

A COLLISIONAL TRANSFER MECHANISM FOR SULFUR MASS INDEPENDENT FRACTIONATION IN WEAKLY INTERACTING EXCITED ELECTRONIC STATES OF S₂

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The Great Oxygenation Event, the introduction of O₂ into the Earth's atmosphere approximately 2.5 billion years ago, is a critical stage in the development of life on Earth. The exact timing of this event is thought to be correlated with the disappearance 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 a reducing atmosphere is still unknown. This talk explores the B-X system of S₂ where the short-lifetime B state is extensively perturbed by a long-lifetime B'' state. We employ a master equation model that calculates rotationally and electronically inelastic collisional transfer rates between the B and B'' states. For weakly perturbed B/B'' level crossings (matrix element less than 1 cm⁻¹), these collisional transfer processes can generate significant isotope effects, where one isotopologue has a larger enhancement of excited state population than another. We discuss the effects of mass-dependent vibrational level shifts and nuclear permutation symmetry on this isotopic fractionation, and propose a possible mechanism for the S-MIF pattern observed in the rock record.