ANALYTIC FORMULATION OF ISOTOPE FRACTIONATION DUE TO SELF-SHIELDING. J. R. Lyons[1], [1]School of Earth & Space Exploration, Arizona State University, PO Box 871404, Tempe AZ 85287; jimlyons@asu.edu

Introduction: Ultraviolet self-shielding in small gas-phase molecules is an important mechanism for generating isotopic mass-independent fractionation (MIF) signatures. For oxygen isotopes, CO is the archetypal self-shielding molecule, with numerous astrochemical examples known [1], [2], [3], [4], [5], [6].

Here, I extend earlier work [7] in which I derived analytical expressions for O and S isotope fractionation due to self-shielding for the case of idealized spectra. 'Idealized' means that 1) perturbations to the isotopic cross sections due to interactions among excited electronic states can be neglected, and 2) line wing overlap can be neglected (line wing overlap effects have been treated elsewhere [8]). The present work applies the same method to symmetric molecules and to molecules with band progressions. These two types of molecules are particularly important for understanding the origin of S-MIF signatures in Archean sedimentary rocks [9].

Formulation: Isotopic photodissociation rate coefficients may be computed as

$$J_i(\tau) = \int_{band} \sigma_i(\lambda)\phi_i(\lambda)I_0(\lambda)e^{-\tau(\lambda)}\,d\lambda \quad (1)$$

where σ_i is the absorption cross section for isotope i, ϕ_i is the dissociation probability (assumed constant here), I_0 is the incident photon intensity (also assumed constant), τ is the summed optical depth for all isotopologues, and λ is wavelength. Simplified but representative cross sections are assumed (Figs. 1a, 3a), allowing an analytical evaluation of equation (1). Natural O and S isotope abundances are assumed. The results presented are most relevant to O_2, S_2, SO_2, and CS_2 but are applicable to other similar molecules.

Results and Implications: Symmetric molecules such as O_2, S_2, and CS_2 are symmetric for their abundant isotopologue, but change symmetry upon substitution of a single O or S minor isotope. (Note that molecules such as H_2S and SO_2 do not change symmetry upon S isotope substitution). This change in symmetry alters the number of rotational transitions available, with roughly a factor of two fewer rotational lines present in the symmetric isotopologue. Figure 1a illustrates simplified line-type spectra for a spectral band of a symmetric O-containing molecule, such as $^{16}O^{16}O$ (labeled σ_{16}) together with the denser bands for two asymmetric isotopologues, $^{16}O^{17}O$ and $^{16}O^{18}O$. The results are shown in Figs. 1b show the excellent agreement between the analytical expressions derived (not shown here) and the full integration, and also show that the symmetric case yields results similar, but not identical to, the asymmetric case [7].

Most molecules exhibit a progression of bands in their UV absorption spectrum. In most cases the isotopic shifts associated with each band follow the trend of a harmonic oscillator, and therefore exhibit mass-dependent relationship. Figure 2 demonstrates this for SO_2 bands in the 190-220 nm region. Box-type spectra with 5 bands are shown in Fig. 3a. The isotopic shifts follow the harmonic trend of Fig. 2. Evaluating the rate coefficients yields MDF behavior at low optical depths (Fig. 3b). There are two main implications: 1) Symmetric molecules yield qualitatively similar self-shielding fractionation to that of asymmetric molecules. 2) A harmonic band progression follows a MDF trend, a result important to understanding laboratory experiments. Archean S-MIF cannot derive from MDF self-shielding but may have a contribution from line-type self-shielding.

References: [1] Bally J. and Langer W.D. (1982) *ApJ 255*, 143-148. [2] Heidenreich and Thiemens M. (1983) *Science 219*, 1073-1075 [3] Navon O. and Wasserburg G. (1985) *EPSL 73*, 1-16. [4] Clayton R. N. (2002) *Nature 415*, 860-861. [5] Lyons J.R. and Young E.D. *Nature 435*, 317-320. [6] Smith R.L. et al. (2009) *ApJ 701*, 163-175. [7] Lyons J.R. (2016) 49th *LPSC*, abs. 2792. [8] Lyons J.R. et al. (2018) *JQSRT* 210, 156-164. [9] Farquhar J. et al. (2000) *Science 289*, 756-759. [10] Lyons J.R. (2008) *Adv. Quant. Chem. 55*, 57-74.
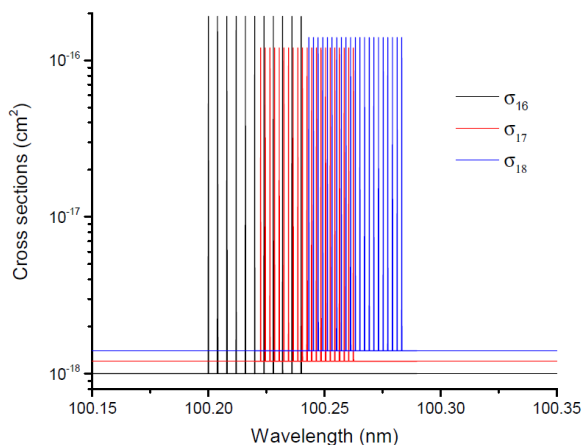
Fig. 1a Isotopic cross sections for a non-overlapping line-type spectral band representative of a predissociating symmetric diatomic molecule such as O_2. Vertical offset for clarity.
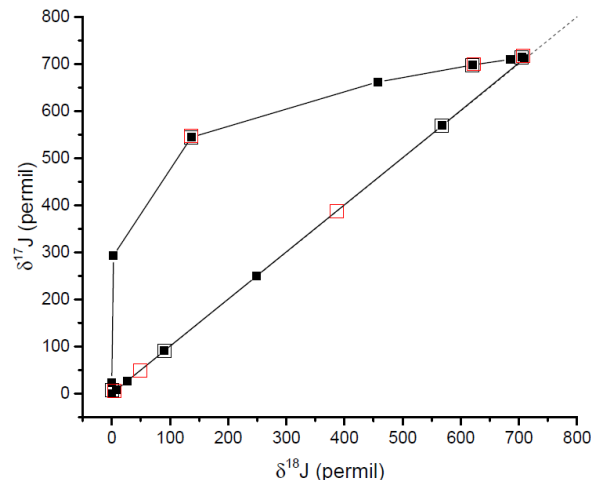

Fig. 1b Delta-values of photodissociation rate coefficients for the cross sections shown in Fig. 1a. With increasing optical depth, the δ-vales progress up a slope-1 line (dashed). $\delta^{18}J$ values reduce as the ^{18}O isotopologue becomes optically thick. Open black squares are results from exact integration of (1). These results are also applicable to S_2. Open red squares show results for a purely asymmetric molecule [7].
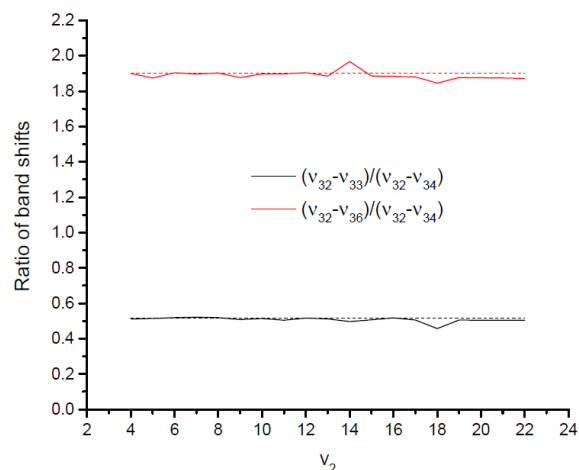

Fig. 2 Ratios of isotopic band shifts for SO_2 from estimates in [10] for a bending mode progression in the 190-220 nm wavelength region. The band shift ratios are very nearly mass-dependent (dotted lines at .515 and 1.90). SO_2 vibrational bands have been recently reassigned, but that will not affect this MDF behavior.
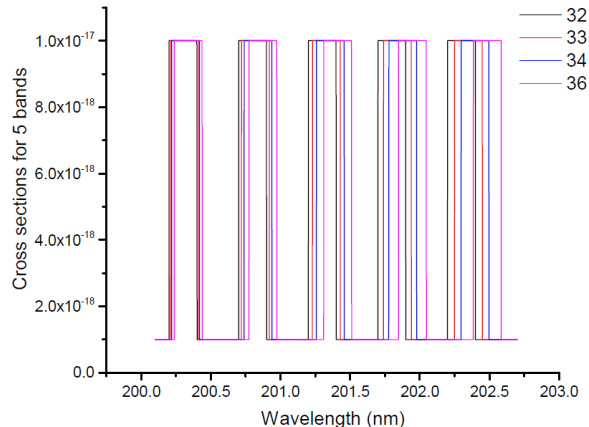

Fig. 3a Shifted box-type cross sections representative of a vibrational progression of bands. The molecule is assumed to be follow a harmonic trend, and the bands are assigned MDF shifts. These cross sections approximate the underlying pseudo-continuum absorption in SO_2 near 200 nm, but not the line-type features in SO_2.
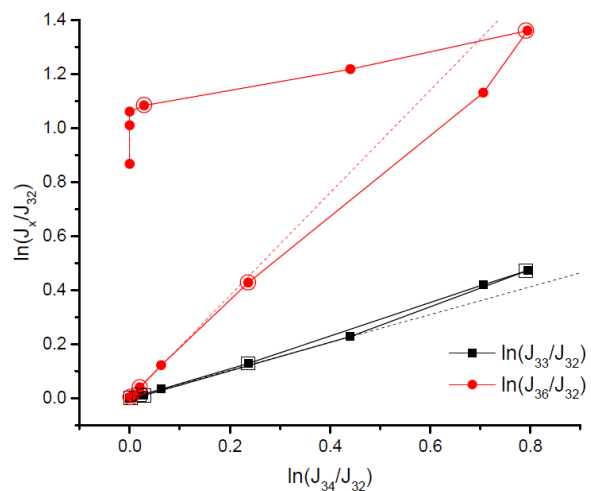

Fig. 3b Ratios of isotopic rate coefficients for the cross sections in Fig. 3a. For optical depth $\tau_{32} < 10$ the fractionation is largely mass-dependent (i.e., close to the dotted lines, slopes .515 and 1.90). The MDF results from the isotopic shifts in Fig. 3a, which are multiples of the zero-point energy of each isotopologue [8]. For $\tau_{32} > 10$ the 32, 33 and 34 isotopologues are largely shielded, but a portion of the 36 cross section is not, resulting in a sustained 36 enrichment.