

Sulfur Isotopic Fractionation in VUV Photodissociation of Sulfur Dioxide: Implications for Meteorite Data

S. Chakraborty¹, Teresa Jackson¹, Bruce Rude², Musahid Ahmed² and M. H. Thieme¹

¹University of California, San Diego, Department of Chemistry and Biochemistry, 9500 Gilman Drive, La Jolla, CA 92093-0356

²Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720



1. Introduction

Mass independent sulfur isotopic compositions have been observed in chondritic chondrules and organics [1, 2] and in bulk CM chondrites, achondrites and iron meteorites [3-6]. A significant excess of $\Delta^{33}\text{S}$ ($= \delta^{33}\text{S} - 0.515 \delta^{34}\text{S}$) was observed in the Dhajala chondrite. Sulfonic acid extracts from the carbonaceous chondrite, Murchison also displayed a significant ^{33}S anomaly and may be associated with deuterium enrichment and it was suggested that methanesulfonic acid could have resulted from gas-phase ultraviolet irradiation of a precursor, carbon disulfide [2]. It was shown through a step wise chemical extraction protocol that the mass independent sulfur component was mostly carried by chondrule rims [7]. Large ^{33}S excesses in sulfides from achondrite meteoritic groups have been found [4]. The ^{33}S excess present in oldhamite from the Norton County aubrite ($\Delta^{33}\text{S} = 0.161 \text{‰}$) suggests that refractory sulfide minerals condensed from a nebular gas with an enhanced carbon to oxygen ratio [3]. In a recent study, a large number of enstatite chondrites were analyzed for quadruple sulfur isotopic composition, but no significant mass-independent signature ($\Delta^{33}\text{S}$, $\Delta^{36}\text{S}$) was measured [7]. However, the oldhamite and aubrite fractions show clear mass-independent character, however, no apparent correlation between $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$. The authors proposed decay of ^{36}Cl (in FeCl_2) as a source of excess ^{36}S . Stellar nucleosynthesis and cosmic ray spallation have been ruled out as the cause of the observed $\Delta^{33}\text{S}$ anomaly [3]. Photochemical reactions in the early solar nebula was inferred to be a leading process to generate mass independent sulfur compositions as it has been shown in laboratory experiments [3, 8]. The other rationale behind this proposition is that the fractionation trend (in $\Delta^{33}\text{S}$ - $\Delta^{36}\text{S}$ space) observed for many meteorites, e.g., iron meteorites, CM chondrites follow the same as that measured for Ly- α photodissociation of H_2S [8]. Though H_2S is the major sulfur bearing species in the solar nebula, especially in the reducing environments, however, within the oxidizing pockets (with lower C/O ratio) in the solar nebula existence of SO_2 could not be ruled out. The goal of the study reported here is to decipher the isotope effect during VUV photodissociation of SO_2 . SO_2 photodissociation have been carried out in the past [9-17], but this is the first ever experiments at the VUV energy regime.

2. Experimental

We performed SO_2 photolysis experiment using a differential pumping system [12] and a 120-cm long reaction chamber. The experiments were performed in a flow condition at a pressure on 200 to 300 mtorr. An appropriate sized high purity (99.99%) Aluminum foil was rolled and inserted inside the reaction chamber (as an inner jacket). The photolysis product- elemental sulfur was collected inside the jacket. The entire jacket was treated as a sample and collected after each photolysis experiment and a fresh jacket for each experiment was utilized. After photolysis, elemental sulfur was extracted from the Al-jacket by CCl_4 treatment. Elemental sulfur was converted to SF_6 through a series of chemical procedures including fluorination of silver sulfide as described in [1]. Several VUV wavelengths from 98.8 through 200 nm was used from the ALS synchrotron.

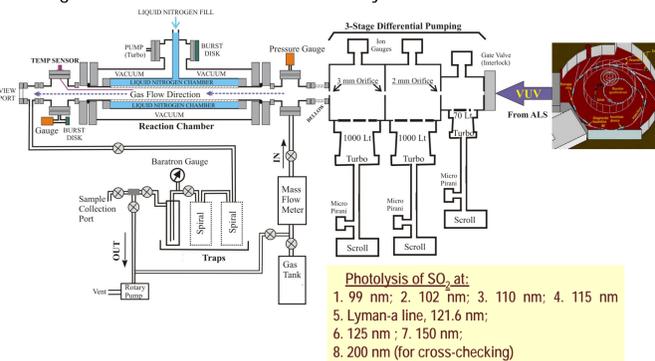


Figure 1. Schematic of experimental apparatus including LN_2 cooled reaction chamber, and three-stage differential pumping system.

3. SO_2 Photodissociation Pathways

The threshold for producing atomic sulfur is 143.3 nm

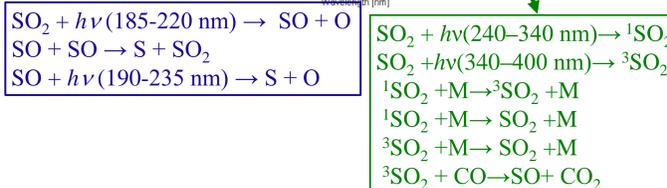
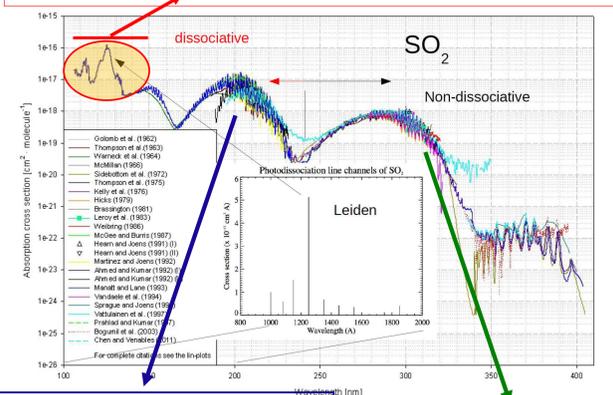
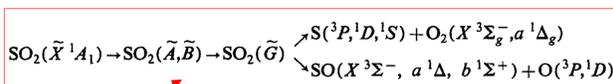


Figure 2. Wavelength dependent photo absorption cross-section data of SO_2 . The entire regime could be divided into three sections based on the dissociation products or pathways as shown. The highlighted VUV regime is the focus of this study, where elemental sulfur could produce in a direct way. The cross-section data taken from the MPI-Mainz UV/VIS Spectral Atlas (http://satellite.mpi.de/spectral_atlas/).

4. SO_2 Photodissociation: Previous Results

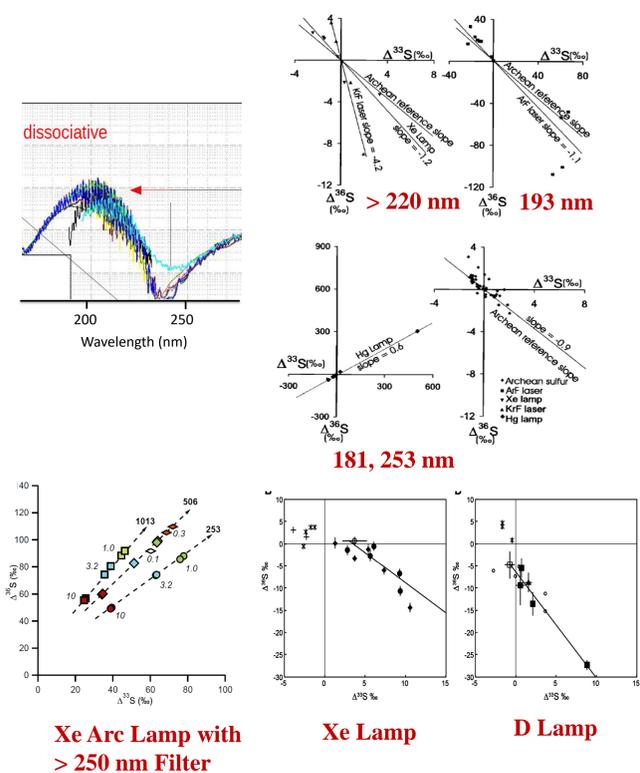


Figure 3. Wavelength dependent (lamp specific) sulfur isotopic fractionation measured previously by different groups in the product of SO_2 photodissociation. Top left: spectral region used previously; top right: data from [9]; bottom: data from [10] and [11]. All these previous experimental results show that the sulfur isotopic fraction in photodissociation/ excitation follow mass-independent trend.

5. Photodissociation Fundamentals

At VUV energy range (8.2 to 12.5 eV used here), SO_2 photodissociates in two different branches: (i) $\text{S} + \text{O}_2$ to (ii) $\text{SO} + \text{O}$ [13]. Based on energy the branching ratio varies also the electronic states of the products (Figure 2).

A molecule predissociates with a certain probability when a bound electronic state couples to a continuous state. Coupling of a bound state to another intermediate bound state, which itself is predissociative may lead to electronic predissociation. Accidental near resonances may occur between vibronic levels of different electronic states as shown by the schematic in Figure 4 (top). For SO_2 the photodissociation is predissociative [14]. Spectroscopic data on SO_2 at VUV is sparse and thus higher energy state definitions are not always available as shown in Figure 4 (bottom).

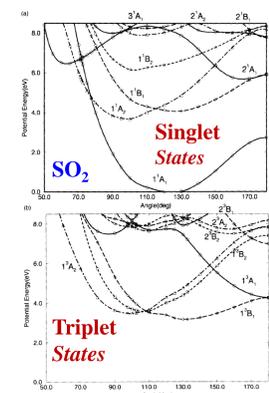
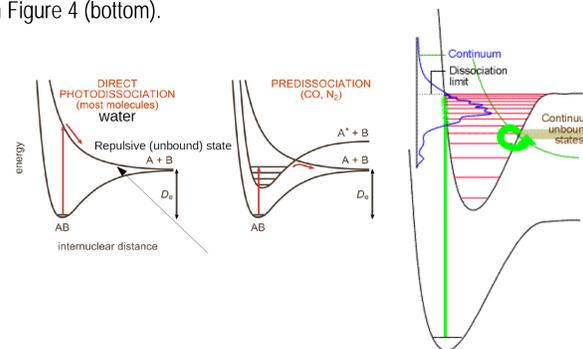


Figure 4. Top: Schematic showing the dissociation dynamics for direct and indirect photo-dissociation. Bottom: The singlet and triplet states of SO_2 [15]. The overlapping (crossing) singlet and triplet states of SO_2 brings the complexity in the pre-dissociative dynamics, which governs the isotopic fractionation in the dissociation product.

6. Results

VUV energy regime provides the threshold energy to dissociation SO_2 to produce elemental sulfur. The measured sulfur isotopic compositions of elemental sulfur in VUV photodissociation of SO_2 are presented here. Figure 5 shows the wavelength dependent $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values, which clearly depict that there is significant variation within a short wavelength shift. Also, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ do not always follow each other which is entirely consistent with quantum mechanical governed inter-electronic state crossing, which is sensitive to the geometry of the surfaces involved in the pre-dissociation process [8]. Figure 6 shows the isotopic compositions in mass-independent space of $\Delta^{33}\text{S}$ vs $\Delta^{36}\text{S}$. Except for the photodissociation at 102 nm, the rest of the data points lie in a zone defined by a slope value of 4.89 ± 0.82 . The data point of 102 nm lies totally in a different quadrant (defining a slope of -1.3). To cross-check with the literature values (Figure 3), one photolysis experiment was performed at 200 nm. The result from that is totally consistent with the literature data and it is in the same quadrant as that of 102 nm data shown in Figure 6.

Acknowledgements: The work is funded through NASA's Cosmochemistry and Emerging Worlds programs. MA and the ALS are supported by the Director, Office of Energy Res., DOE (Contract No. DE-AC02-05CH11231).

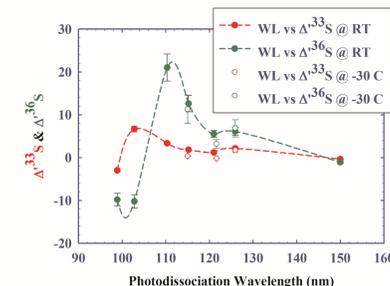


Figure 5. Wavelength dependent sulfur isotopic fractionation ($\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$) as measured in the SO_2 photodissociation product, elemental sulfur.

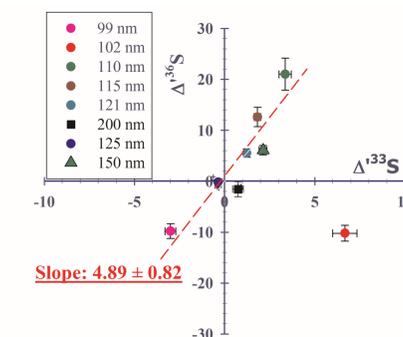


Figure 6. Sulfur isotopic fractionation in mass-independent space ($\Delta^{33}\text{S}$ vs $\Delta^{36}\text{S}$). For most of the wavelengths, the fractionation trend follow a slope of -4.9 , except for 102 nm, where the measured slope value is -1.3 . The results from 200 nm photodissociation show the same trend as that reported in the literature.

7. Discussion

H_2S is one of the major sulfur-bearing species in the gas phase of the solar nebula and was a chemically active environment with VUV photochemistry and ion-molecule chemistry [12, 16]. We have previously shown that elemental sulfur produced from H_2S photodissociation by Ly- α (121.6 nm) produces a slope value of ~ -3 in $\Delta^{33}\text{S}$ vs $\Delta^{36}\text{S}$ space. Data from Iron- meteorites and CM chondrites follow this slope value [5, 6]. Some data from CM chondrites also follow the fractionation trend seen in H_2S photodissociation at 90 and 157 nm. However, all the S-isotopic anomalies measured in meteorites could not be explained only by H_2S photolysis. In that scenario, based on the present photochemical results the effect of VUV photodissociation of SO_2 could not be ruled out. Some of the meteorite measurements could be explained through this new results. As an example, decay of ^{36}Cl to explain excess ^{36}S may be logical for some extremely ^{36}S enrichments measured in water soluble fractions [7]. However, the bulk enstatites and aubrites, though small, show scatter and that could be explained by the wavelength selective SO_2 photodissociation.

8. References

- [1] V. K. Rai, M. H. Thieme (2007) *GCA* 71, 1341-1354.
- [2] G. W. Cooper *et al.* (1997) *Science* 277, 1072-1074.
- [3] V. K. Rai *et al.* (2005) *Science* 309, 1062-1065.
- [4] J. Farquhar *et al.* (2000) *GCA* 64, 1819-1825.
- [5] J. Labidi *et al.* (2017) *GCA* 196, 326-350.
- [6] M. A. Antonelli *et al.* (2014) *PNAS* 111, 17749-17754.
- [7] C. Defouilly *et al.* (2016) *GCA* 172, 393-409.
- [8] S. Chakraborty *et al.* (2013) *PNAS* 110, 44.
- [9] J. Farquhar *et al.* (2001) *JGR: Planets* 106, 32829- 32839.
- [10] Y. Endo *et al.* (2016) *Earth and Planetary Science Letters* 453, 9-22.
- [11] A. R. Whitehill *et al.* (2013) *PNAS* 110.
- [12] S. Chakraborty *et al.* (2014) *PNAS* 111, 14704-14709.
- [13] J. R. Appling *et al.* (1992) *JCP* 97, 4041-4049.
- [14] J. M. Ajello *et al.* (1992) *JGR: Space Physics* 97, 10473-10500.
- [15] Katagiri *et al.* (1997) *J. Mol. Structure*, 413-114.
- [16] B. Fegley (1999) *Sp. Sci. Rev.* 90, 239-252.