Pressure broadening in SO_2 and implications for S-MIF

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In the pre-oxygenated Earth atmosphere, the lack of O_3 absorption allowed UV photodissociation of numerous molecules in the lower atmosphere. For molecules with narrow line-type absorption spectra, optically thick columns would have produced isotope fractionation due to self-shielding. In the lower atmosphere pressure broadening would modify or eliminate these isotope signatures. Here, we report pressure broadening coefficients for natural abundance SO_2 at 215 nm. We find broadening coefficients of 0.30 ± 0.03 cm^{-1} atm^{-1} and 0.40 ± 0.04 cm^{-1} atm^{-1} for N_2 and CO_2, respectively [1]. Using a simple model of pressure broadening we show that S-MIF signatures are diminished as bath (or self) gas pressure is increased. The model replicates SO_2 experiments that used a D_2 lamp [2] fairly well, but overestimates the decrease in S-MIF for experiments that used a Xe arc lamp [3]. For the early Earth atmosphere, pressure broadening of SO_2 would have decreased the magnitude of S-MIF from an optically-thick column of SO_2. Taken together with the large MDF associated with SO_2 self-shielding, this argues that photodissociation of optically-thick SO_2 was at most a minor isotopic process on early Earth.

[1] Lyons JR et al. (*in press*). [2] Masterson AL et al., Earth Plan. Sci. Lett. 2011;306 253-60. [3] Ono S et al., J. Geophys. Res. 2013;118: 2444–54.