

ISOTOPE FRACTIONATION DUE TO SELF-SHIELDING FOR IDEALIZED MOLECULAR SPECTRA.

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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 derive 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 overlap can be neglected. The objective is to illustrate the origin of self-shielding fractionation effects, and to explore the range of possible MIF from self-shielding, particularly for sulfur isotopes with application to Archean S-MIF signatures [7].

Formulation: Isotopic photodissociation rate coefficients may be computed as

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

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 CO (O isotopes) and SO and SO₂ (S isotopes), but are applicable to other similar molecules.

Results and Implications: The results are shown in Figs. 1b, 2, 3b and 4, with detailed descriptions in the captions. There are two main implications: 1) It is straightforward to derive fairly accurate expressions for MIF and MDF signatures due to self-shielding for idealized spectra by accounting for peak heights, continuum levels, linewidths and numbers of lines, as done in [3]. For vibrationally excited upper states, or for a vibrational progression, as occurs in SO₂, large MDF signatures arise from the spectral shifts, which are given approximately as vibrational quantum number * ZPE [8]. 2) The latter yields an accurate description of laboratory SO₂ photolysis [9], and may be relevant to modern sulfate aerosols [8], [9], but does not explain the Archean S-MIF record. Archean S-MIF likely derives from a process other than self-shielding.

References: [1] Bally J. and Langer W.D. (1982) *ApJ* 255, 143-148. [2] Heidenreich and Thieme 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] Farquhar J. et al. (2000) *Science* 289, 756-759. [8] Lyons J. R. (2008) *Adv. Quant. Chem.* 55, 57-74. [9] Ono et al. (2013) *JGR Atmos.* 118, 2444-2454.

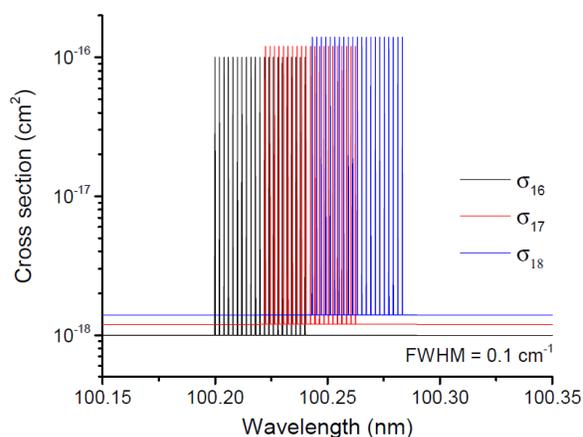


Fig. 1a Isotopic cross sections for a non-overlapping line-type spectral band representative of a predissociating diatomic molecule such as CO. Vertical offset for clarity.

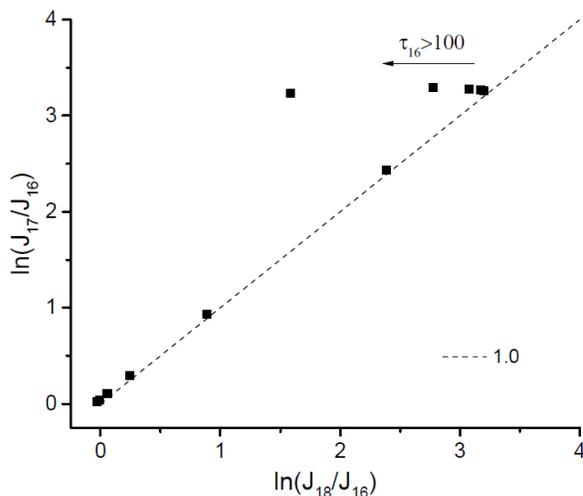


Fig. 1b Ratios of isotopic rate coefficients for cross sections in Fig. 1a. Simple self-shielding with a fractionation slope of unity is evident. At high optical depth ($\tau_{16} > 100$) the ^{18}O -containing molecule also becomes self-shielding, increasing the slope to > 1 .

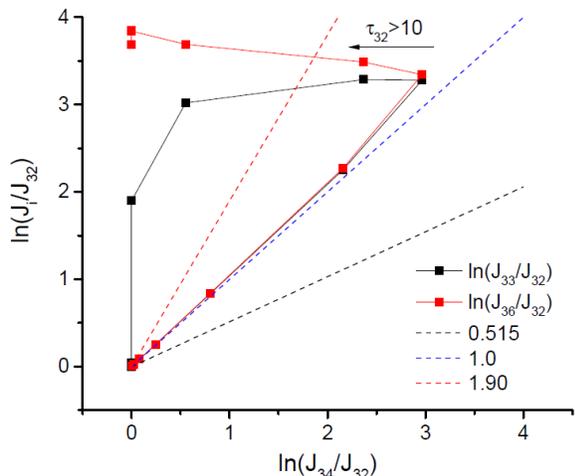


Fig. 2 Ratios of isotopic rate coefficients for a S-containing predissociating molecule such as SO. Cross sections for ^{32}S , ^{33}S , and ^{34}S are non-overlapping, as in Fig. 1a for O isotopes, but with a 4th cross section added for ^{36}S . Self-shielding with slope ~ 1 is present up to optical depth $\tau_{32} \sim 10$ for all 3 rare isotopes. The trends seen do not reproduce Archean S isotope signatures.

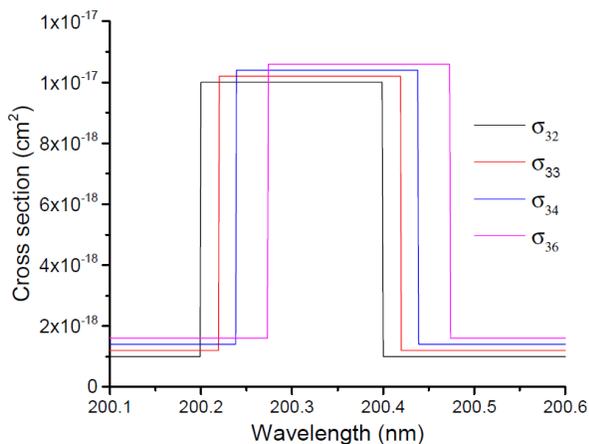


Fig. 3a Shifted box-type cross sections representative of a continuum band with a vibrationally excited upper state which yields large isotopic shifts. These cross sections approximate the underlying pseudo-continuum absorption in SO_2 near 200 nm. Cross sections are vertically offset for clarity.

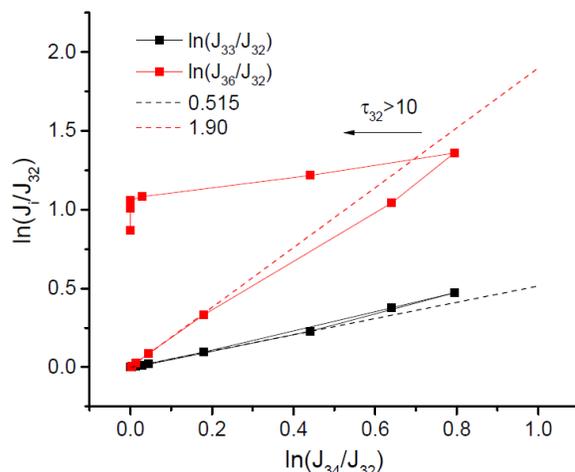


Fig. 3b Ratios of isotopic rate coefficients for the cross sections in Fig. 3a. For optical depth $\tau_{32} < 10$ the fractionation is largely mass-dependent (i.e., close to the dotted lines). The MDF results from the isotopic shifts in Fig. 3a, which are multiples of the zero-point energy of each isotopologue [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.

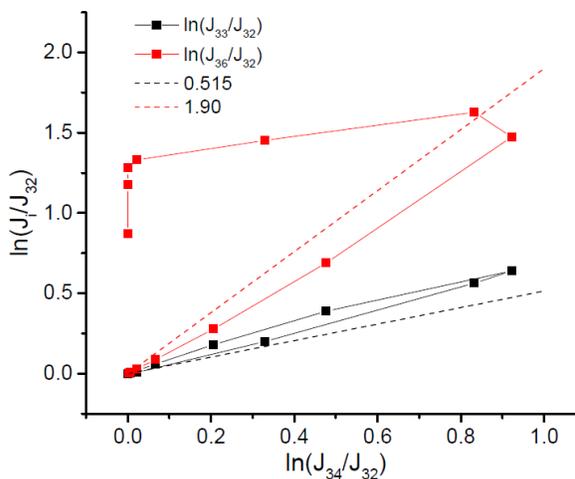


Fig. 4 Ratios of isotopic rate coefficients for spectra that are a combination of those shown in Fig. 3a and Fig. 1a. SO_2 spectra near 200 nm are well approximated by shifted box-type spectra (Fig. 3a), each topped with line-type features (Fig. 1a). The line-type features produce a sulfur MIF signature, and the shifted box-features produce a large sulfur MDF. These results reproduce numerical simulations for SO_2 photofractionation [8], and also laboratory experiments on SO_2 photolysis [9]. However, they do not reproduce Archean sulfur MIF signatures.