Two mechanisms for the production of mass-independent fractionation during the photochemistry of SO_2

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Sulfur dioxide is known to produce different patterns of sulfur mass-independent isotope fractionation (S-MIF) in two different absorption bands. SO_2 photolysis at wavelengths between 180 and 220 nm produces significant S-MIF only at high optical densities ($>10^{-16}$ molecules/cm^2), suggesting a dominant contribution from optical shielding effects[1]. Both mass-dependent and mass-independent isotope effects become larger at higher SO_2 column densities (up to optical saturation) and at lower temperatures. Mass-dependent isotope effects are consistent with cross-section calculations. SO_2 photolysis occurs due to coupling of a bound state ($^1B_2$) with the dissociative continuum of the ground state ($^1A_1$) [2]. The high density of states in the $^1A_1$ state makes it unlikely that there is a considerable difference in photolysis quantum yields between isotopologues.

In contrast, photoexcitation of SO_2 in the 250 to 350 nm region produces S-MIF that is not due to self-shielding. Its pattern differs considerably from that predicted by cross-sections. Photoexcitation produces larger S-MIF signatures at lower SO_2 pressures and produces very large S-MIF signatures even under optically thin conditions. The isotope effects in this absorption region are due to an isotopologue-specific dependence on intersystem crossing rates between the excited singlet (coupled $^1B_1/^1A_2$) states and reactive triplet ($^3B_1$) states [3], both of which have a low density of states in the crossing region.

Understanding the mechanisms for the production of mass-independent fractionation allows us to predict other molecules that might display similar effects (e.g. CS_2 and SO) and explain the mechanism responsible for the production of S-MIF signatures in the modern atmosphere [4].

[1] Ono *et al* (2013) *J. Geophys. Res. Atmos.* **118**, 2444 [2] Katagiri *et al* (1997) *J. Molec. Struct.* **413-414**, 589 [3] Whitehill *et al* (2013) *PNAS* **110**, 17697 [4] Savarino *et al* (2003) *Geophys. Res. Lett.* **30**, 2131