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Ultraviolet Spectroscopy of ^{32}S, ^{33}S, ^{34}S and ^{36}S Sulphur Dioxide: Isotopic model for the SO_2* reaction.

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We present a model study of the non-mass dependent (NMD) fractionation produced during the photochemical oxidation involving the SO_2* molecule. For this study we used a recently reported spectra of the ultraviolet absorption cross sections of 32SO_2, 33SO_2, 34SO_2 and 36SO_2 isotopologue recorded between 40,000 and 30,300 cm-1 (250 to 330 nm) at 293 K with a resolution of 8 cm-1 and a previously reported spectra recorded at 25cm-1. The B1B1-X1A1 band absorbs UV light below the dissociation threshold and therefore produces a photoexited molecule denoted as SO_2*. The fate of the trapped extra energy within this molecule is a combination of luminescence, internal energy conversion and energy transfer by collision with surrounding molecules. Given suitable broadband or single wavelength photolysis conditions NMD distribution of 32/33/34/36SO_2* isotopologues is generated and given suitable conditions this signal is preserved in reaction products. We present the results of a model study compared them to several chamber experiments. We conclude that planetary atmospheres will exhibit isotopic fractionation from both photoexcitation and photodissociation, and that experiments in the literature have isotopic imprints arising from both the B1B1-X1A1 and the C1B1-X1A1 bands.