HIGH-RESOLUTION SO2 ISOTOPOLOGUE SPECTRA AND SULFUR NON-MASS-DEPENDENT ISOTOPE FRACTIONATION DUE TO SO2 PHOTOLYSIS.  J. R. Lyons1, G. Stark2, D. Blackie2, J. C. Pickering3. 

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Introduction: Full interpretation of the Archean record of sulfur isotope anomalies [1] requires knowledge of the fractionation mechanism. Photolysis of atmospheric SO2 is believed to be the source of sulfur isotope NMDF measured in early Earth sedimentary rocks. It is well known that photolysis of some gas-phase molecules can lead to isotopic non-mass-dependent fractionation (NMDF), as demonstrated in laboratory experiments on SO2 [2]. Several mechanisms for photolytic NMDF have been proposed including 1) self-shielding during photon absorption, 2) variations in band oscillator strengths, 3) hyperfine effects, and 4) resonant curve crossing. Self-shielding, a result of line saturation in molecules with line-type absorption spectra, is observed (and predicted) in CO and N2, both of which undergo predissociation. Here, we focus on the role of self-shielding in SO2, also a predissociating molecule. Quantitative evaluation of SO2 self-shielding requires accurate and high-resolution absorption cross section data. Below we compare moderate resolution spectra with recently obtained low resolution data, and demonstrate the risk in using low resolution spectra for a molecule with a highly structured spectrum such as SO2 (Figure 1).

FTS results: We have completed 1 cm-1 resolution measurements of 32SO2, 33SO2 and 34SO2 isotopologues using a Fourier transform spectrometer (FTS) at Imperial College (IC). Here, we present a brief overview of the data (a more compete discussion of the data will be presented elsewhere by coauthor D. Blackie), comparison with recently obtained lower resolution cross section data. Below we compare moderate resolution spectra with recently obtained low resolution data, and demonstrate the risk in using low resolution spectra for a molecule with a highly structured spectrum such as SO2 (Figure 1).

Modeling results: Interpretation of the isotopic spectra with respect to sulfur NMDF effects is made through the use of radiative transfer modeling [3]. Radiative transfer calculations comparing several sets of cross section data in a 1-D atmospheric chemistry code (assuming 10 ppb SO2) yield very different photolytic sulfur NMDF. Model results using the approximate spectra in [3] demonstrate that a positive $\Delta^{33}S$ is produced in SO (Figure 3), the principal product of SO2 photolysis. The Danielache et al. spectra [5] yield $\Delta^{34}S > 0$ and $\Delta^{33}S < 0$ (Figure 4), and do not demonstrate line-type self-shielding. The sulfur NMDF effects are due to broad variations in the intensities of the isotopic spectra [5].

The Imperial College cross sections yield increasing $\delta^{34}S$, $\delta^{33}S$ and $\Delta^{33}S$ values for photoproduction SO with deceasing altitude in the atmosphere, as expected for self-shielding of 32SO2 rotational lines [3], and qualitatively consistent with laboratory experiments of Pen and Clayton [6]. Due to uncertainties in the total column density of gas, an additive correction is needed to the baseline of the cross section data of 33SO2. We are planning experiments that will allow make this correction unnecessary. Because the sulfur NMDF effect arises from the rotational features, we expect even larger NMDF effects from the high-resolution data (black, Fig. 2). This work is in progress.

Atmospheric OCS: Ueno et al. [7] recently proposed that the negative $\Delta^{33}S$(SO) signature predicted by the low-resolution spectra [5] could be converted to a positive $\Delta^{33}S$ signature if a large quantity (~1-10 ppm) of OCS was in the atmosphere. Although the higher resolution 32SO2 spectra obtain the correct sign, precluding the need for absorption effects by OCS, Ueno et al. have raised the interesting possibility of NMDF effects due to OCS photolysis. The possibility of a hyperfine interaction (electron spin-nuclear spin interaction) exists for 33SO2 (spin 3/2), and could yield an excess of 33SO during OCS photolysis. One of us (JRL) recently discounted this mechanism in OCS [8], but in fact the spin-forbidden photolysis pathway is present at a wide range of wavelengths, and cannot be so easily discounted.

Fig. 1 Illustration of band shifts in SO₂ sulfur isotopologue absorption spectra. Black = $^{32}$SO₂, green = $^{33}$SO₂, red = $^{34}$SO₂, blue = $^{36}$SO₂. (Figure from [3]). The $^{32}$SO₂ data are from [4].

Fig. 2 Comparison of absorption spectra data for $^{34}$SO₂ at several resolutions. Green = low resolution (~20 cm$^{-1}$) data from [5]; red = moderate resolution (1 cm$^{-1}$) data from Imperial College; black = high resolution (0.12 cm$^{-1}$) data from Imperial College.

Fig. 3 Sulfur NMDF from a 1-D atmospheric model using estimated $^{3}$SO₂ spectra [3]. $\Delta^{33}$S(SO) > 0 and $\Delta^{33}$S(SO₂) < 0. This agrees with the general trend seen in pyrites ($\Delta^{33}$S>0) and barites ($\Delta^{33}$S<0), where SO is a precursor to elemental sulfur.

Fig. 4 Model calculations using the low-resolution spectra of [5]. Here, $J_{SO2}$ is the photodissociation rate coefficient. Line-type self-shielding is clearly not present ($\delta^{33}$S and $\delta^{34}$S should be the same sign), and is not expected given the lack of rotational detail in the spectra (green, Fig. 2).

Fig. 5 Model calculations using the moderate-resolution 1 cm$^{-1}$ spectra from the Imperial College FTS. Line-type self-shielding is clearly present ($\delta^{33}$S and $\delta^{34}$S increase with depth), as is expected from the rotational detail in the spectra (red, Fig. 2).