A SPECTROSCOPIC PERTURBATION ORIGIN FOR SULFUR MASS INDEPENDENT FRACTIONATION VIA THE B-X SYSTEM OF S_2

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The Great Oxygenation Event (GOE), the introduction of O_2 into the Earth's atmosphere approximately 2.4 billion years ago, is a critical signpost in the development of life on Earth. The vanishing of sulfur isotope anomalies, called Sulfur Mass-Independent Fractionation (S-MIF), in the rock record is thought to be correlated with oxygenation of the early atmosphere. However, the mechanism for the generation of S-MIF in an anoxic atmosphere is unknown. Here, I propose a mechanism that involves spectroscopic perturbations in the B-X UV band system of S_2. This proposal is based on a global deperturbation analysis done by Green and Western[a] [b] and work that I presented previously at this conference in 2015 (MG12) and 2016 (MG08). Specifically, perturbations of the "bright" B state by a "dark" B" state cause some isotopologues to have longer average excited state lifetimes than others. I demonstrate a difference between the shorter-lifetime symmetric (e.g. ^{32}S-^{32}S) isotopologues of S2, for which nuclear permutation symmetry causes half of the rotational lines to be missing, and the longer-lifetime asymmetric isotopologues (e.g. ^{33}S-^{32}S). I also comment on general features of the B/B" system of S_2 that make it uniquely well-suited to generate a large MIF isotope effect.

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[a] M.E. Green, C.M. Western, A deperturbation analysis of the B $^3\Sigma_u^-$ (v' = 0-6) and the B" $^3\Pi_u$ (v' = 2-12) states of S_2, J. Chem. Phys. 104 (3) (1996) 848-864.

[b] M.E. Green, C.M. Western, Upper vibrational states of the B" $^3\Pi_u$ state of $^{32}S_2$, J. Chem. Soc., Faraday Trans. 93 (3) (1997) 365-372.