³SO₂, ³⁴SO₂, and ³⁶SO₂

- for the $\tilde{B}^1B_1-\tilde{X}^1A_1$ band over the wavelength range 240 to 320 nm at a resolution of 0.4 cm⁻¹.
- 25 The resolution is improved by 20 times compared to a previous study (Danielache et al., 2012).
- 26 A least absolute deviation linear regression method was applied to calculate the cross-sections
- and spectral errors from a set of measurements recorded at a wide range of pressure to ensure
- optimal signal-to-noise ratio at all wavelengths. Based on this analysis, error bars on the
 measured cross-sections ranged between 3 and 10%. The overall features of measured cross-
- 30 sections, such as peak positions of isotopologues, are consistent with previous studies. We
- 31 provide improved spectral data for studying sulfur mass-independent fraction (S-MIF)
- 32 signatures in SO₂ photoexcitation. Our spectral measurements predict that SO₂ photoexcitation
- 33 produces ${}^{33}E = -0.8 \pm 0.2\%$ and ${}^{36}E = -4.0 \pm 0.4\%$, whose magnitudes are smaller than those
- reported by Danielache et al. (2012).
- 35

36 1 Introduction

37 Sulfur dioxide (SO₂) is the most common reduced sulfur compound present in many planetary

38 atmospheres. This molecule has been known to exist in Earth, Venus, and Io for many years

39 (Yung and DeMore, 1999). It has also been reported the presence of SO_2 in the atmosphere of

40 WASP-39b (Tsai et al., 2023). Understanding the photochemical properties of this molecule is

41 essential for geochemical studies of planetary atmospheres. Its interactions with UV light

- 42 trigger a cascade of chemical reactions that produce a variety of compounds, such as sulfuric 42 acid (USO) or S_{1} depending on the strager barie redevised as state
- 43 acid (H_2SO_4) or S_8 , depending on the atmospheric redox state.
- 44 Stable isotopes are a powerful tool for studying and understanding a variety of geochemical 45 processes. Such applications involve singly substituted isotopes, a combination of the same 46 isotope with different masses which creates mass-dependent and mass-independent relations, and more than one isotope within the same molecule known as clumped isotopes (e.g., Eiler et 47 al., 2014). The sulfur mass-independent fractionation (S-MIF) signatures (non-zero Δ^{33} S and 48 Δ^{36} S values) in the geological record have been shown to be non-zero before ~2.3 Ga 49 50 coinciding with the rise of oxygen levels in the atmosphere (Farquhar et al., 2000; Ono, 2017). Studies by Farquhar and co-workers (Farquhar et al., 2001; Masterson et al., 2011) and 51 52 subsequent chemical chamber experiments (Endo et al., 2019; Endo et al., 2016) have shown 53 that SO₂ photodissociation and photoexcitation reactions under conditions free of oxygen produce large S-MIF signatures, although the previous experiments have not fully reproduced 54 the Archean record such as relationships between $\Delta^{33}S$ and $\Delta^{36}S$ and between $\delta^{34}S$ and $\Delta^{33}S$ 55 (e.g., Ono, 2017; Endo et al., 2022b). An atmospheric photochemical model study by Pavlov 56 and Kasting (2002) showed that SO radical produced during photolysis rapidly oxidized back 57 to SO₂ with 10^{-5} of present atmospheric levels of O₂ and therefore setting a maximum level of 58 59 atmospheric oxygen abundance in which the S-MIF can be preserved, yet no model study has 60 succussed into reproducing the geological record. The work done to constrain the mechanisms
- 61 and the atmospheric conditions that explain the S-MIF in the geological record is extensive and

62 a full summary is beyond the scope of this report (e.g., Ono, 2017; Thiemens and Lin, 2019) 63 but current understanding points to a combination of mechanisms including the photoexcitation 64 $\tilde{B}^1 B_1 - \tilde{X}^1 A_1$ band of the SO₂ molecule (Endo et al., 2016).

In the present earth, sulfur aerosols produced in the lower stratosphere from material uplifted 65 66 by plumes during Plinian eruptions and collected from Antarctic and Greenland ice cores show 67 an S-MIF signature distinct from Archean sulfides and sulfates (Baroni et al., 2007). Hattori et 68 al. (2013), based on the data reported by Danielache et al. (2012), reported that SO₂ 69 photoexcitation in the lower stratosphere produce signals compatible with the ice core record. A subsequent study presented by Whitehill et al. (2013) showed that the fate of the photoexcited 70 71 fragment is not only direct oxidation by O₂, as assumed in the Hattori et al. (2013) study, but 72 follows a branching mechanism due to quenching in which a fraction of the molecules in the 73 $\tilde{A}^1 A_2 / \tilde{B}^1 B_1$ state are converted to the $\tilde{a}^3 B_1$ state. They further show an isotope selective spinorbit interaction between the singlet $(\tilde{A}^1 A_2 / \tilde{B}^1 B_1)$ and triplet $(\tilde{a}^3 B_1)$ manifolds. Despite the 74 75 extensive work done so far, further quantification of the isotopic effect during the $\tilde{B}^1 B_1$ - $\tilde{X}^1 A_1$ and $\tilde{A}^1 A_2 - \tilde{X}^1 A_1$ excitation is needed. 76

77 The highly structured SO₂ UV absorption spectrum directly results from electronic transitions and a complex and nuanced set of vibrational and rotational energy levels (Herzberg, 1945). 78 79 The single report on the ${}^{32}SO_2$, ${}^{33}SO_2$, ${}^{34}SO_2$, and ${}^{36}SO_2$ (hereafter ${}^{32,33,34,36}SO_2$) \tilde{B}^1B_1 - $\tilde{X}^{1}A_{1}$ absorption spectrum from Danielache et al. (2012) has a spectral resolution of 8 cm⁻¹ 80 which is still far from fully resolved (Stark et al., 1999). Although from the $\tilde{C}^1B_2-\tilde{X}^1A_1$ 81 absorption band, spectral measurements by Endo et al. (2015), SO₂ column density dependence 82 on cross-sections were observed (especially, this apparent column density and cross-sections 83 84 relation was stronger at absorption peaks; see Endo et al., 2015 Figure 1). Further analysis 85 suggested that insufficient spectral resolution relative to absorption line width explains this 86 phenomenon (Endo et al., 2015). The lack of resolution directly affects the peak separation and 87 further interferes with the accuracy of S-MIF calculations, which would significantly impact 88 the study of light-induced isotopic effects (See Endo et al., 2015 Figure S1). High-resolution 89 spectrum is therefore necessary for better understanding spectroscopic properties and 90 accurately the absorption spectra (Wu et al., 2000). Fully resolved spectra (Koplow et al., 1998) 91 with a low level of noise would be the authoritative yet near unachievable measurement for an 92 entire absorption band.

93 Recent studies by Lyons et al. (2018) have reported pressure room temperature broadening coefficients of 0.30 ± 0.03 cm⁻¹ atm⁻¹ and 0.40 ± 0.04 cm⁻¹ atm⁻¹ for N₂ and CO₂ respectively 94 for the \tilde{C} - \tilde{X} absorption band and Leonard (1989) reported broadening coefficients of 0.237 95 ± 0.0011 cm⁻¹ atm⁻¹ and 0.325 ± 0.0015 cm⁻¹ atm⁻¹ for N₂ and CO₂ respectively for the \tilde{B} -96 97 \tilde{X} absorption band. There are studies suggesting a largely congested line profile for the SO₂ 98 electronic spectra. The basis for such an assertion are from theoretical calculations of the 99 bound-type exited electronic states coupled to rotational-vibrational transitions (Kumar et al., 100 2015). Models reported by Lyons et al. (2018) used a line spacing of 0.25 cm⁻¹ for the \tilde{C} - \tilde{X} 101 band which is not the absorption band concerned in this report, but it might show a similar 102 behavior. A quantitative assessment of natural widths and line congestion at different spectral 103 regions is yet to be reported. The computational requirement for a theoretical calculation of a

104 high J electronic spectrum is a challenge to be reckoned with. Reports on J and K values (J and

105 K stand for rotational and vibrational wavefunction, not to be confused with the integrated 106 photo-dissociation rate constant J) such as the reported by Kumar et al. (2015) for total angular 107 momentum J = 0-10 are illustrative of the amount of computations needed for a full spectrum calculated at high J. Pressure broadening coefficients put together with the above suggested 108 line density of these systems will cause line profile overlap and thus creating a pseudo-109 110 broadened spectra or sections of the most congested parts of the rovibrational progression and 111 thus reducing the minimal requirement of spectral resolution for meaningful photo-induced isotopic effects. In summary, a combination of spectral resolution, pressure broadening, and 112 profile overlap suggests that the data in this report might be suitable for the study of isotopic 113 114 effects happening in a planetary atmosphere with a total atmospheric pressure close to 1 atm.

An additional known issue is that even if a fully resolved spectrum is achieved, it is difficult to obtain high precision with high-resolution measurements because the noise increases at highresolution measurements (see comparison in Table 1). The issue would lead to large errors of calculated photodissociation rate constants and associated isotopic effects. In order to address this issue we have implemented a linear regression method that has been widely used in Fourier

transform spectroscopy to reduce noise and increase spectral precision (Barra et al., 2021;
Dreissig et al., 2009; Meyer-Jacob et al., 2014; Santos et al., 2021).

122 In this study, an experimental setup of a Fourier transform spectrometer (VERTEX 80v, Bruker, 123 Japan) was optimized to adapt measurements in the UV band. We used the least absolute 124 deviation (LAD) linear regression for data calibration and measured the ${}^{32}SO_2$, ${}^{33}SO_2$, ${}^{34}SO_2$, 125 and ${}^{36}SO_2$, $\tilde{B}^1B_1-\tilde{X}^1A_1$ absorption spectrum ranges from 240 to 320 nm with a resolution of 126 0.4 cm⁻¹ and 3–10% of error.

127 2 Experimental

128 2.1 SO₂ isotopologues samples

129 The isotopically enriched ${}^{32,33,34,36}SO_2$ gas samples were prepared from elemental ${}^{32}S, {}^{33}S, {}^{34}S,$ 130 and ${}^{36}S$ powder (Isoflex USA) sealed with CuO in quartz tubes under vacuum, heated at 950°C 131 for 15 min. Separation of SO₂ samples and unreacted O₂ was done by freeze-pump-thaw 132 cycling. The components of the gas phase labeled samples were confirmed and purified using 133 a GC-MS, and the products purity was checked by quantitative IR spectroscopy (Danielache et 134 al., 2012). Details of sample preservation are described in Endo et al. (2022a).

135 2.2 Instrument setups

The gas cell and inlet gas system follows Endo et al. (2022a). The UV absorption cross-sections were determined using a Fourier transform spectrometer (VERTEX 80v, Bruker, Japan) with an external deuterium lamp (L6301-50, Hamamatsu, Japan) equipped at the inlet port on the right spectrometer side. Two capacitance manometers (CMR362 and CMR364, Pfeiffer, Germany) calibrated the pressure using a full-range gauge (PGE500, INFICON, Germany) and local weather reports. An oil pump was added to the gas line system for pre-vacuuming to extend the lifetime of the turbopump system (Pfeiffer, Germany).

143 Signal drifting from the light source was observed, where the signal intensity decreases over144 time. Following a commonly used method (Danielache et al., 2008; Danielache et al., 2012;

145 Endo et al., 2022a; Vandaele et al., 2009), where the background signal intensity at the time of

146 the sample signal measurement was derived by alternating the background and sample signal 147 measurements and calculating the average of the two background signal before and after each

148 sample signal measurement.

149 Numerous measurement parameters were adjusted to balance high-resolution and relatively low noise levels while limiting the measurement time to avoid excessive errors brought by 150 signal drift. The interferogram from a single measurement was derived from an average of 150 151 scans at a resolution of 0.4 cm⁻¹ using single-sided and bi-directional acquisition mode and 152 153 was converted to signal intensity spectrum by Fourier transform using boxcar apodization function and Mertz phase correction mode to preserve the most original data possible. A 154 frequency window from 0 to 60,000 cm⁻¹ and a zero-filling number of 2 produced a spectrum 155 ranging from 41666 to 29400 cm⁻¹ with a data point spacing of ca. 0.12055 cm⁻¹. No prominent 156 157 peaks spread due to the grazing-incidence light in the UV region measurement was observed, 158 and an 8 mm aperture size was selected. The VERTEX 80v instrument used in our measurements is capable of a maximum spectral resolution of 0.1 cm^{-1} . However, the optimal 159 trade-off between spectral resolution and spectral noise was found to be 0.4 cm^{-1} which is 160 between 5 to 10 times lower in resolving power than the suggested optimal spectral resolution 161 162 (Rufus et al., 2003).

163 2.3 Measurements

164 The Beer-Lambert law,

165
$$A = \ln \frac{I_0}{I} = \ln \frac{1}{Trans} = \sigma l \rho$$
(1)

Shows that absorbance A is proportional to attenuating number density of the gas sample ρ (in 166 167 this report approximated as gas pressure, assuming a constant temperature). The radiant power intensity is reduced from I_0 to *I*, *Trans* is the transmittance, σ is the absorption cross-sections, 168 and l is the optical path length. Both logarithm and natural logarithm definition formats of 169 170 absorbance are widely used. Which format is used does not affect the $A \propto C$ relationship, we 171 used the natural logarithm format for a more convenient calculation of cross-sections. In this 172 report, SO₂ absorption cross-section (σ) at each wavelength (λ) was calculated through the 173 application of the Beer-Lambert law,

174
$$\sigma(\lambda) = -\frac{RT}{PN_A z} \ln \frac{2I(\lambda)}{I_{0a}(\lambda) + I_{0b}(\lambda)} = -\frac{1}{\rho z} \ln \frac{I(\lambda)}{I_{0ave}(\lambda)} = -\frac{1}{\rho z} \ln Trans(\lambda)$$
(2)

175 Where *R* is the gas constant, *T* is the room temperature in the laboratory, *P* is the sample 176 pressure during measurement, N_A is the Avogadro number, *z* is the sample cell length (10.0 177 cm) through which the light passes, *I* is the measured sample signal intensity, I_{0a} and I_{0b} are 178 the measured background signal intensity before and after a single sample measurement as 179 mentioned above, and I_{0ave} is the mean signal intensity of I_{0a} and I_{0b} , Substituting (1) into 180 (2) yields the following,

181
$$\sigma(\lambda) = -\frac{RT}{PN_A z} \ln T(\lambda) = k_1 \cdot \frac{A(\lambda)}{P}$$
(3)

182 Where
$$k_1 = \frac{RT}{N_A z}$$
, and

$$\sigma(\lambda) = -\frac{RT}{PN_A z} \ln T(\lambda) = k_2 \cdot TA(\lambda)$$
(4)

184 Where
$$k_2 = \frac{R}{PN_A z}$$
.

185 Equations (3) and (4) indicate that when σ is either pressure or temperature dependent, the 186 linear relationship between A and P is not valid. In this study, the temperature is assumed to be 187 constant since variability was within a range of a few digress. The measured data showed no 188 pressure-dependent cross-sections. Figure 1 shows the relation between sample pressure in the 189 gas cell and measured absorption-cross sections. Previous absorption cross-section 190 measurements of various gas and liquid species have acknowledged deviations from the Beer-191 Lambert law, that is an apparent cross-section pressure dependency (e.g., Kostkowski and Bass, 192 1956; Anderson and Griffiths, 1975; Mellqvist and Rosén, 1996; Endo et al., 2015; Li et al., 193 2022).In both reports the origin of such non-linear behavior is attributed to low spectral 194 resolution of the instrument. The data presented in this report, which was recorded at spectral 195 resolution of 0.4 cm⁻¹, shows no apparent pressure-dependent cross-section variability (Figure 196 1). Thus, it is not required to correct the apparent cross-section pressure dependency.



- Figure 1: Individual cross-section data of each peak and valley at different pressures from
 280–300 nm for ³⁴SO₂. The ³⁴SO₂ pressure ranges from 200–2200 Pa. No apparent pressure dependent cross-section phenomenon was observed.
- 201

202 In actual measurements, many sources of uncertainty can affect the linear relationship between 203 A and P. In the case of a high-precision Fourier transform spectrometer, the dark current and 204 amplifier noise from regions where source intensity and detector sensitivity are low, the photon detector shot noise, the cell positioning uncertainties, etc., making different orders of impact 205 206 on the relative signal intensity uncertainty (Skoog et al., 2017). These random noises are almost 207 impossible to distinguish from each other thoroughly. Common solutions include averaging multiple sets of measurements (Blackie et al., 2011; Rufus et al., 2003; Stark et al., 1999; 208 209 Vandaele et al., 2009), adding weights to the parameters that characterize the data (Danielache 210 et al., 2008; Danielache et al., 2012), and calibration of SO₂ column density dependence on 211 measured cross-sections with a least squares method (Endo et al., 2015). Nonetheless, 212 conventional methods still do not resolve the bias that noise from different sources introduce to the actual absorptivity. 213

In this study, we implemented a linear regression technique to rule out the effect of random noise. The LAD method was deployed to clarify the linear relationship between A and P, following the purpose of minimizing the sum of the absolute values of the residuals S between raw data y_i to the fitted data $f(x_i)$,

218
$$\operatorname{argmin} S = \sum_{i=1}^{n} |y_i - f(x_i)|$$
 (5)

219 A universal algorithm from the Scikit-Learn machine learning library (Pedregosa et al., 2011) 220 for the Python programming language was used for computational efficiency considerations. 221 Based on the degree of data dispersion, scenarios that linear regression needs to target can be 222 categorized into three. Case 1: Little effect of random noise on the data, where A and P have 223 good linear fit, and there is little difference compared to the commonly used least squares (LS) 224 linear regression. Case 2: The effect of random noise on individual data creates outliers, and 225 the LAD method excludes the impact from outliers much better than the LS method. Case 3: 226 Highly discrete data in high noise regions, the linear relationship between A and P is almost 227 indistinguishable, and all current methods do not guarantee noise removal.

228 The number of valid measurements at a given wavelength used in the LAD linear regression 229 ranged between 10 and 70 depending on signal-to-noise and the amount of available sample 230 (Figure S2). The increased number of measurements are a necessary condition for reducing 231 the errors associated with signal-to-noise issues. Previous measurements on isotopic effects of 232 ultraviolet absorption cross sections reported by the authors (Danielache et al., 2008, 2012; 233 Hattori et al., 2011; Endo et al., 2015, 2022a) have been aware of this issue but limitations on 234 sample and instrument accessibility have limited the number of measurements. In this report 235 the number of measurements were increased to a number where an analysis of the limit of noise 236 reduction by number pf measurements was conducted. At least 10 measurements are required to reduce the LAD algorithm error. 15–25 sets of measurements are recommended, and the
improvement in error is no longer apparent after more than 30 sets.

239 With the above reference parameters, the final cross-sections are calculated as follows. Firstly, 240 the collected raw data were prefiltered to retain the data with transmittance from 0.1 to 0.95. 241 which not only excluded the data with too low signal intensity but also the transmittance range 242 was chosen to consider the effect of instrument noise on the measurement precision (Skoog et 243 al., 2017). Next, data with signal-to-noise ratio (SNR) less than 20 were excluded to further improve data quality. The filtered data are involved in the following data correction of the 244 linear relationship between A and P by the LAD method. Finally, the corrected A allows the 245 246 calculation of the cross-sections at the corresponding wavelength.

247 2.4 Error budgets

The errors in this study came mainly from four main sources. (1) The temperature variation of the experimental environment was within 2.5 K, introducing an error of 0.85% to the final cross-sections. (2) The mechanical error of the pressure gauge, according to the manufacturer's instructions, has a validity of about 0.2%. (3) Each measurement took about 20 min, and the pressure change due to SO₂ adsorption to the sample cell and stainless tube wall introduced an error of about 0.2%. (4) The errors from instrumental random noises are mostly reflected in the dispersion of the linear relationship between *A* and *P*, following,

255
$$S_{y/x} = \sqrt{\frac{\sum (y_i - f(x_i))^2}{n - 2}}$$
(6)

256 3 Results and discussions

257 3.1 Comparisons with previous studies

The measured ${}^{32}SO_2$ absorption spectrum in the present study is compared to four previous 258 studies on SO₂ in the $\tilde{B}^1 B_1 - \tilde{X}^1 A_1$ absorption band (Figure 2) and spectral summary listed in 259 Table 1. There are two previous studies about the SO₂ isotopologues with spectral resolution 260 of 25 cm⁻¹ (Danielache et al., 2008) and 8 cm⁻¹ (Danielache et al., 2012) and errors of 1.2–2.5% 261 and 1.2-8.2% respectively. For comparison, two naturally abundant SO₂ studies with high 262 resolution are presented. The study from Vandaele et al. (2009) with spectral resolution of 2 263 cm⁻¹ and 4–6% error. A high-resolution natural abundance measurement from Rufus et al. 264 (2003) with spectral resolution of 0.04-0.13 cm⁻¹ resolution and 5% error. This study improves 265 the spectral resolution of the existing isotopic spectrum by a factor of 20, while the error in the 266 267 260-300 nm band is comparable to spectra of natural abundance at about ten times higher 268 resolution.



Figure 2: Comparison of measured ³²SO₂ absorption spectrum in this study with spectra 270 reported by Rufus et al. (2003), Vandaele et al. (2009), Danielache et al. (2008) (³²SO₂, 25 271 cm⁻¹), and Danielache et al. (2012) at the 293.5–295.5 nm spectral range. All the reported 272 273 spectra were measured at room temperature (293-298 K) therefore spectral differences are not 274 expected to be produced by temperature differences. Spectra reported by Rufus et al. (2003), Vandaele et al. (2009) are for natural abundance SO₂ samples. ³²SO₂ spectrum data in 275 276 Danielache et al. (2008) used natural abundance samples and calibrated with measured ${}^{33}SO_2$ and ³⁴SO₂ spectra. Spectra in this report and Danielache et al., (2008) are from isotopically 277 enriched ³²SO₂ samples. 278

279

Table 1: Summary and comparison of studies on SO₂ absorption b-band.

Reference	Isotope	Resolution	Average	Temperature
		(cm^{-1})	Error (%)	(K)
Present study	^{32,33,34,36} S	0.4	~5.1(³² SO ₂)	293
			~4.0(³³ SO ₂)	
			~4.5(³⁴ SO ₂)	
			~4.1(³⁶ SO ₂)	

Rufus et al. (2003)	Natural abundance	0.04-0.13	~5	295
Vandaele et al. (2009)	Natural abundance	2	~4-6	298
Danielache et al. (2012)	^{32,33,34,36} S	8	~2.2(³² SO ₂) ~1.8(³³ SO ₂) ~1.2(³⁴ SO ₂) ~2.5(³⁶ SO ₂)	293
Danielache et al. (2008)	Nat.,33,34 S	25	~1.2(Nat.) ~3.8(³³ SO ₂) ~8.2(³⁴ SO ₂)	293

281 Note. Comparison of peaks at different resolutions show that the spectrum in this study exhibits 282 significantly better peak separation than the low-resolution studies (Danielache et al., 2008; Danielache et al., 2012; Vandaele et al., 2009). Even the spectrum from Vandaele et al. (2009), 283 284 which has only a five-times difference in resolution, can observe much more resolved peaks. 285 This study also shows excellent control of baseline noise, which is about the same as the lower 286 resolution spectrums compared to the ten times higher resolution spectrum from Rufus et al. 287 (2003). The peak position in this study fits the result from Danielache et al. (2012), while the 288 spectrum from Danielache et al. (2008) is unsuitable for comparison due to band shape 289 distortion by low resolution. The peak position in the spectrum from Vandaele et al. (2009) 290 shows a slightly blue shift compared to the spectrum from Rufus et al. (2003), which is also of 291 natural abundance.

292 The cross-sections calculated using the LAD method are also compared to those calculated 293 using the averaging method as illustrated in Figure 3. The new LAD method perfectly 294 reproduces the peak positions and peak intensities derived from the averaging method over the 295 entire measurement band. From Figure 3 (b), it can be concluded that the subtle differences 296 between the two methods are mainly reflected in the position of the spectral peaks, and the magnitude of the difference increases with the intensity of the peaks. Figure 3 (c) shows that 297 the difference is about 10^{-2} of the intensity of the cross-sections, and there is a relatively high 298 299 difference of about 2-3% at the low SNR positions at both ends of the measurement band, and 300 about 1% at the high SNR positions in the middle of the measurement band. The comparison of errors between two methods are shown in Figure 4, where the spectral data of ${}^{32}SO_2$ 301 302 measured in this study are used. The error calculation of averaging method follows Stark et al. (1999) that includes uncertainty in the absorbing column density N of SO₂, uncertainties in the 303 values of $I(\lambda)$ and $I_{ave}(\lambda)$ associated with the measurement SNR for $I_{0ave}(\lambda)$, and the 304 305 systematic errors associated with inadequate spectral resolution, following,

306
$$\frac{\Delta\sigma}{\sigma} = \left[\left(\frac{\Delta N}{N}\right)^2 + \left(\frac{1}{(SNR)N\sigma}\right)^2 \{1 + e^{2N\sigma}\} \right]^{0.5}$$
(7)

The averaging method shows higher error than the LAD method, with 20-40% error in low SNR regions at both ends of the measurement band range and 10% in high SNR regions. The mean error for the averaging method is 15.1% in the 240-320 nm band range, compared with the 5.1% error using the LAD method, indicating the new algorithm reduces the error by a factor of about three. Since the LAD method does not require separating multiple sources of

- 312 noise and calculating the errors brought by each type of noise individually, it treats them as a
- 313 whole and discriminates the errors by the dispersion of the linear relationship between
- absorbance and gas pressure, as well as introducing a sufficiently large number of measurement

315 groups to improve the reliability of the data.



316

Figure 3: Comparison of spectra obtained the LAD and averaging methods (panel a), and difference between both methods grey color line for the 240–320 nm spectral range. Panel (b) shows an enlarged comparison for the 290–300 nm spectral range. Panel (c) shows the relative of difference between the two methods respect to the spectrum obtained by the LAD method. From the panel c can be seen that both methods yield spectra with a maximum difference of c.a. $\pm 4\%$.



Figure 4: Error comparison between the LAD method and the averaging method for the spectral data of ${}^{32}SO_2$ measured in this study. The error calculation of the averaging method follows Stark et al. (1999) that includes the uncertainty in the column density, the uncertainties in the value of $I(\lambda)$ and $I_{0ave}(\lambda)$ associated with the measurement SNR for $I_{0ave}(\lambda)$, and the systematic errors associated with inadequate spectral resolution.

- 329
- **330** 3.2 Isotopic Fractionation in SO₂ Photoexcitation

331 The measured absorption cross-sections are shown in **Figure 5**, where values of σ for 332 $^{32,33,34}SO_2$ at 240–320 nm were successfully measured. However, due to insufficient samples 333 as illustrated in **Figure S3**, $^{36}SO_2$ in the 240–245 nm band could not be measured. The errors 334 in the measured cross-sections are in the range of 3–10% shown in **Figure 6**, with relatively 335 high errors in the 240–260 nm and 310–320 nm bands.



Figure 5: Measured absorption cross-sections of ³²SO₂, ³³SO₂, ³⁴SO₂, and ³⁶SO₂, absorption cross-sections and estimated errors. For clarity panels a,b,c and d divide the spectrum in four spectral ranges 240–260nm, 260–280 nm, 280–300 nm and 300–320 nm respectively. Subsets in panels a and d show an expanded fraction of the spectra to make more readable the associated error bars to each wavelength. As the mass of the 13sotopologues increases a significant redshift in the position of the peak of the absorption spectrum can be observed starting at the spectral band origin near 317 nm.



Figure 6: Relative error of ³²SO₂, ³³SO₂, ³⁴SO₂, and ³⁶SO₂ respect to measured absorption
cross-sections. Lack of precision due to insufficient signal-to-noise ratio is more pronounced
at edges of the measurement spectral band.

349 The redshift of the SO₂ rare isotopologues relative to 32 SO₂ at each peak position is more 350 pronounced for heavier isotopes. The wavelength-dependent isotopic fractionation constant 351 ${}^{3x}\varepsilon(\lambda)$ was calculated to describe the isotopic effect (Ueno et al., 2009), following,

352
$${}^{3x}\varepsilon(\lambda) = 1000 \times \ln\left[\frac{\sigma^{3x}SO_2(\lambda)}{\sigma^{32}SO_2(\lambda)}\right] [\%_0]$$
(8)

where $\sigma^{3x}(\lambda)$ is the absorption cross-section for a given 14sotopologues (^{3x}S, namely ³²S, ³³S, ³⁴S, or ³⁶S) at wavelength λ . The result is shown in **Figure 7**, this study extends the existing value of fractionation constant by 10 nm at shorter wavelengths compared to the previous study (Danielache et al., 2012). The peak positions in the highly structured absorption cross-sections are consistent with Danielache et al. (2012), but the values at both ends of the measurement band are slightly smaller.



Figure 7: Fractionation constant of ${}^{33,34,36}\varepsilon$ as a function of wavelength from measured absorption cross-sections (${}^{3x}\varepsilon(\lambda)$) compared to the previous study (Danielache et al., 2012). Newly reported spectra show a large wavelength specific isotopic effect which are similar to previously reported spectra. Significant differences can be seen at edges of the measured spectra in the ~250 nm and ~315 nm region.

369

The magnitudes of S-MIF for the four stable sulfur isotopologues are given by the linearexpressions as follows,

$${}^{33}E_{\lambda} = {}^{33}\varepsilon_{\lambda} - 0.515 \times {}^{34}\varepsilon_{\lambda} \tag{9}$$

$${}^{36}E_{\lambda} = {}^{33}\varepsilon_{\lambda} - 1.9 \times {}^{34}\varepsilon_{\lambda} \tag{10}$$

where the values 0.515 and 1.9 are the high-temperature limit values for the equilibrium partition function ratio for isotope exchange reactions (Hulston and Thode, 1965). As shown in **Figure 8**, the S-MIF constant of ${}^{33}E$ and ${}^{36}E$ largely agree to the previous study (Danielache et al., 2012), with the values at both ends of the measurement band are slightly deviated.



Figure 8: The Mass-independent fractionation constant ${}^{33}E$ and ${}^{36}E$ calculated from standard S-MIF values of 0.515 and 1.9 as a function of wavelength compared to Danielache et al. (2012). Newly reported spectra show a large wavelength specific isotopic effect which are similar to previously reported spectra. Significant differences can be seen at edges of the measured spectra in the ~250 nm and ~315 nm region.

380

381 Generally, ${}^{33,34,36}\varepsilon$ and ${}^{33,36}E$ mostly reproduced the results from the previous study 382 (Danielache et al., 2012) regardless of the higher resolution of this report. The deviation at both 383 ends of the measurement band could come from many factors, the largest of which is likely to 384 be the low SNR brought about by insufficient background signal intensity.

385 The sulfur isotopic fractionation for SO₂ photodissociation in $\tilde{C}^1B_2-\tilde{X}^1A_1$ absorption band and 386 photoexcitation in $\tilde{B}^1B_1-\tilde{X}^1A_1$ absorption band were also calculated. The photochemistry 387 reaction rates for each sulfur 16sotopologues in the atmosphere follows,

388
$${}^{3x}J = \int_{\lambda_0}^{\lambda_1} \Phi(\lambda) \cdot I(\lambda) \cdot {}^{3x}\sigma(\lambda) \, \mathrm{d}\lambda \tag{11}$$

389 Where Φ is the quantum yield (assumed as 1) and *I* is the actinic solar flux derived from 390 Gueymard (2004). The S-MIF signatures ^{33,36}*E* of sulfur isotopes by SO₂ photochemical 391 reactions are then calculated from ^{3x}*J* follow,

392
$${}^{3x}\varepsilon = 1000 \ln \frac{{}^{3x}J}{{}^{32}J} [\%_0]$$
 (12)

393
$${}^{33}E = {}^{33}\varepsilon - 0.515 \times {}^{34}\varepsilon$$
 (13)

394
$${}^{36}E = {}^{36}\varepsilon - 1.9 \times {}^{34}\varepsilon$$
 (14)

395 The errors derived from the LAD method produce a simple standard deviation which in this 396 report is represented as σ ($\sigma^{3x}J$, $\sigma^{3x}\varepsilon$ and $\sigma^{3x}E$). For a detailed description on the error propagation procedure see the corresponding section in the additional information. Calculated 397 398 ^{3x}J values from cross-sections obtained by the LAD and averaging methods are presented and compared in Figure 9 and Table 2. As presented in Figure 2a, cross-sections obtained by both 399 methods are almost identical and therefore the calculated ${}^{3x}J$ values are numerically similar. 400 The propagated errors are significantly different where the robustness of the LAD method is 401 402 reflected in the propagated $\sigma^{3x}J$ values which are roughly 2 orders of magnitude smaller to 403 those obtained by the averaging method. The reduction of the calculated $\sigma^{3x}J$ values represent a breakthrough since they do not overlap with each other (Figure 9 red and blue data sets) 404 405 while the averaging method show significant overlap making the derived $\sigma^{3x}\varepsilon$ and $\sigma^{3x}E$ 406 unreliable for geochemical predictions. The source in propagated error values can be traced to 407 random errors produced by noise in the measured signal intensity (I or I_0 in Equation 1). Noise 408 in the measured signal intensity I or I_0 for single measurements falls into the category of random 409 errors. However, repeated measurements (See Figure S3 for the number reliable measurements 410 at each wavelength and 17sotopologues) provide the necessary data required by the LAD method to systematically dismiss outlier data points produced by noisy conditions. The 411 implementation of the LAD method reduces the random character of noise in the measured 412 intensities to partially convert it into a systematic error. Calculated ${}^{3x}J$ values were compared 413 414 to calculations under the same solar spectra for cross-sections reported by Danielache et al. (2008, 2012) measured at 25 cm⁻¹ and 8 cm⁻¹ numbers respectively. Figure 10 compares these 415 three data sets. One clear and counter intuitive trend is that the higher the spectral resolution 416 the smaller the differences among ${}^{3x}J$ values. This trend has also been observed by Endo et al. 417 (2015) for the $\tilde{C} - \tilde{X}$ absorption band. The comparison is a clear reminder that when 418 419 considering light induced isotopic effects predictions from single or a narrow band of wavelengths. Error bars for values measured at 8 cm⁻¹ spectral resolution for ${}^{33}J$ and ${}^{34}J$ clearly 420 421 overlap casting shadows on the reliability of the derived isotopic enrichment factors. The J422 values presented in this report present error bars which are far smaller than the J values themselves. Calculated ${}^{3x}\varepsilon$ and ${}^{3x}E$ are, as expected, similar in both methods while $\sigma^{3x}\varepsilon$ and 423 424 $\sigma^{3x}E$ values obtained from the cross-sections calculated with the LAD are 1 order of magnitude 425 smaller than those obtained by the averaging method (Tables 3 and 4).

Table 2. Calculated photoexcitation rate constants $({}^{3x}J)$ and propagated standard deviations $(\sigma^{3x}J)$. All values are in molecules cm⁻³ s⁻¹ units.

	^{32}J	^{33}J	^{34}J	^{36}J	$\sigma^{32}J$	$\sigma^{33}J$	$\sigma^{34}J$	$\sigma^{36}J$
LAD Method	3.0913x10 ⁻³	3.0982x10 ⁻³	3.1097x10 ⁻³	3.1137x10 ⁻³	7.03x10 ⁻⁷	4.41x10 ⁻⁷	4.42x10 ⁻⁷	3.96x10 ⁻⁷
Averaging Method	3.090x10 ⁻³	3.097x10 ⁻³	3.108x10 ⁻³	3.113x10 ⁻³	1.42x10 ⁻⁵	1.42x10 ⁻⁵	1.44x10 ⁻⁵	1.44x10 ⁻⁵

428

429

430	Table 3. Calculated isotopic enrichment factors $({}^{3x}\varepsilon)$ during photoexcitation and propagated
431	standard deviations ($\sigma^{3x}\varepsilon$). All values are in permil (‰) units.

	³³ ε	$^{34}\varepsilon$	³⁶ ε	$\sigma^{33}\epsilon$	$\sigma^{34} \epsilon$	$\sigma^{36}\!\epsilon$
LAD Method	5.91	2.22	7.22	0.26	0.26	0.26
Averaging Method	5.84	2.13	7.29	6.51	6.49	6.52

Table 4. Calculated mass independent isotopic enrichment factors $({}^{3x}E)$ during photoexcitation and propagated standard deviations $(\sigma^{3x}E)$. All values are in permil (‰) units.

	³³ E	³⁶ E	σ ³³ E	$\sigma^{36}E$
LAD Method	-0.83	-4.02	0.19	0.36
Averaging Method	-0.88	-3.81	5.64	10.76

435

436 The introduction of the LAD method has made possible the reduction of propagated error bars 437 to a point where reliable geochemical predictions are possible. Spectral resolution has also been 438 a topic of concern. Previous measurements by Danielache et al. (2008, 2012) carried out at a 439 spectral resolution of 25 cm^{-1} and 8 cm^{-1} respectively, the relation between spectral resolution and predicted isotopic effect has been so far acknowledged but not properly addressed. A 440 441 definite study on the quantitative relation between isotopic effect and spectral resolution is yet to be done. Rufus et al. (2003) reported absorption cross for this band at a spectral resolution 442 between 0.04 cm⁻¹ and 0.13 cm⁻¹, which is according with their assessment sufficient to resolve 443 all natural line widths. For the measurements in this report the optimal trade-off between 444 spectral resolution and spectral noise was set to 0.4 cm⁻¹. Based on recent reports on pressure 445 446 broadening (Lyons et al., 2018) and line profile density (Kumar et al., 2015) suggest that a spectral resolution 0.4 cm⁻¹ could be sufficient for the study of photochemical induced isotopic 447 448 effects at about 1 atm of pressure.

The calculated ${}^{34,33,36}\varepsilon$ and ${}^{33,36}E$ (Figure 11) enrichment factors derived from this and previous 449 measurements are compared respect to spectral resolution at each measurement. All ${}^{3x}J$ values 450 451 were calculated for a top of the atmosphere with a solar flux reported by Gueymard (2004) and 452 adjusted to the spectral resolution of this report. Danielache et al. (2008) first presented spectrum of ^{32,33,34}SO₂ but used natural abundance SO₂ as ³²S 18sotopologues, and a spectral 453 454 resolution ~ 25 cm⁻¹. These first measurements were conducted at the very early stages of this decade long enquiry, they were designed for the \tilde{C} - \tilde{X} absorption band and issues of spectral 455 456 resolution were not properly taken into account. Danielache et al. (2012) later improved the 457 sample preparation and conducted the measurements at a higher resolution data ($\sim 8 \text{ cm}^{-1}$), and 458 higher S/N ratios achieving propagated small error bars. This study introduced a new algorithm 459 to further reduce the errors associated with increased resolution and the number of 460 measurements at each pressure were extended the statistical maximum. The comparison in Figure 11 suggest, yet do not quantitively prove, that the higher the spectral resolution, the 461 smaller the isotopic effect for all ${}^{34,33,36}\varepsilon$ and ${}^{33,36}E$ values. 462





464 Figure 9: Photoexcitation rate constants calculated for a present Earth top of the atmosphere 465 (TOA) conditions with actinic flux reported by (Gueymard, 2004)) for measured ${}^{32}SO_2$, ${}^{33}SO_2$, 466 ${}^{34}SO_2$, and ${}^{36}SO_2$ isotopologues. The red and blue data sets represent cross-sections derived the 467 LAD and averaging methods respectively. Both methods yield nearly the same *J* values. 468 Propagated errors by the averaging method (red) produce error bars that overlap *J* values 469 rendering them unreliable to geochemical predictions. The implemented LAD method (blue 470 data sets) solves this problem.

472





478 between calculated *J* values therefore making them reliable for geochemical predictions.



480 Figure 11: Relationship between isotopic fractionation ${}^{34,33,36}\varepsilon$ and ${}^{33,36}E$ vs. spectral resolution 481 calculated from data in this report and compared to previously reported data by Danielache at 482 al. (2008, 2012). The comparison of the data sets shows a clear trend where isotopic effects 483 tend to be smaller with increased spectral resolution.

484

485 3.2 Comparison with isotope fractionation observed in SO₂ photochemical experiments

Sulfur isotope fractionation during SO₂ photoexcitation at wavelengths in the \tilde{B} - \tilde{X} band 486 487 was investigated by UV irradiating SO₂ with natural isotope ratios and examining the sulfur 488 isotope ratios of the products (referred to as SO₂ photochemical experiments below) (Endo et al., 2016; Whitehill and Ono, 2012; Whitehill et al., 2013)). Quadruple sulfur isotope analysis 489 of the products show large S-MIF, with Δ^{33} S up to 78% (Whitehill et al., 2013) and up to 142% 490 (Endo et al., 2016) with positive $\Delta^{36}S/\Delta^{36}S$ ratios. In this section, we compare isotope 491 fractionation factors predicted from our absorption cross-section measurements with those 492 493 previously observed in SO₂ photochemical experiments. Then, we discuss the origin of S-MIF, 494 which occurs in SO₂ photoexcitation or related to the reaction.

Whitehill et al. (2013)) irradiated SO₂ with UV light under N₂ bath gas and measured quadruple
sulfur isotopes of produced organics. They used a Xe arc lamp as a broadband UV source and

497 controlled UV spectra with UV filters to prevent SO₂ photolysis and examine the wavelength

498 dependence of the isotope fractionations. Acetylene was added as an electron donor in the

experiments. Although reactions are not fully understood, some organic sulfur matter was
produced and collected after UV irradiation. The expected relevant chemical pathways during
this experiment are reactions 1 to 4 (R1-R4) (e.g., Heicklen et al., 1980)

502
$$SO_2(^1A_1) + hv (240-320 \text{ nm}) \rightarrow SO_2(^1A_2 v=n) + SO_2(^1B_1 v=n) (R1)$$

503
$$SO_2(^1A_2 v=n) + M \rightarrow SO_2(^1A_2 v=0) + M (R2)$$

504
$$SO_2(^1A_2 \nu = 0) \rightarrow SO_2(^3B_1)$$
 (R3)

505
$$SO_2(^{3}B_1) + C_2H_2 \rightarrow \text{products (R4)}$$

506 The notation used in reactions 1 to 4 (R1 to R4) describe specific electronic and vibrational 507 states and are not frequent in chemical notation. Starting with R1 $SO_2(^1A_1)$ is the electronic ground state with a given and unspecified rovibrational state. $SO_2(^1A_2 v=n)$ and $SO_2(^1B_1 v=n)$ 508 are the photoexcited electronic ${}^{1}A_{2}/{}^{1}B_{1}$ manifold (mixing of two electronic states) at a given n 509 vibrational state (this fragment is also commonly known as SO₂*). In R2 M is a third body 510 511 collider (e.g., N_2) which triggers a quenching reaction to produce the electronic ¹A₂ state at its 512 ground rovibrational state (v=0). R3 shows the intersystem crossing (ISC) from the singlet ¹A₂ (v=0) state to the triplet $({}^{3}B_{1})$. Because SO₂ $({}^{3}B_{1})$ is more reactive than SO₂ $({}^{1}A_{2}/{}^{1}B_{1})$ (Kroll et 513 514 al., 2018) $SO_2({}^{3}B_1)$ reacts (R3) selectively with acetylene. The details of the reaction R4 have 515 yet to be understood, but they are unlikely to significantly contribute to S-MIF.

516 Isotopic fractionation factor in reaction R1 is predicted with absorption cross-sections of SO₂ isotopologues measured by this study and Danielache et al. (2012). Reactions other than 517 518 reaction R1 also may contribute to the isotopic fractionation observed in photochemical 519 experiments. Whitehill et al. (2013) suggested that reaction R2 mainly originated the observed 520 S-MIF in their experiments, mainly because (1) their theoretical study suggests that isotope 521 selective intersystem crossing might potentially contribute to the observed S-MIF and (2) their 522 results significantly differ from the S-MIF in reaction R1 predicted with SO₂ absorption cross-523 sections measured by Danielache et al. (2012) (Fig. 13).

- 524 Furthermore, the observed MIF signature is considerably different from those predicted by
- 525 isotopologue-specific absorption cross-sections. They also show that excitation wavelength
- **526** range produces isotopic effects in the order of 20-60‰ for Δ^{36} S and 10-40‰ for Δ^{33} S. The
- 527 wavelength range-isotopic effect is significant yet not as large as the pressure dependency $\tilde{1}$
- 528 observed when the full spectral region of the $\tilde{A}^1 A_2 / \tilde{B}^1 B_1$ manifold was photoexcited
- **529** (Whitehill et al., 2013, Fig. 2).
- 530 To compare our results with those of Whitehill et al. (2013), we calculate fractionation factors
- using SO₂ absorption cross-sections of this study and Danielache et al. (2012) from Eqs. (11)
- to (14), assuming a 150 W Xenon arc lamp spectrum and absorption spectra with UV filters.
- 533 The comparisons are shown in **Figures 12** and **13** where the isotopic effect produced during
- the photoexcitation process (R1) is compared to the results from chamber experiments.
- **Figure 12** compares Δ^{33} S, ^{33}E values to δ^{34} S, $^{34}\varepsilon$. The values reported by Whitehill et al. (2013), regardless of excitation wavelength region or P_{SO2} do not match the ones calculated from the

537 spectra reported by Danielache et al. (2008) neither the ones calculated from the spectra in this report. Large discrepancies are also observed on Figure 13 where small and negative values of 538 ^{33}E and ^{36}E from spectra in this report show no correlation with large and positive $\Delta^{36}S$ and 539 Δ^{33} S isotopic ratios from the chamber experiments. Self-shielding calculations reported by 540 Whitehill et al. (2013) and photoexcitation induced enrichment factors calculated from data 541 542 reported by Danielache et al. (2008) and photoexcitation effects from the same spectra at 543 different spectral ranges independently calculated in this report, show large negative ${}^{36}E$ and large positive ${}^{33}E$ values which don't match chamber experiments either. 544

545

From the comparisons in **Figures 12** and **13** the data presented in this report tend to support the conclusions reported by Whitehill et al. (2013) that the MIF isotopic ratios measured in collected organosulfur are likely produced by the ISC process in R3. Furthermore, the data in this report in which values of ${}^{34}\varepsilon$, ${}^{33}E$ and ${}^{36}E$ being small and quite unsensitive to the excitation wavelength band could contribute to the final organosulfur product MIF. This hypothesis does not provide any explanation to the large $\Delta^{33}S$, $\Delta^{36}S$ values to $\delta^{34}S$ values reported from chamber

552 experiments under different band-pass filters, partial SO_2 and total N_2 pressures.

553



Figure 12: Calculated ${}^{34}\varepsilon$ vs. ${}^{33}E$ isotopic effects from spectra reported by Danielache et al. (2012) and from spectra reported in this study using a 150W Xenon arc lamp spectrum and compared to experiments by Whitehill et al. (2013)) (δ^{34} S and Δ^{33} S). The units of the spectral range are in nm, while P_{tot} (total gas pressures) and P_{SO2} (partial pressures of SO₂) are in mbar. 560



Figure 13: Calculated ³³*E* vs. ³⁶*E* isotopic effects from spectra reported by Danielache et al. (2012) and from spectra reported in this study using a 150W Xenon arc lamp spectrum and compared to experiments by Whitehill et al. (2013) (Δ^{33} S and Δ^{36} S). P_{tot} (total gas pressures) and P_{SO2} (partial pressures of SO₂) are expressed in mbar units.

In order to assess the difference between the isotopic imprint between R1 and R3, next
photoexcitation rate constants from isotopic-specific spectra in the 250–320 nm region were
calculated and compared to chamber experiments reported by Whitehill and Ono (2012).

- 570
- 571



573 **Figure 14:** Calculated ${}^{34}\varepsilon$ vs. ${}^{33}E$ isotopic effects from spectra reported in this study using a 574 150W Xenon arc lamp spectrum and compared to experiments by Whitehill et al., 2013) (δ^{34} S 575 and Δ^{33} S).

576

Experiments conducted by Whitehill and Ono (2012) where they focused on isotopic mixing 577 ratios (δ^{34} S vs. Δ^{33} S and Δ^{33} S vs. Δ^{36} S) of oxydation products of photoexcited (${}^{1}B_{1} {}^{1}A_{2}$)SO₂ 578 and residual ground state SO₂. For additional insight a simple self-shielded photoexcited 579 580 enrichement factors (${}^{34}\varepsilon$ vs. ${}^{33}E$ and ${}^{33}E$ vs. ${}^{36}E$) at pressures ranging from 4.48 to 25.7 mbar using a 150W Xenon arc lamp spectrum was added to the analysis. The results are presented 581 in Figures 14 and 15. Figure 14 shows that calculated enrichment factors ${}^{34}\varepsilon$ and ${}^{33}E$ present 582 clearly different values to isotopic mixing ratios δ^{34} S vs. Δ^{33} S for produced ⁰S (Whitehill and 583 Ono, 2012). Residual SO₂ show negative values of δ^{34} S and Δ^{33} S, for experiments conducted 584 at 25.7 mbar of partial pressure of SO₂, are quite similar to those calculated in this report. Most 585 significantly, the calculated ${}^{34}\varepsilon$ and ${}^{33}E$ values are not only very close to those reported by 586 Whitehill and Ono (2012) for produced SO_3 , but they also have a very similar slope (inset **a**). 587 The comparisons in **Figure 15** are even more revealing since ${}^{33}E$ vs. ${}^{36}E$ slope calculated from 588 spectra in this report almost perfectly match the ${}^{33}E$ vs. ${}^{36}E$ slope reported by Whitehill and 589 Ono (2012) for produced SO₃, and residual SO₂. Furthermore, in both cases the ${}^{36}E/{}^{33}E$ and 590 591 Δ^{36} S/ Δ^{33} S slopes are particularly identical (**Figure 15** inset **a** for clarity). From the above discussion it can be suggested that the $({}^{1}B_{1} {}^{1}A_{2})SO_{2}$ photoexcitation band is likely to have a 592

593 small isotopic effect that is transported to the SO_3 products. A quantitative mass balance 594 analysis of the reaction products and residuals is necessary for obtaining further insight into 595 the processes taking place at the chamber experiments reported by Whitehill and Ono (2012) 596 and Whitehill et al. (2013).

- 597
- 598



599

Figure 15: Calculated ³³*E* vs. ³⁶*E* isotopic effects from spectra reported in this study using a 150W Xenon arc lamp spectrum and compared to experiments by Whitehill et al. (2013)) (Δ^{33} S and Δ^{36} S).

603

604 3.4 Geochemical implications

The origin of S-MIF found in stratospheric sulfate aerosols (SSA) is still debated. Savarino et al. (2003) attributed the S-MIF to SO₂ photoexcitation, because the SSA array of Δ^{36} S/ Δ^{33} S \approx -4.3 matched early photoexcitation experimental results where KrF excimer laser (248 nm of narrow band) was used (Δ^{36} S vs Δ^{33} S slope \approx -4.2; Farquhar et al., 2001). It is suspected that experiments using narrow-band UV spectra, which are significantly different from the sunlight spectrum, do not simulate isotope fractionation in the atmosphere (e.g., Claire et al., 2014). Subsequently, Danielache et al. (2012) reported ^{32,33,34,36}SO₂ absorption cross-section

measurements for the $\tilde{B}^1 B_1 - \tilde{X}^1 A_1$ band, allowing predictions of sulfur isotopic compositions 612 in sulfate aerosols under various atmospheric conditions. Then, Hattori et al. (2013) modeled 613 chemical reaction networks with a one-box model and calculated the isotope ratio of sulfate, 614 assuming that SO₂ photoexcitation causes MIF with the ^{32,33,34,36}SO₂ absorption cross-section 615 measurements. The results of Δ^{33} S magnitudes and Δ^{36} S/ Δ^{33} S ratios in sulfates reproduce those 616 617 within the SSA array. Thus, it is suggested that SO₂ photoexcitation (reaction R1) is the origin 618 of the S-MIF in SSA. However, this result strongly depends on the results of the absorption cross-section measurements by Danielache et al. (2012). In this section we compare 619 620 photoexcitation induced enrichment factors calculated from reported cross-sections to ice core data reported by Gautier et al. (2018), Shaheen et al. (2013) and Baroni et al. (2008). Gautier 621 et al. (2018) have updated $\Delta^{36}S/\Delta^{33}S$ ratio to -1.56 ± 0.25 for records of the past 2,600 years. 622 further modeling is required to explain the discrepancies between models based on spectra and 623 observations. However, the Δ^{36} S/ Δ^{33} S's difference of the updated data by Gautier et al. (2018) 624 may not be significant to determine the origin of S-MIF. The $\Delta^{36}S/\Delta^{33}S$ slope can be changed 625 by mixing processes between mass-independent and mass-dependent sulfur species, that is, 626 when non-zero Δ^{33} S signature is "diluted." This process happens because of the non-linearity 627 character of the Δ^{33} S and Δ^{36} S definitions (Endo et al. under review). 628

- Attenuation by atmospheric shielding of UV light below 300 nm renders all possible 629 630 photoexcitations unlikely below 10 km. At an altitude of 30 km, the band of available UV 631 radiation expands to 290 nm, and at an altitude of 40 km, UV light with wavelength longer than 280 nm can participate in the reaction. At 50 km of altitude, the atmospheric shielding 632 effect significantly weakens, and the entire SO₂ UV absorption $\tilde{B}^1B_1-\tilde{X}^1A_1$ band contributes 633 to the photoexcitation process (See Figure S7). Solar flux at different altitudes generates 634 635 different S-MIF signatures on the SO₂ photoexcitation reaction. Solar flux at different altitudes 636 used in the calculation of altitude dependent photoexcitation rate constants were obtained from modelled current atmosphere (Danielache et al., 2023) using actinic solar flux (Gueymard, 637 638 2004) at the top of atmosphere. The results of isotopic fractionation of self-shielding free SO₂ 639 photoexcitation reaction (250-320 nm) are shown in Figure 16 (brown circles).
- The same calculation at different altitudes combined with self-shielding under an SO₂ column 640 density ranging from 1.21×10^{14} to 1.21×10^{16} molecules cm⁻² are shown in Figure 16 (violet 641 and yellow tringles), and for SO₂ column densities up to 1.21×10^{17} molecules cm⁻² which are 642 643 closer to those reported during the Pinatubo eruption are presented in **Figure 17**. For a further 644 comparison, comparisons isotopic effects calculated by Hattori et al. (2013) are added to Figure 17. Figure 16 also shows volcanic data from Gautier et al. (2018) (red stars), Shaheen et al., 645 (2014) (black stars) and Baroni et al., (2008) (violet stars). Self-shielding free photoexcitation 646 effect is almost 0 in ${}^{33}E$ and stays unchanged with altitude, ${}^{36}E$ range from -10% at 10 km to 647 4‰ at 30 km. Altitude variability do not produce any significant ${}^{36}E/{}^{33}E$ slope but it they show 648 649 an interesting overlap with volcanic data suggesting that the ${}^{36}E$ variability is produced by altitude. Self-shielding calculations show a more revealing result in which increased column 650 density (up to 1.21×10^{16} molecules cm⁻²) creates a ${}^{36}E/{}^{33}E$ slope compatible with the reported 651 652 volcanic data. The data presented in Figure 17 includes the data in Figure 16 but it has expanded both ${}^{33}E$ and ${}^{36}E$ axis. By expanding the ${}^{33}E$ and ${}^{36}E$ axis, self-shielding calculations 653 more realistic to a stratospheric eruption $(1.21 \times 10^{17} \text{ molecules cm}^{-2})$ shows that the slope does 654 655 not change but also is compatible and of reverse signs to the altitude and self-shielding
656 calculations of Hattori et al. (2013) and also ${}^{36}E/{}^{33}E$ slope compatible with volcanic reported 657 data.

658



659

Figure 16: The isotopic fractionation from SO₂ photoexcitation using modern atmospheric solar flux at different altitudes and comparison with Hattori et al. (2013). (a) ${}^{34}\varepsilon$ and ${}^{33}E$. (b) ${}^{33}E$ and ${}^{36}E$. The volcanic data is from Gautier et al. (2018) (red stars), Shaheen et al. (2013) (black stars) and Baroni et al. (2008) (violet stars).

664



666

Figure 17: Photoexcitation enrichment factors calculated from this report compared to those reported by Hattori et al. (2013). Self-shielding calculation with column densities of 10^{19} molecules cm⁻² (530 DU) as suggested by Guo et al. (2004) produced values of ${}^{36}E = 1.314\%$ and ${}^{33}E = 1.163\%$ which fall well outside of the range in the plot.

672 4 Conclusions

This study presents the cross-sections of ${}^{32}SO_2$, ${}^{33}SO_2$, ${}^{34}SO_2$, and ${}^{36}SO_2$ for the $\tilde{B}^1B_1-\tilde{X}^1A_1$ 673 absorption band at 293.15 K measured at a resolution of 0.4 cm⁻¹ with an error of 3–10%. In 674 this report we implemented an algorithm using the LAD linear regression which was applied 675 676 to finely calibrate the linear relationship between absorbance and pressure and then achieve the 677 cross-section data at each wavelength. The overall features of measured cross-sections, that is, 678 the peak positions of isotopologues, are consistent with previous studies (Danielache et al., 679 2008; Danielache et al., 2012). We obtained both more detail in the absorption peaks and a significant improvement in errors derived from noise during the measurement. For S-MIF 680 related to SO₂ photochemistry, S-MIF predicted from our new spectral measurements do not 681 reproduce results of S-MIF observed in SO₂ photochemical experiments performed by 682 683 Whitehill et al. (2013). The discrepancy supports Whitehill's argument that large S-MIF 684 originates in the intersystem crossing rather than photoexcitation alone.

685

686 Acknowledgements

This study does not have real or perceived financial conflict of interest for any author. We
would like to thank Shohei Hattori and Naohiro Yoshida for sample preparation and Matthew
S. Johnson for technical advice. We also wish to thank Yi Ding for his consultation and advice
on machine learning and algorithms. This research was funded by JSPS KAKENHI (grant
numbers 22H05150 and 20H01975).

692 Data Availability Statement

693 The spectral data presented in this manuscript was recorded at the Tokyo Institute of 694 Technologies with experimental devices described in the experimental section. Reported data set in this study are available at Harvard Dataverse repository of research data via 695 696 https://doi.org/10.7910/DVN/AP8ISE with CC0 1.0 license/Data use agreement. Figures were 697 made with Origin Ver. 2022 (Origin Lab). The code used in this manuscript for the calculation 698 of absorption cross-sections is licensed under MIT and Published on GitHub 699 https://github.com/PatrickYLi/LAD-Regression/tree/multi-core and Zenodo 700 (doi/10.5281/zenodo.10836723)

701

702 References

- Anderson, R. J., and P. R. Griffiths (1975), Errors in absorbance measurements in infrared Fourier
- transform spectrometry because of limited instrument resolution, *Analytical Chemistry*, 47(14), 23392347, doi:10.1021/ac60364a030.
- 706 Baroni, M., J. Savarino, J. Cole-Dai, V. K. Rai, and M. H. Thiemens (2008), Anomalous sulfur
- isotope compositions of volcanic sulfate over the last millennium in Antarctic ice cores, J. Geophys.
- 708 Res. Atmos., 113(D20).
- 709 Baroni, M., M. H. Thiemens, R. J. Delmas, and J. Savarino (2007), Mass-independent sulfur isotopic
- 710 compositions in stratospheric volcanic eruptions, *Science*, *315*(5808), 84-87,
- 711 doi:10.1126/science.1131754.
- 712 Barra, I., L. Khiari, S. M. Haefele, R. Sakrabani, and F. Kebede (2021), Optimizing setup of scan
- 713 number in FTIR spectroscopy using the moment distance index and PLS regression: application to
- 714 soil spectroscopy, *Scientific reports*, *11*(1), 1-9, doi:10.1038/s41598-021-92858-w.
- 715 Blackie, D., R. Blackwell-Whitehead, G. Stark, J. C. Pickering, P. L. Smith, J. Rufus, and A. P.
- 716 Thorne (2011), High-resolution photoabsorption cross-section measurements of SO₂ at 198 K from
- 717 213 to 325 nm, J. Geophys. Res., 116(E3), doi:10.1029/2010je003707.
- 718 Claire, M. W., J. F. Kasting, S. D. Domagal-Goldman, E. E. Stüeken, R. Buick, and V. S. Meadows
- 719 (2014), Modeling the signature of sulfur mass-independent fractionation produced in the Archean
- 720 atmosphere, *Geochimica et Cosmochimica Acta*, *141*, 365-380, doi:10.1016/j.gca.2014.06.032.
- 721 Danielache, S. O., C. Eskebjerg, M. S. Johnson, Y. Ueno, and N. Yoshida (2008), High-precision
- **722** spectroscopy of ³²S, ³³S, and ³⁴S sulfur dioxide: Ultraviolet absorption cross sections and isotope
- 723 effects, J. Geophys. Res. Atmos., 113(D17), doi:10.1029/2007JD009695.

- 724 Danielache, S. O., S. Hattori, M. S. Johnson, Y. Ueno, S. Nanbu, and N. Yoshida (2012),
- 725 Photoabsorption cross-section measurements of ${}^{32}S$, ${}^{33}S$, ${}^{34}S$, and ${}^{36}S$ sulfur dioxide for the $B^{I}B_{I}-X^{I}A_{I}$
- 726 absorption band, J. Geophys. Res. Atmos., 117(D24), doi:10.1029/2012jd017464.
- 727 Danielache, S. O., G. Iwama, M. Shinkai, M. Oinuma, E. Simoncini, and T. Grassi (2023),
- 728 Introducing atmospheric photochemical isotopic processes to the PATMO atmospheric code,
- 729 *Geochem. J.*, 57(2), 42-58, doi:10.2343/geochemj.GJ23004.
- 730 Dreissig, I., S. Machill, R. Salzer, and C. Krafft (2009), Quantification of brain lipids by FTIR
- 731 spectroscopy and partial least squares regression, Spectrochimica Acta Part A: Molecular and
- 732 *Biomolecular Spectroscopy*, *71*(5), 2069-2075, doi:10.1016/j.saa.2008.08.008.
- 733 Eiler, J. M., B. Bergquist, I. Bourg, P. Cartigny, J. Farquhar, A. Gagnon, W. Guo, I. Halevy, A.
- Hofmann, and T. E. Larson (2014), Frontiers of stable isotope geoscience, *Chem. Geol.*, 372, 119-
- 735 143, doi:10.1016/j.chemgeo.2014.02.006.
- 736 Endo, Y., S. O. Danielache, and Y. Ueno (2019), Total pressure dependence of sulfur mass-
- independent fractionation by SO₂ photolysis, *Geophys Res Lett*, 46(1), 483-491,
- 738 doi:10.1029/2018gl080730.
- 739 Endo, Y., S. O. Danielache, Y. Ueno, S. Hattori, M. S. Johnson, N. Yoshida, and H. G.
- 740 Kjaergaard (2015), Photoabsorption cross-section measurements of ³²S, ³³S, ³⁴S, and ³⁶S
- sulfur dioxide from 190 to 220 nm, Journal of Geophysical Research: Atmospheres, 120(6),
- 742 2546-2557, doi:10.1002/2014JD021671.
- 743 Endo, Y., S. O. Danielache, M. Ogawa, and Y. Ueno (2022a), Absorption spectra
- measurements at $\sim 1 \text{ cm}^{-1}$ spectral resolution of ³²S, ³³S, ³⁴S, and ³⁶S sulfur dioxide for the
- 745 206–220 nm region and applications to modeling of the isotopic self-shielding, *Geochemical*
- 746 *Journal*, 56(1), 40-56, doi:10.2343/geochemj.GJ22004.
- 747 Endo, Y., Sekine, Y., and Ueno, Y. (2022b). Sulfur mass-independent fractionation during
- **748** SO₂ photolysis in low-temperature/pressure atmospheres. *Chemical Geology*, 609, 121064.
- 749 doi.org/10.1016/j.chemgeo.2022.121064
- 750 Endo, Y., Y. Ueno, S. Aoyama, and S. O. Danielache (2016), Sulfur isotope fractionation by
- broadband UV radiation to optically thin SO₂ under reducing atmosphere, *Earth and*
- 752 *Planetary Science Letters*, 453, 9-22, doi:10.1016/j.epsl.2016.07.057.
- 753 Farquhar, J., H. Bao, and M. Thiemens (2000), Atmospheric influence of Earth's earliest sulfur cycle,
- 754 *Science*, 289(5480), 756-758, doi:science.289.5480.756.
- 755 Farquhar, J., J. Savarino, S. Airieau, and M. H. Thiemens (2001), Observation of wavelength-
- sensitive mass-independent sulfur isotope effects during SO₂ photolysis: Implications for the early
- atmosphere, *Journal of Geophysical Research: Planets*, *106*(E12), 32829-32839,
- 758 doi:10.1029/2000JE001437.
- 759 Gautier, E., J. Savarino, J. Erbland, and J. Farquhar (2018), SO₂ oxidation kinetics leave a consistent
- isotopic imprint on volcanic ice core sulfate, J. Geophys. Res. Atmos., 123(17), 9801-9812.
- 761 Gueymard, C. A. (2004), The sun's total and spectral irradiance for solar energy applications and
- 762 solar radiation models, *Solar energy*, 76(4), 423-453, doi:10.1016/j.solener.2003.08.039.
- 763 Guo, S., Bluth, G. J. S., Rose, W. I., Watson, I. M., & Prata, A. J. (2004). Re-evaluation of
- 764 SO₂ release of the 15 June 1991 Pinatubo eruption using ultraviolet and infrared satellite
- response to the sensors. *Geochemistry, Geophysics, Geosystems*, 5(4).
- 766 https://doi.org/10.1029/2003GC000654

- 767 Hattori, S., J. A. Schmidt, M. S. Johnson, S. O. Danielache, A. Yamada, Y. Ueno, and N. Yoshida
- 768 (2013), SO₂ photoexcitation mechanism links mass-independent sulfur isotopic fractionation in
- 769 cryospheric sulfate to climate impacting volcanism, *Proceedings of the National Academy of*
- 770 *Sciences*, *110*(44), 17656-17661, doi:10.1073/pnas.1213153110.
- Heicklen, J., N. Kelly, and K. Partymiller (1980), The photophysics and photochemistry of SO2,
- 772 *Reviews of Chemical Intermediates*, *3*(3-4), 315-404, doi:10.1007/bf03052425.
- 773 Herzberg, G. (1945), *Molecular spectra and molecular structure*, D. van Nostrand.
- Hulston, J., and H. Thode (1965), Variations in the S^{33} , S^{34} , and S^{36} contents of meteorites and their
- relation to chemical and nuclear effects, J. Geophys. Res., 70(14), 3475-3484,
- 776 doi:10.1029/JZ070i014p03475.
- Koplow, J. P., D. A. Kliner, and L. Goldberg (1998), Development of a narrow-band, tunable,
- frequency-quadrupled diode laser for UV absorption spectroscopy, *Applied optics*, *37*(18), 3954-3960,
 doi:10.1364/AO.37.003954.
- 780 Kostkowski, H. J., and A. M. Bass (1956), Slit function effects in the direct measurement of
- 781 absorption line half-widths and intensities, *JOSA*, *46*(12), 1060-1064, doi:10.1364/JOSA.46.001060.
- 782 Kroll, J. A., B. N. Frandsen, R. J. Rapf, H. G. Kjaergaard, and V. Vaida (2018), Reactivity of
- 783 Electronically Excited SO₂ with Alkanes, *The Journal of Physical Chemistry A*, 122(39), 7782-7789,
- 784 doi:10.1021/acs.jpca.8b04643.
- Kumar, P., J. Ellis, and B. Poirier (2015), Rovibrational bound states of SO₂ isotopologues. I: Total
 angular momentum *J*=0–10, *Chem. Phys.*, *450*, 59-73.
- 787 Leonard C. Entwicklung eines UV-laserspektroskopischen nachweisverfahrens für OH-
- 788 Radikals und spektroskopische untersuchungen an spurengasen unter troposphärischen
 789 bedingungen, Germany: University of Hannover; 1989. Doctoral dissertation in physics.
- 790 Li, L., H. Zhao, N. Ni, Y. Wang, J. Gao, Q. Gao, Y. Zhang, and Y. Zhang (2022), Study on the origin
- 791 of linear deviation with the Beer-Lambert law in absorption spectroscopy by measuring sulfur
- 792 dioxide, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 275, 121192,
- 793 doi:10.1016/j.saa.2022.121192.
- 794 Lyons, J., H. Herde, G. Stark, D. Blackie, J. Pickering, and N. de Oliveira (2018), VUV pressure-
- broadening in sulfur dioxide, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 210, 156164.
- 797 Masterson, A. L., J. Farquhar, and B. A. Wing (2011), Sulfur mass-independent fractionation patterns
- in the broadband UV photolysis of sulfur dioxide: Pressure and third body effects, *Earth and*
- 799 *Planetary Science Letters*, *306*(3), 253-260, doi:10.1016/j.epsl.2011.04.004.
- 800 Mellqvist, J., and A. Rosén (1996), DOAS for flue gas monitoring—II. Deviations from the Beer-
- 801 Lambert law for the UV/visible absorption spectra of NO, NO₂, SO₂ and NH₃, *Journal of Quantitative*
- 802 Spectroscopy and Radiative Transfer, 56(2), 209-224, doi:10.1016/0022-4073(96)00043-X.
- 803 Meyer-Jacob, C., H. Vogel, F. Boxberg, P. Rosén, M. E. Weber, and R. Bindler (2014), Independent
- 804 measurement of biogenic silica in sediments by FTIR spectroscopy and PLS regression, *Journal of*
- 805 *paleolimnology*, *52*, 245-255, doi:10.1007/s10933-014-9791-5.
- 806 Ono, S. (2017), Photochemistry of sulfur dioxide and the origin of mass-independent isotope
- fractionation in Earth's atmosphere, *Annual Review of Earth and Planetary Sciences*, 45(1), 301-329,
- 808 doi:10.1146/annurev-earth-060115-012324.
- 809 Origin, Version 2022. OriginLab Corporation, Northampton, MA, USA.

- 810 Pavlov, A., and J. Kasting (2002), Mass-independent fractionation of sulfur isotopes in Archean
- 811 sediments: strong evidence for an anoxic Archean atmosphere, *Astrobiology*, 2(1), 27-41,
 812 doi:10.1089/153110702753621321.
- 813 Pedregosa, F., G. Varoquaux, A. Gramfort, V. Michel, B. Thirion, O. Grisel, M. Blondel, P.
- 814 Prettenhofer, R. Weiss, and V. Dubourg (2011), Scikit-learn: Machine learning in Python, *The*
- 815 *Journal of machine Learning research*, *12*, 2825-2830.
- 816 Rufus, J., G. Stark, P. L. Smith, J. C. Pickering, and A. P. Thorne (2003), High-resolution
- photoabsorption cross section measurements of SO₂, 2: 220 to 325 nm at 295 K, *Journal of Geophysical Research: Planets*, *108*(E2), doi:10.1029/2002je001931.
- 819 Santos, V. H. J. M. D., D. Pontin, G. G. D. Ponzi, A. S. D. G. E. Stepanha, R. B. Martel, M. K.
- 820 Schütz, S. M. O. Einloft, and F. Dalla Vecchia (2021), Application of Fourier Transform infrared
- spectroscopy (FTIR) coupled with multivariate regression for calcium carbonate (CaCO3)
- quantification in cement, *Construction and Building Materials*, 313, 125413,
- 823 doi:10.1016/j.conbuildmat.2021.125413.
- 824 Savarino, J., A. Romero, J. Cole-Dai, S. Bekki, and M. Thiemens (2003), UV induced mass-
- 825 independent sulfur isotope fractionation in stratospheric volcanic sulfate, *Geophys. Res. Lett*, 30(21),
- **826** doi:10.1029/2003GL018134.
- 827 Shaheen, R., M. Abauanza, T. L. Jackson, J. McCabe, J. Savarino, and M. H. Thiemens (2013), Tales
- 828 of volcanoes and El-Niño southern oscillations with the oxygen isotope anomaly of sulfate aerosol,
- 829 Proceedings of the National Academy of Sciences, 110(44), 17662-17667.
- 830 Skoog, D. A., F. J. Holler, and S. R. Crouch (2017), *Principles of instrumental analysis*, Cengage831 learning.
- 832 Stark, G., P. L. Smith, J. Rufus, A. Thorne, J. Pickering, and G. Cox (1999), High-resolution
- 833 photoabsorption cross-section measurements of SO₂ at 295 K between 198 and 220 nm, *Journal of*
- 834 *Geophysical Research: Planets*, 104(E7), 16585-16590, doi:10.1029/1999JE001022.
- 835 Tsai, S.-M., E. K. Lee, D. Powell, P. Gao, X. Zhang, J. Moses, E. Hébrard, O. Venot, V. Parmentier,
- and S. Jordan (2023), Photochemically produced SO2 in the atmosphere of WASP-39b, *Nature*,
- **837** *617*(7961), 483-487.
- 838 Ueno, Y., M. S. Johnson, S. O. Danielache, C. Eskebjerg, A. Pandey, and N. Yoshida (2009),
- 839 Geological sulfur isotopes indicate elevated OCS in the Archean atmosphere, solving faint young sun
- paradox, *Proceedings of the National Academy of Sciences*, *106*(35), 14784-14789,
- **841** doi:10.1073/pnas.0903518106.
- 842 Vandaele, A. C., C. Hermans, and S. Fally (2009), Fourier transform measurements of SO₂ absorption
- 843 cross sections: II.: Temperature dependence in the 29 000–44 000 cm⁻¹ (227–345 nm) region, *Journal*
- 844 of Quantitative Spectroscopy and Radiative Transfer, 110(18), 2115-2126,
- 845 doi:10.1016/j.jqsrt.2009.05.006.
- 846 Whitehill, A., and S. Ono (2012), Excitation band dependence of sulfur isotope mass-independent
- fractionation during photochemistry of sulfur dioxide using broadband light sources, *Geochimica et Cosmochimica Acta*, 94, 238-253, doi:10.1016/j.gca.2012.06.014.
- 849 Whitehill, A. R., C. Xie, X. Hu, D. Xie, H. Guo, and S. Ono (2013), Vibronic origin of sulfur mass-
- 850 independent isotope effect in photoexcitation of SO₂ and the implications to the early earth's
- atmosphere, *Proceedings of the National Academy of Sciences*, 110(44), 17697-17702,
- **852** doi:10.1073/pnas.1306979110.

- 853 Wu, C. R., B. Yang, F. Chen, D. Judge, J. Caldwell, and L. Trafton (2000), Measurements of high-,
- room-, and low-temperature photoabsorption cross sections of SO₂ in the 2080- to 2950-Å region,
- with application to Io, *Icarus*, *145*(1), 289-296, doi:10.1006/icar.1999.6322.
- 856 Yung, Y. L., and W. B. DeMore (1999), *Photochemistry of planetary atmospheres*, Oxford University
- 857 Press, USA, doi:10.1093/oso/9780195105018.001.0001.
- 858
- 859
- 860
- 861
- 862
- 863

Figure 1.



Figure 2.



Figure 3.



Figure 4.



Figure 5.



Figure 6.



Figure 7.



Figure 8.



Figure 9.



Figure 10.



Figure 11.



Figure 12.



Figure 13.



Figure 14.



Figure 15.


Figure 16.



Figure 17.



1 High-Resolution UV Absorption Cross-section Measurements of ³²S, ³³S,

2 ³⁴S, and ³⁶S Sulfur Dioxide for the \tilde{B}^1B_1 - \tilde{X}^1A_1 Absorption Band

3 Y. Li¹, S. O. Danielache¹, Y. Endo², S. Nanbu¹, Y. Ueno^{2,3,4}

- 4 ¹Department of Materials and Life Science, Faculty of Science and Technology, Sophia
- 5 University, Japan
- ⁶ ²Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Tokyo, Japan
- ³Earth-Life Science Institute, Tokyo Institute of Technology, Tokyo, Japan
- ⁴Institute for Extra-cutting-edge Science and Technology Avant-garde Research (X-star),
- 9 Super-cutting-edge Grand and Advanced Research (SUGAR) Program, Japan Agency for
- 10 Marine-Earth Science and Technology (JAMSTEC), Yokosuka, Japan
- 11 Corresponding author: Yuanzhe Li (<u>liyuanzhe@eagle.sophia.ac.jp</u>)

12 Key Points:

- We report measured cross-sections of ${}^{32}SO_2$, ${}^{33}SO_2$, ${}^{34}SO_2$, ${}^{36}SO_2$ for the $\tilde{B}^1B_1-\tilde{X}^1A_1$ absorption band over the wavelength range 240 to 320 nm at a resolution of 0.4 cm⁻¹.
- A least absolute deviation linear regression method was applied to calculate the cross-sections, and the error bars on the measured cross-sections ranged between 3 and 10%.
- Reported absorption cross-sections predict relatively small mass-independent fractionation (${}^{33}E = -0.8 \pm 0.2\%$ and ${}^{36}E = -4.0 \pm 0.4\%$) during SO₂ photoexcitation for top of the atmosphere solar spectra.
- 20

21 Abstract

High-resolution and high-precision spectrum data presents a challenging measurement. We
 report newly measured ultraviolet absorption cross-sections of ³²SO₂, ³³SO₂, ³⁴SO₂, and ³⁶SO₂

- for the $\tilde{B}^1B_1-\tilde{X}^1A_1$ band over the wavelength range 240 to 320 nm at a resolution of 0.4 cm⁻¹.
- 25 The resolution is improved by 20 times compared to a previous study (Danielache et al., 2012).
- A least absolute deviation linear regression method was applied to calculate the cross-sections
- and spectral errors from a set of measurements recorded at a wide range of pressure to ensure
- optimal signal-to-noise ratio at all wavelengths. Based on this analysis, error bars on the
 measured cross-sections ranged between 3 and 10%. The overall features of measured cross-
- 30 sections, such as peak positions of isotopologues, are consistent with previous studies. We
- 31 provide improved spectral data for studying sulfur mass-independent fraction (S-MIF)
- 32 signatures in SO₂ photoexcitation. Our spectral measurements predict that SO₂ photoexcitation
- 33 produces ${}^{33}E = -0.8 \pm 0.2\%$ and ${}^{36}E = -4.0 \pm 0.4\%$, whose magnitudes are smaller than those
- 34 reported by Danielache et al. (2012).
- 35

36 1 Introduction

37 Sulfur dioxide (SO₂) is the most common reduced sulfur compound present in many planetary

38 atmospheres. This molecule has been known to exist in Earth, Venus, and Io for many years

39 (Yung and DeMore, 1999). It has also been reported the presence of SO_2 in the atmosphere of

40 WASP-39b (Tsai et al., 2023). Understanding the photochemical properties of this molecule is

41 essential for geochemical studies of planetary atmospheres. Its interactions with UV light

- 42 trigger a cascade of chemical reactions that produce a variety of compounds, such as sulfuric 42 acid (USO) or S_{1} depending on the strager barie redevised as state
- 43 acid (H_2SO_4) or S_8 , depending on the atmospheric redox state.
- 44 Stable isotopes are a powerful tool for studying and understanding a variety of geochemical 45 processes. Such applications involve singly substituted isotopes, a combination of the same 46 isotope with different masses which creates mass-dependent and mass-independent relations, and more than one isotope within the same molecule known as clumped isotopes (e.g., Eiler et 47 al., 2014). The sulfur mass-independent fractionation (S-MIF) signatures (non-zero Δ^{33} S and 48 Δ^{36} S values) in the geological record have been shown to be non-zero before ~2.3 Ga 49 50 coinciding with the rise of oxygen levels in the atmosphere (Farquhar et al., 2000; Ono, 2017). Studies by Farquhar and co-workers (Farquhar et al., 2001; Masterson et al., 2011) and 51 52 subsequent chemical chamber experiments (Endo et al., 2019; Endo et al., 2016) have shown 53 that SO₂ photodissociation and photoexcitation reactions under conditions free of oxygen produce large S-MIF signatures, although the previous experiments have not fully reproduced 54 the Archean record such as relationships between $\Delta^{33}S$ and $\Delta^{36}S$ and between $\delta^{34}S$ and $\Delta^{33}S$ 55 (e.g., Ono, 2017; Endo et al., 2022b). An atmospheric photochemical model study by Pavlov 56 and Kasting (2002) showed that SO radical produced during photolysis rapidly oxidized back 57 to SO₂ with 10^{-5} of present atmospheric levels of O₂ and therefore setting a maximum level of 58 59 atmospheric oxygen abundance in which the S-MIF can be preserved, yet no model study has 60 succussed into reproducing the geological record. The work done to constrain the mechanisms
- 61 and the atmospheric conditions that explain the S-MIF in the geological record is extensive and

62 a full summary is beyond the scope of this report (e.g., Ono, 2017; Thiemens and Lin, 2019) 63 but current understanding points to a combination of mechanisms including the photoexcitation 64 $\tilde{B}^1 B_1 - \tilde{X}^1 A_1$ band of the SO₂ molecule (Endo et al., 2016).

In the present earth, sulfur aerosols produced in the lower stratosphere from material uplifted 65 66 by plumes during Plinian eruptions and collected from Antarctic and Greenland ice cores show 67 an S-MIF signature distinct from Archean sulfides and sulfates (Baroni et al., 2007). Hattori et 68 al. (2013), based on the data reported by Danielache et al. (2012), reported that SO₂ 69 photoexcitation in the lower stratosphere produce signals compatible with the ice core record. A subsequent study presented by Whitehill et al. (2013) showed that the fate of the photoexcited 70 71 fragment is not only direct oxidation by O₂, as assumed in the Hattori et al. (2013) study, but 72 follows a branching mechanism due to quenching in which a fraction of the molecules in the 73 $\tilde{A}^1 A_2 / \tilde{B}^1 B_1$ state are converted to the $\tilde{a}^3 B_1$ state. They further show an isotope selective spinorbit interaction between the singlet $(\tilde{A}^1 A_2 / \tilde{B}^1 B_1)$ and triplet $(\tilde{a}^3 B_1)$ manifolds. Despite the 74 75 extensive work done so far, further quantification of the isotopic effect during the $\tilde{B}^1 B_1$ - $\tilde{X}^1 A_1$ and $\tilde{A}^1 A_2 - \tilde{X}^1 A_1$ excitation is needed. 76

77 The highly structured SO₂ UV absorption spectrum directly results from electronic transitions and a complex and nuanced set of vibrational and rotational energy levels (Herzberg, 1945). 78 79 The single report on the ${}^{32}SO_2$, ${}^{33}SO_2$, ${}^{34}SO_2$, and ${}^{36}SO_2$ (hereafter ${}^{32,33,34,36}SO_2$) \tilde{B}^1B_1 - $\tilde{X}^{1}A_{1}$ absorption spectrum from Danielache et al. (2012) has a spectral resolution of 8 cm⁻¹ 80 which is still far from fully resolved (Stark et al., 1999). Although from the $\tilde{C}^1B_2-\tilde{X}^1A_1$ 81 absorption band, spectral measurements by Endo et al. (2015), SO₂ column density dependence 82 on cross-sections were observed (especially, this apparent column density and cross-sections 83 84 relation was stronger at absorption peaks; see Endo et al., 2015 Figure 1). Further analysis 85 suggested that insufficient spectral resolution relative to absorption line width explains this 86 phenomenon (Endo et al., 2015). The lack of resolution directly affects the peak separation and 87 further interferes with the accuracy of S-MIF calculations, which would significantly impact 88 the study of light-induced isotopic effects (See Endo et al., 2015 Figure S1). High-resolution 89 spectrum is therefore necessary for better understanding spectroscopic properties and 90 accurately the absorption spectra (Wu et al., 2000). Fully resolved spectra (Koplow et al., 1998) 91 with a low level of noise would be the authoritative yet near unachievable measurement for an 92 entire absorption band.

93 Recent studies by Lyons et al. (2018) have reported pressure room temperature broadening coefficients of 0.30 ± 0.03 cm⁻¹ atm⁻¹ and 0.40 ± 0.04 cm⁻¹ atm⁻¹ for N₂ and CO₂ respectively 94 for the \tilde{C} - \tilde{X} absorption band and Leonard (1989) reported broadening coefficients of 0.237 95 ± 0.0011 cm⁻¹ atm⁻¹ and 0.325 ± 0.0015 cm⁻¹ atm⁻¹ for N₂ and CO₂ respectively for the \tilde{B} -96 97 \tilde{X} absorption band. There are studies suggesting a largely congested line profile for the SO₂ 98 electronic spectra. The basis for such an assertion are from theoretical calculations of the 99 bound-type exited electronic states coupled to rotational-vibrational transitions (Kumar et al., 100 2015). Models reported by Lyons et al. (2018) used a line spacing of 0.25 cm⁻¹ for the \tilde{C} - \tilde{X} 101 band which is not the absorption band concerned in this report, but it might show a similar 102 behavior. A quantitative assessment of natural widths and line congestion at different spectral 103 regions is yet to be reported. The computational requirement for a theoretical calculation of a

104 high J electronic spectrum is a challenge to be reckoned with. Reports on J and K values (J and

105 K stand for rotational and vibrational wavefunction, not to be confused with the integrated 106 photo-dissociation rate constant J) such as the reported by Kumar et al. (2015) for total angular 107 momentum J = 0-10 are illustrative of the amount of computations needed for a full spectrum calculated at high J. Pressure broadening coefficients put together with the above suggested 108 line density of these systems will cause line profile overlap and thus creating a pseudo-109 110 broadened spectra or sections of the most congested parts of the rovibrational progression and 111 thus reducing the minimal requirement of spectral resolution for meaningful photo-induced isotopic effects. In summary, a combination of spectral resolution, pressure broadening, and 112 profile overlap suggests that the data in this report might be suitable for the study of isotopic 113 114 effects happening in a planetary atmosphere with a total atmospheric pressure close to 1 atm.

An additional known issue is that even if a fully resolved spectrum is achieved, it is difficult to obtain high precision with high-resolution measurements because the noise increases at highresolution measurements (see comparison in Table 1). The issue would lead to large errors of calculated photodissociation rate constants and associated isotopic effects. In order to address this issue we have implemented a linear regression method that has been widely used in Fourier

transform spectroscopy to reduce noise and increase spectral precision (Barra et al., 2021;
Dreissig et al., 2009; Meyer-Jacob et al., 2014; Santos et al., 2021).

122 In this study, an experimental setup of a Fourier transform spectrometer (VERTEX 80v, Bruker, 123 Japan) was optimized to adapt measurements in the UV band. We used the least absolute 124 deviation (LAD) linear regression for data calibration and measured the ${}^{32}SO_2$, ${}^{33}SO_2$, ${}^{34}SO_2$, 125 and ${}^{36}SO_2$, $\tilde{B}^1B_1-\tilde{X}^1A_1$ absorption spectrum ranges from 240 to 320 nm with a resolution of 126 0.4 cm⁻¹ and 3–10% of error.

127 2 Experimental

128 2.1 SO₂ isotopologues samples

129 The isotopically enriched ${}^{32,33,34,36}SO_2$ gas samples were prepared from elemental ${}^{32}S, {}^{33}S, {}^{34}S,$ 130 and ${}^{36}S$ powder (Isoflex USA) sealed with CuO in quartz tubes under vacuum, heated at 950°C 131 for 15 min. Separation of SO₂ samples and unreacted O₂ was done by freeze-pump-thaw 132 cycling. The components of the gas phase labeled samples were confirmed and purified using 133 a GC-MS, and the products purity was checked by quantitative IR spectroscopy (Danielache et 134 al., 2012). Details of sample preservation are described in Endo et al. (2022a).

135 2.2 Instrument setups

The gas cell and inlet gas system follows Endo et al. (2022a). The UV absorption cross-sections were determined using a Fourier transform spectrometer (VERTEX 80v, Bruker, Japan) with an external deuterium lamp (L6301-50, Hamamatsu, Japan) equipped at the inlet port on the right spectrometer side. Two capacitance manometers (CMR362 and CMR364, Pfeiffer, Germany) calibrated the pressure using a full-range gauge (PGE500, INFICON, Germany) and local weather reports. An oil pump was added to the gas line system for pre-vacuuming to extend the lifetime of the turbopump system (Pfeiffer, Germany).

143 Signal drifting from the light source was observed, where the signal intensity decreases over144 time. Following a commonly used method (Danielache et al., 2008; Danielache et al., 2012;

145 Endo et al., 2022a; Vandaele et al., 2009), where the background signal intensity at the time of

146 the sample signal measurement was derived by alternating the background and sample signal 147 measurements and calculating the average of the two background signal before and after each

148 sample signal measurement.

149 Numerous measurement parameters were adjusted to balance high-resolution and relatively low noise levels while limiting the measurement time to avoid excessive errors brought by 150 signal drift. The interferogram from a single measurement was derived from an average of 150 151 scans at a resolution of 0.4 cm⁻¹ using single-sided and bi-directional acquisition mode and 152 153 was converted to signal intensity spectrum by Fourier transform using boxcar apodization function and Mertz phase correction mode to preserve the most original data possible. A 154 frequency window from 0 to 60,000 cm⁻¹ and a zero-filling number of 2 produced a spectrum 155 ranging from 41666 to 29400 cm⁻¹ with a data point spacing of ca. 0.12055 cm⁻¹. No prominent 156 157 peaks spread due to the grazing-incidence light in the UV region measurement was observed, 158 and an 8 mm aperture size was selected. The VERTEX 80v instrument used in our measurements is capable of a maximum spectral resolution of 0.1 cm^{-1} . However, the optimal 159 trade-off between spectral resolution and spectral noise was found to be 0.4 cm^{-1} which is 160 between 5 to 10 times lower in resolving power than the suggested optimal spectral resolution 161 162 (Rufus et al., 2003).

163 2.3 Measurements

164 The Beer-Lambert law,

165
$$A = \ln \frac{I_0}{I} = \ln \frac{1}{Trans} = \sigma l \rho$$
(1)

Shows that absorbance A is proportional to attenuating number density of the gas sample ρ (in 166 167 this report approximated as gas pressure, assuming a constant temperature). The radiant power intensity is reduced from I_0 to *I*, *Trans* is the transmittance, σ is the absorption cross-sections, 168 and l is the optical path length. Both logarithm and natural logarithm definition formats of 169 170 absorbance are widely used. Which format is used does not affect the $A \propto C$ relationship, we 171 used the natural logarithm format for a more convenient calculation of cross-sections. In this 172 report, SO₂ absorption cross-section (σ) at each wavelength (λ) was calculated through the 173 application of the Beer-Lambert law,

174
$$\sigma(\lambda) = -\frac{RT}{PN_A z} \ln \frac{2I(\lambda)}{I_{0a}(\lambda) + I_{0b}(\lambda)} = -\frac{1}{\rho z} \ln \frac{I(\lambda)}{I_{0ave}(\lambda)} = -\frac{1}{\rho z} \ln Trans(\lambda)$$
(2)

175 Where *R* is the gas constant, *T* is the room temperature in the laboratory, *P* is the sample 176 pressure during measurement, N_A is the Avogadro number, *z* is the sample cell length (10.0 177 cm) through which the light passes, *I* is the measured sample signal intensity, I_{0a} and I_{0b} are 178 the measured background signal intensity before and after a single sample measurement as 179 mentioned above, and I_{0ave} is the mean signal intensity of I_{0a} and I_{0b} , Substituting (1) into 180 (2) yields the following,

181
$$\sigma(\lambda) = -\frac{RT}{PN_A z} \ln T(\lambda) = k_1 \cdot \frac{A(\lambda)}{P}$$
(3)

182 Where
$$k_1 = \frac{RT}{N_A z}$$
, and

$$\sigma(\lambda) = -\frac{RT}{PN_A z} \ln T(\lambda) = k_2 \cdot TA(\lambda)$$
(4)

184 Where
$$k_2 = \frac{R}{PN_A z}$$
.

185 Equations (3) and (4) indicate that when σ is either pressure or temperature dependent, the 186 linear relationship between A and P is not valid. In this study, the temperature is assumed to be 187 constant since variability was within a range of a few digress. The measured data showed no 188 pressure-dependent cross-sections. Figure 1 shows the relation between sample pressure in the 189 gas cell and measured absorption-cross sections. Previous absorption cross-section 190 measurements of various gas and liquid species have acknowledged deviations from the Beer-191 Lambert law, that is an apparent cross-section pressure dependency (e.g., Kostkowski and Bass, 192 1956; Anderson and Griffiths, 1975; Mellqvist and Rosén, 1996; Endo et al., 2015; Li et al., 193 2022).In both reports the origin of such non-linear behavior is attributed to low spectral 194 resolution of the instrument. The data presented in this report, which was recorded at spectral 195 resolution of 0.4 cm⁻¹, shows no apparent pressure-dependent cross-section variability (Figure 196 1). Thus, it is not required to correct the apparent cross-section pressure dependency.



- Figure 1: Individual cross-section data of each peak and valley at different pressures from
 280–300 nm for ³⁴SO₂. The ³⁴SO₂ pressure ranges from 200–2200 Pa. No apparent pressure dependent cross-section phenomenon was observed.
- 201

202 In actual measurements, many sources of uncertainty can affect the linear relationship between 203 A and P. In the case of a high-precision Fourier transform spectrometer, the dark current and 204 amplifier noise from regions where source intensity and detector sensitivity are low, the photon detector shot noise, the cell positioning uncertainties, etc., making different orders of impact 205 206 on the relative signal intensity uncertainty (Skoog et al., 2017). These random noises are almost 207 impossible to distinguish from each other thoroughly. Common solutions include averaging multiple sets of measurements (Blackie et al., 2011; Rufus et al., 2003; Stark et al., 1999; 208 209 Vandaele et al., 2009), adding weights to the parameters that characterize the data (Danielache 210 et al., 2008; Danielache et al., 2012), and calibration of SO₂ column density dependence on 211 measured cross-sections with a least squares method (Endo et al., 2015). Nonetheless, 212 conventional methods still do not resolve the bias that noise from different sources introduce to the actual absorptivity. 213

In this study, we implemented a linear regression technique to rule out the effect of random noise. The LAD method was deployed to clarify the linear relationship between A and P, following the purpose of minimizing the sum of the absolute values of the residuals S between raw data y_i to the fitted data $f(x_i)$,

218
$$\operatorname{argmin} S = \sum_{i=1}^{n} |y_i - f(x_i)|$$
 (5)

219 A universal algorithm from the Scikit-Learn machine learning library (Pedregosa et al., 2011) 220 for the Python programming language was used for computational efficiency considerations. 221 Based on the degree of data dispersion, scenarios that linear regression needs to target can be 222 categorized into three. Case 1: Little effect of random noise on the data, where A and P have 223 good linear fit, and there is little difference compared to the commonly used least squares (LS) 224 linear regression. Case 2: The effect of random noise on individual data creates outliers, and 225 the LAD method excludes the impact from outliers much better than the LS method. Case 3: 226 Highly discrete data in high noise regions, the linear relationship between A and P is almost 227 indistinguishable, and all current methods do not guarantee noise removal.

228 The number of valid measurements at a given wavelength used in the LAD linear regression 229 ranged between 10 and 70 depending on signal-to-noise and the amount of available sample 230 (Figure S2). The increased number of measurements are a necessary condition for reducing 231 the errors associated with signal-to-noise issues. Previous measurements on isotopic effects of 232 ultraviolet absorption cross sections reported by the authors (Danielache et al., 2008, 2012; 233 Hattori et al., 2011; Endo et al., 2015, 2022a) have been aware of this issue but limitations on 234 sample and instrument accessibility have limited the number of measurements. In this report 235 the number of measurements were increased to a number where an analysis of the limit of noise 236 reduction by number pf measurements was conducted. At least 10 measurements are required to reduce the LAD algorithm error. 15–25 sets of measurements are recommended, and the
improvement in error is no longer apparent after more than 30 sets.

239 With the above reference parameters, the final cross-sections are calculated as follows. Firstly, 240 the collected raw data were prefiltered to retain the data with transmittance from 0.1 to 0.95. 241 which not only excluded the data with too low signal intensity but also the transmittance range 242 was chosen to consider the effect of instrument noise on the measurement precision (Skoog et 243 al., 2017). Next, data with signal-to-noise ratio (SNR) less than 20 were excluded to further improve data quality. The filtered data are involved in the following data correction of the 244 linear relationship between A and P by the LAD method. Finally, the corrected A allows the 245 246 calculation of the cross-sections at the corresponding wavelength.

247 2.4 Error budgets

The errors in this study came mainly from four main sources. (1) The temperature variation of the experimental environment was within 2.5 K, introducing an error of 0.85% to the final cross-sections. (2) The mechanical error of the pressure gauge, according to the manufacturer's instructions, has a validity of about 0.2%. (3) Each measurement took about 20 min, and the pressure change due to SO₂ adsorption to the sample cell and stainless tube wall introduced an error of about 0.2%. (4) The errors from instrumental random noises are mostly reflected in the dispersion of the linear relationship between *A* and *P*, following,

255
$$S_{y/x} = \sqrt{\frac{\sum (y_i - f(x_i))^2}{n - 2}}$$
(6)

256 3 Results and discussions

257 3.1 Comparisons with previous studies

The measured ${}^{32}SO_2$ absorption spectrum in the present study is compared to four previous 258 studies on SO₂ in the $\tilde{B}^1 B_1 - \tilde{X}^1 A_1$ absorption band (Figure 2) and spectral summary listed in 259 Table 1. There are two previous studies about the SO₂ isotopologues with spectral resolution 260 of 25 cm⁻¹ (Danielache et al., 2008) and 8 cm⁻¹ (Danielache et al., 2012) and errors of 1.2–2.5% 261 and 1.2-8.2% respectively. For comparison, two naturally abundant SO₂ studies with high 262 resolution are presented. The study from Vandaele et al. (2009) with spectral resolution of 2 263 cm⁻¹ and 4–6% error. A high-resolution natural abundance measurement from Rufus et al. 264 (2003) with spectral resolution of 0.04-0.13 cm⁻¹ resolution and 5% error. This study improves 265 the spectral resolution of the existing isotopic spectrum by a factor of 20, while the error in the 266 267 260-300 nm band is comparable to spectra of natural abundance at about ten times higher 268 resolution.



Figure 2: Comparison of measured ³²SO₂ absorption spectrum in this study with spectra 270 reported by Rufus et al. (2003), Vandaele et al. (2009), Danielache et al. (2008) (³²SO₂, 25 271 cm⁻¹), and Danielache et al. (2012) at the 293.5–295.5 nm spectral range. All the reported 272 273 spectra were measured at room temperature (293-298 K) therefore spectral differences are not 274 expected to be produced by temperature differences. Spectra reported by Rufus et al. (2003), Vandaele et al. (2009) are for natural abundance SO₂ samples. ³²SO₂ spectrum data in 275 276 Danielache et al. (2008) used natural abundance samples and calibrated with measured ${}^{33}SO_2$ and ³⁴SO₂ spectra. Spectra in this report and Danielache et al., (2008) are from isotopically 277 enriched ³²SO₂ samples. 278

279

Table 1: Summary and comparison of studies on SO₂ absorption b-band.

Reference	Isotope	Resolution	Average	Temperature
		(cm^{-1})	Error (%)	(K)
Present study	^{32,33,34,36} S	0.4	~5.1(³² SO ₂)	293
			~4.0(³³ SO ₂)	
			~4.5(³⁴ SO ₂)	
			~4.1(³⁶ SO ₂)	

Rufus et al. (2003)	Natural abundance	0.04-0.13	~5	295
Vandaele et al. (2009)	Natural abundance	2	~4-6	298
Danielache et al. (2012)	^{32,33,34,36} S	8	~2.2(³² SO ₂) ~1.8(³³ SO ₂) ~1.2(³⁴ SO ₂) ~2.5(³⁶ SO ₂)	293
Danielache et al. (2008)	Nat.,33,34 S	25	~1.2(Nat.) ~3.8(³³ SO ₂) ~8.2(³⁴ SO ₂)	293

281 Note. Comparison of peaks at different resolutions show that the spectrum in this study exhibits 282 significantly better peak separation than the low-resolution studies (Danielache et al., 2008; Danielache et al., 2012; Vandaele et al., 2009). Even the spectrum from Vandaele et al. (2009), 283 284 which has only a five-times difference in resolution, can observe much more resolved peaks. 285 This study also shows excellent control of baseline noise, which is about the same as the lower 286 resolution spectrums compared to the ten times higher resolution spectrum from Rufus et al. 287 (2003). The peak position in this study fits the result from Danielache et al. (2012), while the 288 spectrum from Danielache et al. (2008) is unsuitable for comparison due to band shape 289 distortion by low resolution. The peak position in the spectrum from Vandaele et al. (2009) 290 shows a slightly blue shift compared to the spectrum from Rufus et al. (2003), which is also of 291 natural abundance.

292 The cross-sections calculated using the LAD method are also compared to those calculated 293 using the averaging method as illustrated in Figure 3. The new LAD method perfectly 294 reproduces the peak positions and peak intensities derived from the averaging method over the 295 entire measurement band. From Figure 3 (b), it can be concluded that the subtle differences 296 between the two methods are mainly reflected in the position of the spectral peaks, and the magnitude of the difference increases with the intensity of the peaks. Figure 3 (c) shows that 297 the difference is about 10^{-2} of the intensity of the cross-sections, and there is a relatively high 298 299 difference of about 2-3% at the low SNR positions at both ends of the measurement band, and 300 about 1% at the high SNR positions in the middle of the measurement band. The comparison of errors between two methods are shown in Figure 4, where the spectral data of ${}^{32}SO_2$ 301 302 measured in this study are used. The error calculation of averaging method follows Stark et al. (1999) that includes uncertainty in the absorbing column density N of SO₂, uncertainties in the 303 values of $I(\lambda)$ and $I_{ave}(\lambda)$ associated with the measurement SNR for $I_{0ave}(\lambda)$, and the 304 305 systematic errors associated with inadequate spectral resolution, following,

306
$$\frac{\Delta\sigma}{\sigma} = \left[\left(\frac{\Delta N}{N}\right)^2 + \left(\frac{1}{(SNR)N\sigma}\right)^2 \{1 + e^{2N\sigma}\} \right]^{0.5}$$
(7)

The averaging method shows higher error than the LAD method, with 20-40% error in low SNR regions at both ends of the measurement band range and 10% in high SNR regions. The mean error for the averaging method is 15.1% in the 240-320 nm band range, compared with the 5.1% error using the LAD method, indicating the new algorithm reduces the error by a factor of about three. Since the LAD method does not require separating multiple sources of

- 312 noise and calculating the errors brought by each type of noise individually, it treats them as a
- 313 whole and discriminates the errors by the dispersion of the linear relationship between
- absorbance and gas pressure, as well as introducing a sufficiently large number of measurement

315 groups to improve the reliability of the data.



316

Figure 3: Comparison of spectra obtained the LAD and averaging methods (panel a), and difference between both methods grey color line for the 240–320 nm spectral range. Panel (b) shows an enlarged comparison for the 290–300 nm spectral range. Panel (c) shows the relative of difference between the two methods respect to the spectrum obtained by the LAD method. From the panel c can be seen that both methods yield spectra with a maximum difference of c.a. $\pm 4\%$.



Figure 4: Error comparison between the LAD method and the averaging method for the spectral data of ${}^{32}SO_2$ measured in this study. The error calculation of the averaging method follows Stark et al. (1999) that includes the uncertainty in the column density, the uncertainties in the value of $I(\lambda)$ and $I_{0ave}(\lambda)$ associated with the measurement SNR for $I_{0ave}(\lambda)$, and the systematic errors associated with inadequate spectral resolution.

- 329
- **330** 3.2 Isotopic Fractionation in SO₂ Photoexcitation

331 The measured absorption cross-sections are shown in **Figure 5**, where values of σ for 332 $^{32,33,34}SO_2$ at 240–320 nm were successfully measured. However, due to insufficient samples 333 as illustrated in **Figure S3**, $^{36}SO_2$ in the 240–245 nm band could not be measured. The errors 334 in the measured cross-sections are in the range of 3–10% shown in **Figure 6**, with relatively 335 high errors in the 240–260 nm and 310–320 nm bands.



Figure 5: Measured absorption cross-sections of ³²SO₂, ³³SO₂, ³⁴SO₂, and ³⁶SO₂, absorption cross-sections and estimated errors. For clarity panels a,b,c and d divide the spectrum in four spectral ranges 240–260nm, 260–280 nm, 280–300 nm and 300–320 nm respectively. Subsets in panels a and d show an expanded fraction of the spectra to make more readable the associated error bars to each wavelength. As the mass of the 13sotopologues increases a significant redshift in the position of the peak of the absorption spectrum can be observed starting at the spectral band origin near 317 nm.



Figure 6: Relative error of ³²SO₂, ³³SO₂, ³⁴SO₂, and ³⁶SO₂ respect to measured absorption
cross-sections. Lack of precision due to insufficient signal-to-noise ratio is more pronounced
at edges of the measurement spectral band.

349 The redshift of the SO₂ rare isotopologues relative to 32 SO₂ at each peak position is more 350 pronounced for heavier isotopes. The wavelength-dependent isotopic fractionation constant 351 ${}^{3x}\varepsilon(\lambda)$ was calculated to describe the isotopic effect (Ueno et al., 2009), following,

352
$${}^{3x}\varepsilon(\lambda) = 1000 \times \ln\left[\frac{\sigma^{3x}SO_2(\lambda)}{\sigma^{32}SO_2(\lambda)}\right] [\%_0]$$
(8)

where $\sigma^{3x}(\lambda)$ is the absorption cross-section for a given 14sotopologues (^{3x}S, namely ³²S, ³³S, ³⁴S, or ³⁶S) at wavelength λ . The result is shown in **Figure 7**, this study extends the existing value of fractionation constant by 10 nm at shorter wavelengths compared to the previous study (Danielache et al., 2012). The peak positions in the highly structured absorption cross-sections are consistent with Danielache et al. (2012), but the values at both ends of the measurement band are slightly smaller.



Figure 7: Fractionation constant of ${}^{33,34,36}\varepsilon$ as a function of wavelength from measured absorption cross-sections (${}^{3x}\varepsilon(\lambda)$) compared to the previous study (Danielache et al., 2012). Newly reported spectra show a large wavelength specific isotopic effect which are similar to previously reported spectra. Significant differences can be seen at edges of the measured spectra in the ~250 nm and ~315 nm region.

369

The magnitudes of S-MIF for the four stable sulfur isotopologues are given by the linearexpressions as follows,

$${}^{33}E_{\lambda} = {}^{33}\varepsilon_{\lambda} - 0.515 \times {}^{34}\varepsilon_{\lambda} \tag{9}$$

$${}^{36}E_{\lambda} = {}^{33}\varepsilon_{\lambda} - 1.9 \times {}^{34}\varepsilon_{\lambda} \tag{10}$$

where the values 0.515 and 1.9 are the high-temperature limit values for the equilibrium partition function ratio for isotope exchange reactions (Hulston and Thode, 1965). As shown in **Figure 8**, the S-MIF constant of ${}^{33}E$ and ${}^{36}E$ largely agree to the previous study (Danielache et al., 2012), with the values at both ends of the measurement band are slightly deviated.



Figure 8: The Mass-independent fractionation constant ${}^{33}E$ and ${}^{36}E$ calculated from standard S-MIF values of 0.515 and 1.9 as a function of wavelength compared to Danielache et al. (2012). Newly reported spectra show a large wavelength specific isotopic effect which are similar to previously reported spectra. Significant differences can be seen at edges of the measured spectra in the ~250 nm and ~315 nm region.

380

381 Generally, ${}^{33,34,36}\varepsilon$ and ${}^{33,36}E$ mostly reproduced the results from the previous study 382 (Danielache et al., 2012) regardless of the higher resolution of this report. The deviation at both 383 ends of the measurement band could come from many factors, the largest of which is likely to 384 be the low SNR brought about by insufficient background signal intensity.

385 The sulfur isotopic fractionation for SO₂ photodissociation in $\tilde{C}^1B_2-\tilde{X}^1A_1$ absorption band and 386 photoexcitation in $\tilde{B}^1B_1-\tilde{X}^1A_1$ absorption band were also calculated. The photochemistry 387 reaction rates for each sulfur 16sotopologues in the atmosphere follows,

388
$${}^{3x}J = \int_{\lambda_0}^{\lambda_1} \Phi(\lambda) \cdot I(\lambda) \cdot {}^{3x}\sigma(\lambda) \, \mathrm{d}\lambda \tag{11}$$

389 Where Φ is the quantum yield (assumed as 1) and *I* is the actinic solar flux derived from 390 Gueymard (2004). The S-MIF signatures ^{33,36}*E* of sulfur isotopes by SO₂ photochemical 391 reactions are then calculated from ^{3x}*J* follow,

392
$${}^{3x}\varepsilon = 1000 \ln \frac{{}^{3x}J}{{}^{32}J} [\%_0]$$
 (12)

393
$${}^{33}E = {}^{33}\varepsilon - 0.515 \times {}^{34}\varepsilon$$
 (13)

394
$${}^{36}E = {}^{36}\varepsilon - 1.9 \times {}^{34}\varepsilon$$
 (14)

395 The errors derived from the LAD method produce a simple standard deviation which in this 396 report is represented as σ ($\sigma^{3x}J$, $\sigma^{3x}\varepsilon$ and $\sigma^{3x}E$). For a detailed description on the error propagation procedure see the corresponding section in the additional information. Calculated 397 398 ^{3x}J values from cross-sections obtained by the LAD and averaging methods are presented and compared in Figure 9 and Table 2. As presented in Figure 2a, cross-sections obtained by both 399 methods are almost identical and therefore the calculated ${}^{3x}J$ values are numerically similar. 400 The propagated errors are significantly different where the robustness of the LAD method is 401 402 reflected in the propagated $\sigma^{3x}J$ values which are roughly 2 orders of magnitude smaller to 403 those obtained by the averaging method. The reduction of the calculated $\sigma^{3x}J$ values represent a breakthrough since they do not overlap with each other (Figure 9 red and blue data sets) 404 405 while the averaging method show significant overlap making the derived $\sigma^{3x}\varepsilon$ and $\sigma^{3x}E$ 406 unreliable for geochemical predictions. The source in propagated error values can be traced to 407 random errors produced by noise in the measured signal intensity (I or I_0 in Equation 1). Noise 408 in the measured signal intensity I or I_0 for single measurements falls into the category of random 409 errors. However, repeated measurements (See Figure S3 for the number reliable measurements 410 at each wavelength and 17sotopologues) provide the necessary data required by the LAD method to systematically dismiss outlier data points produced by noisy conditions. The 411 implementation of the LAD method reduces the random character of noise in the measured 412 intensities to partially convert it into a systematic error. Calculated ${}^{3x}J$ values were compared 413 414 to calculations under the same solar spectra for cross-sections reported by Danielache et al. (2008, 2012) measured at 25 cm⁻¹ and 8 cm⁻¹ numbers respectively. Figure 10 compares these 415 three data sets. One clear and counter intuitive trend is that the higher the spectral resolution 416 the smaller the differences among ${}^{3x}J$ values. This trend has also been observed by Endo et al. 417 (2015) for the $\tilde{C} - \tilde{X}$ absorption band. The comparison is a clear reminder that when 418 419 considering light induced isotopic effects predictions from single or a narrow band of wavelengths. Error bars for values measured at 8 cm⁻¹ spectral resolution for ${}^{33}J$ and ${}^{34}J$ clearly 420 421 overlap casting shadows on the reliability of the derived isotopic enrichment factors. The J422 values presented in this report present error bars which are far smaller than the J values themselves. Calculated ${}^{3x}\varepsilon$ and ${}^{3x}E$ are, as expected, similar in both methods while $\sigma^{3x}\varepsilon$ and 423 424 $\sigma^{3x}E$ values obtained from the cross-sections calculated with the LAD are 1 order of magnitude 425 smaller than those obtained by the averaging method (Tables 3 and 4).

Table 2. Calculated photoexcitation rate constants $({}^{3x}J)$ and propagated standard deviations $(\sigma^{3x}J)$. All values are in molecules cm⁻³ s⁻¹ units.

	^{32}J	^{33}J	^{34}J	^{36}J	$\sigma^{32}J$	$\sigma^{33}J$	$\sigma^{34}J$	$\sigma^{36}J$
LAD Method	3.0913x10 ⁻³	3.0982x10 ⁻³	3.1097x10 ⁻³	3.1137x10 ⁻³	7.03x10 ⁻⁷	4.41x10 ⁻⁷	4.42x10 ⁻⁷	3.96x10 ⁻⁷
Averaging Method	3.090x10 ⁻³	3.097x10 ⁻³	3.108x10 ⁻³	3.113x10 ⁻³	1.42x10 ⁻⁵	1.42x10 ⁻⁵	1.44x10 ⁻⁵	1.44x10 ⁻⁵

428

429

430	Table 3. Calculated isotopic enrichment factors $({}^{3x}\varepsilon)$ during photoexcitation and propagated
431	standard deviations ($\sigma^{3x}\varepsilon$). All values are in permil (‰) units.

	³³ ε	$^{34}\varepsilon$	³⁶ ε	$\sigma^{33}\epsilon$	$\sigma^{34} \epsilon$	$\sigma^{36}\!\epsilon$
LAD Method	5.91	2.22	7.22	0.26	0.26	0.26
Averaging Method	5.84	2.13	7.29	6.51	6.49	6.52

Table 4. Calculated mass independent isotopic enrichment factors $({}^{3x}E)$ during photoexcitation and propagated standard deviations $(\sigma^{3x}E)$. All values are in permil (‰) units.

	³³ E	³⁶ E	σ ³³ E	$\sigma^{36}E$
LAD Method	-0.83	-4.02	0.19	0.36
Averaging Method	-0.88	-3.81	5.64	10.76

435

436 The introduction of the LAD method has made possible the reduction of propagated error bars 437 to a point where reliable geochemical predictions are possible. Spectral resolution has also been 438 a topic of concern. Previous measurements by Danielache et al. (2008, 2012) carried out at a 439 spectral resolution of 25 cm^{-1} and 8 cm^{-1} respectively, the relation between spectral resolution and predicted isotopic effect has been so far acknowledged but not properly addressed. A 440 441 definite study on the quantitative relation between isotopic effect and spectral resolution is yet to be done. Rufus et al. (2003) reported absorption cross for this band at a spectral resolution 442 between 0.04 cm⁻¹ and 0.13 cm⁻¹, which is according with their assessment sufficient to resolve 443 all natural line widths. For the measurements in this report the optimal trade-off between 444 spectral resolution and spectral noise was set to 0.4 cm⁻¹. Based on recent reports on pressure 445 446 broadening (Lyons et al., 2018) and line profile density (Kumar et al., 2015) suggest that a spectral resolution 0.4 cm⁻¹ could be sufficient for the study of photochemical induced isotopic 447 448 effects at about 1 atm of pressure.

The calculated ${}^{34,33,36}\varepsilon$ and ${}^{33,36}E$ (Figure 11) enrichment factors derived from this and previous 449 measurements are compared respect to spectral resolution at each measurement. All ${}^{3x}J$ values 450 451 were calculated for a top of the atmosphere with a solar flux reported by Gueymard (2004) and 452 adjusted to the spectral resolution of this report. Danielache et al. (2008) first presented spectrum of ^{32,33,34}SO₂ but used natural abundance SO₂ as ³²S 18sotopologues, and a spectral 453 454 resolution ~ 25 cm⁻¹. These first measurements were conducted at the very early stages of this decade long enquiry, they were designed for the \tilde{C} - \tilde{X} absorption band and issues of spectral 455 456 resolution were not properly taken into account. Danielache et al. (2012) later improved the 457 sample preparation and conducted the measurements at a higher resolution data ($\sim 8 \text{ cm}^{-1}$), and 458 higher S/N ratios achieving propagated small error bars. This study introduced a new algorithm 459 to further reduce the errors associated with increased resolution and the number of 460 measurements at each pressure were extended the statistical maximum. The comparison in Figure 11 suggest, yet do not quantitively prove, that the higher the spectral resolution, the 461 smaller the isotopic effect for all ${}^{34,33,36}\varepsilon$ and ${}^{33,36}E$ values. 462





464 Figure 9: Photoexcitation rate constants calculated for a present Earth top of the atmosphere 465 (TOA) conditions with actinic flux reported by (Gueymard, 2004)) for measured ${}^{32}SO_2$, ${}^{33}SO_2$, 466 ${}^{34}SO_2$, and ${}^{36}SO_2$ isotopologues. The red and blue data sets represent cross-sections derived the 467 LAD and averaging methods respectively. Both methods yield nearly the same *J* values. 468 Propagated errors by the averaging method (red) produce error bars that overlap *J* values 469 rendering them unreliable to geochemical predictions. The implemented LAD method (blue 470 data sets) solves this problem.

472





478 between calculated *J* values therefore making them reliable for geochemical predictions.



480 Figure 11: Relationship between isotopic fractionation ${}^{34,33,36}\varepsilon$ and ${}^{33,36}E$ vs. spectral resolution 481 calculated from data in this report and compared to previously reported data by Danielache at 482 al. (2008, 2012). The comparison of the data sets shows a clear trend where isotopic effects 483 tend to be smaller with increased spectral resolution.

484

485 3.2 Comparison with isotope fractionation observed in SO₂ photochemical experiments

Sulfur isotope fractionation during SO₂ photoexcitation at wavelengths in the \tilde{B} - \tilde{X} band 486 487 was investigated by UV irradiating SO₂ with natural isotope ratios and examining the sulfur 488 isotope ratios of the products (referred to as SO₂ photochemical experiments below) (Endo et al., 2016; Whitehill and Ono, 2012; Whitehill et al., 2013)). Quadruple sulfur isotope analysis 489 of the products show large S-MIF, with Δ^{33} S up to 78% (Whitehill et al., 2013) and up to 142% 490 (Endo et al., 2016) with positive $\Delta^{36}S/\Delta^{36}S$ ratios. In this section, we compare isotope 491 fractionation factors predicted from our absorption cross-section measurements with those 492 493 previously observed in SO₂ photochemical experiments. Then, we discuss the origin of S-MIF, 494 which occurs in SO₂ photoexcitation or related to the reaction.

Whitehill et al. (2013)) irradiated SO₂ with UV light under N₂ bath gas and measured quadruple
sulfur isotopes of produced organics. They used a Xe arc lamp as a broadband UV source and

497 controlled UV spectra with UV filters to prevent SO₂ photolysis and examine the wavelength

498 dependence of the isotope fractionations. Acetylene was added as an electron donor in the

experiments. Although reactions are not fully understood, some organic sulfur matter was
produced and collected after UV irradiation. The expected relevant chemical pathways during
this experiment are reactions 1 to 4 (R1-R4) (e.g., Heicklen et al., 1980)

502
$$SO_2(^1A_1) + hv (240-320 \text{ nm}) \rightarrow SO_2(^1A_2 v=n) + SO_2(^1B_1 v=n) (R1)$$

503
$$SO_2(^1A_2 v=n) + M \rightarrow SO_2(^1A_2 v=0) + M (R2)$$

504
$$SO_2(^1A_2 \nu = 0) \rightarrow SO_2(^3B_1)$$
 (R3)

505
$$SO_2(^{3}B_1) + C_2H_2 \rightarrow \text{products (R4)}$$

506 The notation used in reactions 1 to 4 (R1 to R4) describe specific electronic and vibrational 507 states and are not frequent in chemical notation. Starting with R1 $SO_2(^1A_1)$ is the electronic ground state with a given and unspecified rovibrational state. $SO_2(^1A_2 v=n)$ and $SO_2(^1B_1 v=n)$ 508 are the photoexcited electronic ${}^{1}A_{2}/{}^{1}B_{1}$ manifold (mixing of two electronic states) at a given n 509 vibrational state (this fragment is also commonly known as SO₂*). In R2 M is a third body 510 511 collider (e.g., N_2) which triggers a quenching reaction to produce the electronic ¹A₂ state at its 512 ground rovibrational state (v=0). R3 shows the intersystem crossing (ISC) from the singlet ¹A₂ (v=0) state to the triplet $({}^{3}B_{1})$. Because SO₂ $({}^{3}B_{1})$ is more reactive than SO₂ $({}^{1}A_{2}/{}^{1}B_{1})$ (Kroll et 513 514 al., 2018) $SO_2({}^{3}B_1)$ reacts (R3) selectively with acetylene. The details of the reaction R4 have 515 yet to be understood, but they are unlikely to significantly contribute to S-MIF.

516 Isotopic fractionation factor in reaction R1 is predicted with absorption cross-sections of SO₂ isotopologues measured by this study and Danielache et al. (2012). Reactions other than 517 518 reaction R1 also may contribute to the isotopic fractionation observed in photochemical 519 experiments. Whitehill et al. (2013) suggested that reaction R2 mainly originated the observed 520 S-MIF in their experiments, mainly because (1) their theoretical study suggests that isotope 521 selective intersystem crossing might potentially contribute to the observed S-MIF and (2) their 522 results significantly differ from the S-MIF in reaction R1 predicted with SO₂ absorption cross-523 sections measured by Danielache et al. (2012) (Fig. 13).

- 524 Furthermore, the observed MIF signature is considerably different from those predicted by
- 525 isotopologue-specific absorption cross-sections. They also show that excitation wavelength
- **526** range produces isotopic effects in the order of 20-60‰ for Δ^{36} S and 10-40‰ for Δ^{33} S. The
- 527 wavelength range-isotopic effect is significant yet not as large as the pressure dependency $\tilde{1}$
- 528 observed when the full spectral region of the $\tilde{A}^1 A_2 / \tilde{B}^1 B_1$ manifold was photoexcited
- **529** (Whitehill et al., 2013, Fig. 2).
- 530 To compare our results with those of Whitehill et al. (2013), we calculate fractionation factors
- using SO₂ absorption cross-sections of this study and Danielache et al. (2012) from Eqs. (11)
- to (14), assuming a 150 W Xenon arc lamp spectrum and absorption spectra with UV filters.
- 533 The comparisons are shown in **Figures 12** and **13** where the isotopic effect produced during
- the photoexcitation process (R1) is compared to the results from chamber experiments.
- **Figure 12** compares Δ^{33} S, ^{33}E values to δ^{34} S, $^{34}\varepsilon$. The values reported by Whitehill et al. (2013), regardless of excitation wavelength region or P_{SO2} do not match the ones calculated from the

537 spectra reported by Danielache et al. (2008) neither the ones calculated from the spectra in this report. Large discrepancies are also observed on Figure 13 where small and negative values of 538 ^{33}E and ^{36}E from spectra in this report show no correlation with large and positive $\Delta^{36}S$ and 539 Δ^{33} S isotopic ratios from the chamber experiments. Self-shielding calculations reported by 540 Whitehill et al. (2013) and photoexcitation induced enrichment factors calculated from data 541 542 reported by Danielache et al. (2008) and photoexcitation effects from the same spectra at 543 different spectral ranges independently calculated in this report, show large negative ${}^{36}E$ and large positive ${}^{33}E$ values which don't match chamber experiments either. 544

545

From the comparisons in **Figures 12** and **13** the data presented in this report tend to support the conclusions reported by Whitehill et al. (2013) that the MIF isotopic ratios measured in collected organosulfur are likely produced by the ISC process in R3. Furthermore, the data in this report in which values of ${}^{34}\varepsilon$, ${}^{33}E$ and ${}^{36}E$ being small and quite unsensitive to the excitation wavelength band could contribute to the final organosulfur product MIF. This hypothesis does not provide any explanation to the large $\Delta^{33}S$, $\Delta^{36}S$ values to $\delta^{34}S$ values reported from chamber

552 experiments under different band-pass filters, partial SO_2 and total N_2 pressures.

553



Figure 12: Calculated ${}^{34}\varepsilon$ vs. ${}^{33}E$ isotopic effects from spectra reported by Danielache et al. (2012) and from spectra reported in this study using a 150W Xenon arc lamp spectrum and compared to experiments by Whitehill et al. (2013)) (δ^{34} S and Δ^{33} S). The units of the spectral range are in nm, while P_{tot} (total gas pressures) and P_{SO2} (partial pressures of SO₂) are in mbar. 560



Figure 13: Calculated ³³*E* vs. ³⁶*E* isotopic effects from spectra reported by Danielache et al. (2012) and from spectra reported in this study using a 150W Xenon arc lamp spectrum and compared to experiments by Whitehill et al. (2013) (Δ^{33} S and Δ^{36} S). P_{tot} (total gas pressures) and P_{SO2} (partial pressures of SO₂) are expressed in mbar units.

In order to assess the difference between the isotopic imprint between R1 and R3, next
photoexcitation rate constants from isotopic-specific spectra in the 250–320 nm region were
calculated and compared to chamber experiments reported by Whitehill and Ono (2012).

- 570
- 571



573 **Figure 14:** Calculated ${}^{34}\varepsilon$ vs. ${}^{33}E$ isotopic effects from spectra reported in this study using a 574 150W Xenon arc lamp spectrum and compared to experiments by Whitehill et al., 2013) (δ^{34} S 575 and Δ^{33} S).

576

Experiments conducted by Whitehill and Ono (2012) where they focused on isotopic mixing 577 ratios (δ^{34} S vs. Δ^{33} S and Δ^{33} S vs. Δ^{36} S) of oxydation products of photoexcited (${}^{1}B_{1} {}^{1}A_{2}$)SO₂ 578 and residual ground state SO₂. For additional insight a simple self-shielded photoexcited 579 580 enrichement factors (${}^{34}\varepsilon$ vs. ${}^{33}E$ and ${}^{33}E$ vs. ${}^{36}E$) at pressures ranging from 4.48 to 25.7 mbar using a 150W Xenon arc lamp spectrum was added to the analysis. The results are presented 581 in Figures 14 and 15. Figure 14 shows that calculated enrichment factors ${}^{34}\varepsilon$ and ${}^{33}E$ present 582 clearly different values to isotopic mixing ratios δ^{34} S vs. Δ^{33} S for produced ⁰S (Whitehill and 583 Ono, 2012). Residual SO₂ show negative values of δ^{34} S and Δ^{33} S, for experiments conducted 584 at 25.7 mbar of partial pressure of SO₂, are quite similar to those calculated in this report. Most 585 significantly, the calculated ${}^{34}\varepsilon$ and ${}^{33}E$ values are not only very close to those reported by 586 Whitehill and Ono (2012) for produced SO_3 , but they also have a very similar slope (inset **a**). 587 The comparisons in **Figure 15** are even more revealing since ${}^{33}E$ vs. ${}^{36}E$ slope calculated from 588 spectra in this report almost perfectly match the ${}^{33}E$ vs. ${}^{36}E$ slope reported by Whitehill and 589 Ono (2012) for produced SO₃, and residual SO₂. Furthermore, in both cases the ${}^{36}E/{}^{33}E$ and 590 591 Δ^{36} S/ Δ^{33} S slopes are particularly identical (**Figure 15** inset **a** for clarity). From the above discussion it can be suggested that the $({}^{1}B_{1} {}^{1}A_{2})SO_{2}$ photoexcitation band is likely to have a 592

593 small isotopic effect that is transported to the SO_3 products. A quantitative mass balance 594 analysis of the reaction products and residuals is necessary for obtaining further insight into 595 the processes taking place at the chamber experiments reported by Whitehill and Ono (2012) 596 and Whitehill et al. (2013).

- 597
- 598



599

Figure 15: Calculated ³³*E* vs. ³⁶*E* isotopic effects from spectra reported in this study using a 150W Xenon arc lamp spectrum and compared to experiments by Whitehill et al. (2013)) (Δ^{33} S and Δ^{36} S).

603

604 3.4 Geochemical implications

The origin of S-MIF found in stratospheric sulfate aerosols (SSA) is still debated. Savarino et al. (2003) attributed the S-MIF to SO₂ photoexcitation, because the SSA array of Δ^{36} S/ Δ^{33} S \approx -4.3 matched early photoexcitation experimental results where KrF excimer laser (248 nm of narrow band) was used (Δ^{36} S vs Δ^{33} S slope \approx -4.2; Farquhar et al., 2001). It is suspected that experiments using narrow-band UV spectra, which are significantly different from the sunlight spectrum, do not simulate isotope fractionation in the atmosphere (e.g., Claire et al., 2014). Subsequently, Danielache et al. (2012) reported ^{32,33,34,36}SO₂ absorption cross-section

measurements for the $\tilde{B}^1 B_1 - \tilde{X}^1 A_1$ band, allowing predictions of sulfur isotopic compositions 612 in sulfate aerosols under various atmospheric conditions. Then, Hattori et al. (2013) modeled 613 chemical reaction networks with a one-box model and calculated the isotope ratio of sulfate, 614 assuming that SO₂ photoexcitation causes MIF with the ^{32,33,34,36}SO₂ absorption cross-section 615 measurements. The results of Δ^{33} S magnitudes and Δ^{36} S/ Δ^{33} S ratios in sulfates reproduce those 616 617 within the SSA array. Thus, it is suggested that SO₂ photoexcitation (reaction R1) is the origin 618 of the S-MIF in SSA. However, this result strongly depends on the results of the absorption cross-section measurements by Danielache et al. (2012). In this section we compare 619 620 photoexcitation induced enrichment factors calculated from reported cross-sections to ice core data reported by Gautier et al. (2018), Shaheen et al. (2013) and Baroni et al. (2008). Gautier 621 et al. (2018) have updated $\Delta^{36}S/\Delta^{33}S$ ratio to -1.56 ± 0.25 for records of the past 2,600 years. 622 further modeling is required to explain the discrepancies between models based on spectra and 623 observations. However, the Δ^{36} S/ Δ^{33} S's difference of the updated data by Gautier et al. (2018) 624 may not be significant to determine the origin of S-MIF. The $\Delta^{36}S/\Delta^{33}S$ slope can be changed 625 by mixing processes between mass-independent and mass-dependent sulfur species, that is, 626 when non-zero Δ^{33} S signature is "diluted." This process happens because of the non-linearity 627 character of the Δ^{33} S and Δ^{36} S definitions (Endo et al. under review). 628

- Attenuation by atmospheric shielding of UV light below 300 nm renders all possible 629 630 photoexcitations unlikely below 10 km. At an altitude of 30 km, the band of available UV 631 radiation expands to 290 nm, and at an altitude of 40 km, UV light with wavelength longer than 280 nm can participate in the reaction. At 50 km of altitude, the atmospheric shielding 632 effect significantly weakens, and the entire SO₂ UV absorption $\tilde{B}^1B_1-\tilde{X}^1A_1$ band contributes 633 to the photoexcitation process (See Figure S7). Solar flux at different altitudes generates 634 635 different S-MIF signatures on the SO₂ photoexcitation reaction. Solar flux at different altitudes 636 used in the calculation of altitude dependent photoexcitation rate constants were obtained from modelled current atmosphere (Danielache et al., 2023) using actinic solar flux (Gueymard, 637 638 2004) at the top of atmosphere. The results of isotopic fractionation of self-shielding free SO₂ 639 photoexcitation reaction (250-320 nm) are shown in Figure 16 (brown circles).
- The same calculation at different altitudes combined with self-shielding under an SO₂ column 640 density ranging from 1.21×10^{14} to 1.21×10^{16} molecules cm⁻² are shown in Figure 16 (violet 641 and yellow tringles), and for SO₂ column densities up to 1.21×10^{17} molecules cm⁻² which are 642 643 closer to those reported during the Pinatubo eruption are presented in **Figure 17**. For a further 644 comparison, comparisons isotopic effects calculated by Hattori et al. (2013) are added to Figure 17. Figure 16 also shows volcanic data from Gautier et al. (2018) (red stars), Shaheen et al., 645 (2014) (black stars) and Baroni et al., (2008) (violet stars). Self-shielding free photoexcitation 646 effect is almost 0 in ${}^{33}E$ and stays unchanged with altitude, ${}^{36}E$ range from -10% at 10 km to 647 4‰ at 30 km. Altitude variability do not produce any significant ${}^{36}E/{}^{33}E$ slope but it they show 648 649 an interesting overlap with volcanic data suggesting that the ${}^{36}E$ variability is produced by altitude. Self-shielding calculations show a more revealing result in which increased column 650 density (up to 1.21×10^{16} molecules cm⁻²) creates a ${}^{36}E/{}^{33}E$ slope compatible with the reported 651 652 volcanic data. The data presented in Figure 17 includes the data in Figure 16 but it has expanded both ${}^{33}E$ and ${}^{36}E$ axis. By expanding the ${}^{33}E$ and ${}^{36}E$ axis, self-shielding calculations 653 more realistic to a stratospheric eruption $(1.21 \times 10^{17} \text{ molecules cm}^{-2})$ shows that the slope does 654 655 not change but also is compatible and of reverse signs to the altitude and self-shielding

656 calculations of Hattori et al. (2013) and also ${}^{36}E/{}^{33}E$ slope compatible with volcanic reported 657 data.

658



659

Figure 16: The isotopic fractionation from SO₂ photoexcitation using modern atmospheric solar flux at different altitudes and comparison with Hattori et al. (2013). (a) ${}^{34}\varepsilon$ and ${}^{33}E$. (b) ${}^{33}E$ and ${}^{36}E$. The volcanic data is from Gautier et al. (2018) (red stars), Shaheen et al. (2013) (black stars) and Baroni et al. (2008) (violet stars).

664



Figure 17: Photoexcitation enrichment factors calculated from this report compared to those reported by Hattori et al. (2013). Self-shielding calculation with column densities of 10^{19} molecules cm⁻² (530 DU) as suggested by Guo et al. (2004) produced values of ${}^{36}E = 1.314\%$ and ${}^{33}E = 1.163\%$ which fall well outside of the range in the plot. **671**

672 4 Conclusions

This study presents the cross-sections of ${}^{32}SO_2$, ${}^{33}SO_2$, ${}^{34}SO_2$, and ${}^{36}SO_2$ for the $\tilde{B}^1B_1-\tilde{X}^1A_1$ 673 absorption band at 293.15 K measured at a resolution of 0.4 cm⁻¹ with an error of 3–10%. In 674 this report we implemented an algorithm using the LAD linear regression which was applied 675 676 to finely calibrate the linear relationship between absorbance and pressure and then achieve the 677 cross-section data at each wavelength. The overall features of measured cross-sections, that is, 678 the peak positions of isotopologues, are consistent with previous studies (Danielache et al., 679 2008; Danielache et al., 2012). We obtained both more detail in the absorption peaks and a significant improvement in errors derived from noise during the measurement. For S-MIF 680 related to SO₂ photochemistry, S-MIF predicted from our new spectral measurements do not 681 reproduce results of S-MIF observed in SO₂ photochemical experiments performed by 682 683 Whitehill et al. (2013). The discrepancy supports Whitehill's argument that large S-MIF 684 originates in the intersystem crossing rather than photoexcitation alone.

686 Acknowledgements

This study does not have real or perceived financial conflict of interest for any author. We
would like to thank Shohei Hattori and Naohiro Yoshida for sample preparation and Matthew
S. Johnson for technical advice. We also wish to thank Yi Ding for his consultation and advice
on machine learning and algorithms. This research was funded by JSPS KAKENHI (grant
numbers 22H05150 and 20H01975).

692 Data Availability Statement

693 The spectral data presented in this manuscript was recorded at the Tokyo Institute of 694 Technologies with experimental devices described in the experimental section. Reported data set in this study are available at Harvard Dataverse repository of research data via 695 696 https://doi.org/10.7910/DVN/AP8ISE with CC0 1.0 license/Data use agreement. Figures were 697 made with Origin Ver. 2022 (Origin Lab). The code used in this manuscript for the calculation 698 of absorption cross-sections is licensed under MIT and Published on GitHub 699 https://github.com/PatrickYLi/LAD-Regression/tree/multi-core and Zenodo 700 (doi/10.5281/zenodo.10836723)

701

702 References

- Anderson, R. J., and P. R. Griffiths (1975), Errors in absorbance measurements in infrared Fourier
- transform spectrometry because of limited instrument resolution, *Analytical Chemistry*, 47(14), 23392347, doi:10.1021/ac60364a030.
- 706 Baroni, M., J. Savarino, J. Cole-Dai, V. K. Rai, and M. H. Thiemens (2008), Anomalous sulfur
- isotope compositions of volcanic sulfate over the last millennium in Antarctic ice cores, J. Geophys.
- 708 Res. Atmos., 113(D20).
- 709 Baroni, M., M. H. Thiemens, R. J. Delmas, and J. Savarino (2007), Mass-independent sulfur isotopic
- 710 compositions in stratospheric volcanic eruptions, *Science*, *315*(5808), 84-87,
- 711 doi:10.1126/science.1131754.
- 712 Barra, I., L. Khiari, S. M. Haefele, R. Sakrabani, and F. Kebede (2021), Optimizing setup of scan
- 713 number in FTIR spectroscopy using the moment distance index and PLS regression: application to
- 714 soil spectroscopy, *Scientific reports*, *11*(1), 1-9, doi:10.1038/s41598-021-92858-w.
- 715 Blackie, D., R. Blackwell-Whitehead, G. Stark, J. C. Pickering, P. L. Smith, J. Rufus, and A. P.
- 716 Thorne (2011), High-resolution photoabsorption cross-section measurements of SO₂ at 198 K from
- 717 213 to 325 nm, J. Geophys. Res., 116(E3), doi:10.1029/2010je003707.
- 718 Claire, M. W., J. F. Kasting, S. D. Domagal-Goldman, E. E. Stüeken, R. Buick, and V. S. Meadows
- 719 (2014), Modeling the signature of sulfur mass-independent fractionation produced in the Archean
- 720 atmosphere, *Geochimica et Cosmochimica Acta*, *141*, 365-380, doi:10.1016/j.gca.2014.06.032.
- 721 Danielache, S. O., C. Eskebjerg, M. S. Johnson, Y. Ueno, and N. Yoshida (2008), High-precision
- **722** spectroscopy of ³²S, ³³S, and ³⁴S sulfur dioxide: Ultraviolet absorption cross sections and isotope
- 723 effects, J. Geophys. Res. Atmos., 113(D17), doi:10.1029/2007JD009695.
- 724 Danielache, S. O., S. Hattori, M. S. Johnson, Y. Ueno, S. Nanbu, and N. Yoshida (2012),
- 725 Photoabsorption cross-section measurements of ${}^{32}S$, ${}^{33}S$, ${}^{34}S$, and ${}^{36}S$ sulfur dioxide for the $B^{I}B_{I}-X^{I}A_{I}$
- 726 absorption band, J. Geophys. Res. Atmos., 117(D24), doi:10.1029/2012jd017464.
- 727 Danielache, S. O., G. Iwama, M. Shinkai, M. Oinuma, E. Simoncini, and T. Grassi (2023),
- 728 Introducing atmospheric photochemical isotopic processes to the PATMO atmospheric code,
- 729 *Geochem. J.*, 57(2), 42-58, doi:10.2343/geochemj.GJ23004.
- 730 Dreissig, I., S. Machill, R. Salzer, and C. Krafft (2009), Quantification of brain lipids by FTIR
- 731 spectroscopy and partial least squares regression, Spectrochimica Acta Part A: Molecular and
- 732 *Biomolecular Spectroscopy*, *71*(5), 2069-2075, doi:10.1016/j.saa.2008.08.008.
- 733 Eiler, J. M., B. Bergquist, I. Bourg, P. Cartigny, J. Farquhar, A. Gagnon, W. Guo, I. Halevy, A.
- Hofmann, and T. E. Larson (2014), Frontiers of stable isotope geoscience, *Chem. Geol.*, 372, 119-
- 735 143, doi:10.1016/j.chemgeo.2014.02.006.
- 736 Endo, Y., S. O. Danielache, and Y. Ueno (2019), Total pressure dependence of sulfur mass-
- independent fractionation by SO₂ photolysis, *Geophys Res Lett*, 46(1), 483-491,
- 738 doi:10.1029/2018gl080730.
- 739 Endo, Y., S. O. Danielache, Y. Ueno, S. Hattori, M. S. Johnson, N. Yoshida, and H. G.
- 740 Kjaergaard (2015), Photoabsorption cross-section measurements of ³²S, ³³S, ³⁴S, and ³⁶S
- sulfur dioxide from 190 to 220 nm, Journal of Geophysical Research: Atmospheres, 120(6),
- 742 2546-2557, doi:10.1002/2014JD021671.
- 743 Endo, Y., S. O. Danielache, M. Ogawa, and Y. Ueno (2022a), Absorption spectra
- measurements at $\sim 1 \text{ cm}^{-1}$ spectral resolution of ³²S, ³³S, ³⁴S, and ³⁶S sulfur dioxide for the
- 745 206–220 nm region and applications to modeling of the isotopic self-shielding, *Geochemical*
- 746 *Journal*, 56(1), 40-56, doi:10.2343/geochemj.GJ22004.
- 747 Endo, Y., Sekine, Y., and Ueno, Y. (2022b). Sulfur mass-independent fractionation during
- **748** SO₂ photolysis in low-temperature/pressure atmospheres. *Chemical Geology*, 609, 121064.
- 749 doi.org/10.1016/j.chemgeo.2022.121064
- 750 Endo, Y., Y. Ueno, S. Aoyama, and S. O. Danielache (2016), Sulfur isotope fractionation by
- broadband UV radiation to optically thin SO₂ under reducing atmosphere, *Earth and*
- 752 *Planetary Science Letters*, 453, 9-22, doi:10.1016/j.epsl.2016.07.057.
- 753 Farquhar, J., H. Bao, and M. Thiemens (2000), Atmospheric influence of Earth's earliest sulfur cycle,
- 754 *Science*, 289(5480), 756-758, doi:science.289.5480.756.
- 755 Farquhar, J., J. Savarino, S. Airieau, and M. H. Thiemens (2001), Observation of wavelength-
- sensitive mass-independent sulfur isotope effects during SO₂ photolysis: Implications for the early
- atmosphere, *Journal of Geophysical Research: Planets*, *106*(E12), 32829-32839,
- 758 doi:10.1029/2000JE001437.
- 759 Gautier, E., J. Savarino, J. Erbland, and J. Farquhar (2018), SO₂ oxidation kinetics leave a consistent
- isotopic imprint on volcanic ice core sulfate, J. Geophys. Res. Atmos., 123(17), 9801-9812.
- 761 Gueymard, C. A. (2004), The sun's total and spectral irradiance for solar energy applications and
- 762 solar radiation models, *Solar energy*, *76*(4), 423-453, doi:10.1016/j.solener.2003.08.039.
- 763 Guo, S., Bluth, G. J. S., Rose, W. I., Watson, I. M., & Prata, A. J. (2004). Re-evaluation of
- 764 SO₂ release of the 15 June 1991 Pinatubo eruption using ultraviolet and infrared satellite
- response to the sensors. *Geochemistry, Geophysics, Geosystems*, 5(4).
- 766 https://doi.org/10.1029/2003GC000654

- 767 Hattori, S., J. A. Schmidt, M. S. Johnson, S. O. Danielache, A. Yamada, Y. Ueno, and N. Yoshida
- 768 (2013), SO₂ photoexcitation mechanism links mass-independent sulfur isotopic fractionation in
- 769 cryospheric sulfate to climate impacting volcanism, *Proceedings of the National Academy of*
- 770 *Sciences*, *110*(44), 17656-17661, doi:10.1073/pnas.1213153110.
- Heicklen, J., N. Kelly, and K. Partymiller (1980), The photophysics and photochemistry of SO2,
- 772 *Reviews of Chemical Intermediates*, *3*(3-4), 315-404, doi:10.1007/bf03052425.
- 773 Herzberg, G. (1945), *Molecular spectra and molecular structure*, D. van Nostrand.
- Hulston, J., and H. Thode (1965), Variations in the S^{33} , S^{34} , and S^{36} contents of meteorites and their
- relation to chemical and nuclear effects, J. Geophys. Res., 70(14), 3475-3484,
- 776 doi:10.1029/JZ070i014p03475.
- Koplow, J. P., D. A. Kliner, and L. Goldberg (1998), Development of a narrow-band, tunable,
- frequency-quadrupled diode laser for UV absorption spectroscopy, *Applied optics*, *37*(18), 3954-3960,
 doi:10.1364/AO.37.003954.
- 780 Kostkowski, H. J., and A. M. Bass (1956), Slit function effects in the direct measurement of
- 781 absorption line half-widths and intensities, *JOSA*, *46*(12), 1060-1064, doi:10.1364/JOSA.46.001060.
- 782 Kroll, J. A., B. N. Frandsen, R. J. Rapf, H. G. Kjaergaard, and V. Vaida (2018), Reactivity of
- 783 Electronically Excited SO₂ with Alkanes, *The Journal of Physical Chemistry A*, 122(39), 7782-7789,
- 784 doi:10.1021/acs.jpca.8b04643.
- Kumar, P., J. Ellis, and B. Poirier (2015), Rovibrational bound states of SO₂ isotopologues. I: Total
 angular momentum *J*=0–10, *Chem. Phys.*, *450*, 59-73.
- 787 Leonard C. Entwicklung eines UV-laserspektroskopischen nachweisverfahrens für OH-
- 788 Radikals und spektroskopische untersuchungen an spurengasen unter troposphärischen
 789 bedingungen, Germany: University of Hannover; 1989. Doctoral dissertation in physics.
- 790 Li, L., H. Zhao, N. Ni, Y. Wang, J. Gao, Q. Gao, Y. Zhang, and Y. Zhang (2022), Study on the origin
- 791 of linear deviation with the Beer-Lambert law in absorption spectroscopy by measuring sulfur
- 792 dioxide, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 275, 121192,
- 793 doi:10.1016/j.saa.2022.121192.
- 794 Lyons, J., H. Herde, G. Stark, D. Blackie, J. Pickering, and N. de Oliveira (2018), VUV pressure-
- broadening in sulfur dioxide, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 210, 156164.
- 797 Masterson, A. L., J. Farquhar, and B. A. Wing (2011), Sulfur mass-independent fractionation patterns
- in the broadband UV photolysis of sulfur dioxide: Pressure and third body effects, *Earth and*
- 799 *Planetary Science Letters*, *306*(3), 253-260, doi:10.1016/j.epsl.2011.04.004.
- 800 Mellqvist, J., and A. Rosén (1996), DOAS for flue gas monitoring—II. Deviations from the Beer-
- 801 Lambert law for the UV/visible absorption spectra of NO, NO₂, SO₂ and NH₃, *Journal of Quantitative*
- 802 Spectroscopy and Radiative Transfer, 56(2), 209-224, doi:10.1016/0022-4073(96)00043-X.
- 803 Meyer-Jacob, C., H. Vogel, F. Boxberg, P. Rosén, M. E. Weber, and R. Bindler (2014), Independent
- 804 measurement of biogenic silica in sediments by FTIR spectroscopy and PLS regression, *Journal of*
- 805 *paleolimnology*, *52*, 245-255, doi:10.1007/s10933-014-9791-5.
- 806 Ono, S. (2017), Photochemistry of sulfur dioxide and the origin of mass-independent isotope
- fractionation in Earth's atmosphere, *Annual Review of Earth and Planetary Sciences*, 45(1), 301-329,
- 808 doi:10.1146/annurev-earth-060115-012324.
- 809 Origin, Version 2022. OriginLab Corporation, Northampton, MA, USA.

- 810 Pavlov, A., and J. Kasting (2002), Mass-independent fractionation of sulfur isotopes in Archean
- 811 sediments: strong evidence for an anoxic Archean atmosphere, *Astrobiology*, 2(1), 27-41,
 812 doi:10.1089/153110702753621321.
- 813 Pedregosa, F., G. Varoquaux, A. Gramfort, V. Michel, B. Thirion, O. Grisel, M. Blondel, P.
- 814 Prettenhofer, R. Weiss, and V. Dubourg (2011), Scikit-learn: Machine learning in Python, *The*
- 815 *Journal of machine Learning research*, *12*, 2825-2830.
- 816 Rufus, J., G. Stark, P. L. Smith, J. C. Pickering, and A. P. Thorne (2003), High-resolution
- photoabsorption cross section measurements of SO₂, 2: 220 to 325 nm at 295 K, *Journal of Geophysical Research: Planets*, 108(E2), doi:10.1029/2002je001931.
- 819 Santos, V. H. J. M. D., D. Pontin, G. G. D. Ponzi, A. S. D. G. E. Stepanha, R. B. Martel, M. K.
- 820 Schütz, S. M. O. Einloft, and F. Dalla Vecchia (2021), Application of Fourier Transform infrared
- spectroscopy (FTIR) coupled with multivariate regression for calcium carbonate (CaCO3)
- quantification in cement, *Construction and Building Materials*, 313, 125413,
- 823 doi:10.1016/j.conbuildmat.2021.125413.
- 824 Savarino, J., A. Romero, J. Cole-Dai, S. Bekki, and M. Thiemens (2003), UV induced mass-
- 825 independent sulfur isotope fractionation in stratospheric volcanic sulfate, *Geophys. Res. Lett*, 30(21),
- **826** doi:10.1029/2003GL018134.
- 827 Shaheen, R., M. Abauanza, T. L. Jackson, J. McCabe, J. Savarino, and M. H. Thiemens (2013), Tales
- 828 of volcanoes and El-Niño southern oscillations with the oxygen isotope anomaly of sulfate aerosol,
- 829 Proceedings of the National Academy of Sciences, 110(44), 17662-17667.
- 830 Skoog, D. A., F. J. Holler, and S. R. Crouch (2017), *Principles of instrumental analysis*, Cengage831 learning.
- 832 Stark, G., P. L. Smith, J. Rufus, A. Thorne, J. Pickering, and G. Cox (1999), High-resolution
- 833 photoabsorption cross-section measurements of SO₂ at 295 K between 198 and 220 nm, *Journal of*
- 834 *Geophysical Research: Planets*, 104(E7), 16585-16590, doi:10.1029/1999JE001022.
- 835 Tsai, S.-M., E. K. Lee, D. Powell, P. Gao, X. Zhang, J. Moses, E. Hébrard, O. Venot, V. Parmentier,
- and S. Jordan (2023), Photochemically produced SO2 in the atmosphere of WASP-39b, *Nature*,
- **837** *617*(7961), 483-487.
- 838 Ueno, Y., M. S. Johnson, S. O. Danielache, C. Eskebjerg, A. Pandey, and N. Yoshida (2009),
- 839 Geological sulfur isotopes indicate elevated OCS in the Archean atmosphere, solving faint young sun
- paradox, *Proceedings of the National Academy of Sciences*, *106*(35), 14784-14789,
- **841** doi:10.1073/pnas.0903518106.
- 842 Vandaele, A. C., C. Hermans, and S. Fally (2009), Fourier transform measurements of SO₂ absorption
- 843 cross sections: II.: Temperature dependence in the 29 000–44 000 cm⁻¹ (227–345 nm) region, *Journal*
- 844 of Quantitative Spectroscopy and Radiative Transfer, 110(18), 2115-2126,
- 845 doi:10.1016/j.jqsrt.2009.05.006.
- 846 Whitehill, A., and S. Ono (2012), Excitation band dependence of sulfur isotope mass-independent
- 847 fractionation during photochemistry of sulfur dioxide using broadband light sources, *Geochimica et*848 *Cosmochimica Acta*, 94, 238-253, doi:10.1016/j.gca.2012.06.014.
- 849 Whitehill, A. R., C. Xie, X. Hu, D. Xie, H. Guo, and S. Ono (2013), Vibronic origin of sulfur mass-
- 850 independent isotope effect in photoexcitation of SO₂ and the implications to the early earth's
- atmosphere, *Proceedings of the National Academy of Sciences*, 110(44), 17697-17702,
- **852** doi:10.1073/pnas.1306979110.

- 853 Wu, C. R., B. Yang, F. Chen, D. Judge, J. Caldwell, and L. Trafton (2000), Measurements of high-,
- room-, and low-temperature photoabsorption cross sections of SO₂ in the 2080- to 2950-Å region,
- with application to Io, *Icarus*, *145*(1), 289-296, doi:10.1006/icar.1999.6322.
- 856 Yung, Y. L., and W. B. DeMore (1999), *Photochemistry of planetary atmospheres*, Oxford University
- 857 Press, USA, doi:10.1093/oso/9780195105018.001.0001.
- 858
- 859
- 860
- 861
- 862
- 863