A possible mechanism for sulfur mass independent fractionation that involves perturbations in the UV spectrum of S2

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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 milestone in the development of life on Earth. The exact timing of the GOE is correlated with the vanishing of sulfur isotope anomalies, called sulfur mass-independent fractionation (S-MIF), in the rock record. However, the mechanism for the generation of S-MIF in an anoxic atmosphere is poorly understood. Here, I propose a mechanism that involves spectroscopic perturbations in the B-X UV band system of S_2, based on an experiments and analysis performed by Green and Western [1]. Specifically, extensive perturbations of the short-lifetime B state (lifetime: 30 ns) by a much longer lifetime B" state (4000 ns) can affect the overall average excited state lifetime of the B~B" system. Crucially, the relative sizes and locations of these perturbations depends on isotopologue, due to factors such as shifts of vibrational quantum energy levels and nuclear permutation symmetry, the latter of which causes half of the rotational levels to be missing in symmetric (e.g. ^{32}S-^{32}S) vs asymmetric (e.g. ^{34}S-^{32}S) istopologues. We also incorporate a steady state master equation kinetic model to account for the impact of rotationally and electronically inelastic (within the B~B" system) collisions between excited state S_2 and inert species in the atmosphere. We find that, in the absense of collisions, there is a ~4% difference in average lifetime between symmetric and asymmetric S_2. This symmetric/asymmetric difference is increases to ~25% at pressures of ~1 atm, and such pressures also generate a differences in lifetime among the different asymetric isotopologues from ~4 to 8%. I will also discuss the aspects of the B~B" system that may make it especially uniquely well suited to generating such large istope effects.

1. Green and Western, 1996, *J. Chem. Phys.,* **104**, 848