MIF and MDF due to self-shielding for idealized molecular spectra

JAMES LYONS[1]

[1]School of Earth & Space Exploration, Arizona State University, Tempe, AZ 85287-1404

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.

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.

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, allowing an analytical evaluation of equation (1).

Implications: There are three main implications of the results: 1) For vibrationally excited upper states as occur in SO_2, large MDF signatures arise from spectral shifts, which are given approximately as vibrational quantum number v*ZPE. 2) The latter yields an accurate description of laboratory SO_2 photolysis, and may be relevant to modern sulfate aerosols, but thus far does not explain the Archean S-MIF record. 3) Many aspects of laboratory experiments on highly optically thick CO can also be understood with this approach. All of these results will be discussed.