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NMD Fractionation Estimated from SO₂ Isotopologues Photolysis UV Spectra

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We report measurements of the ultraviolet absorption cross sections of ³²SO₂, ³³SO₂, ³⁴SO₂ and ³⁶SO₂, recorded using a Bruker vacuum Fourier-transform spectrometer 190 to 220 nm at 293 K with a resolution of 8 cm⁻¹. The samples were produced by combustion of isotopically enriched ³²S, ³³S, ³⁴S and ³⁶S elemental Sulfur. The spectrum of the ³²S, ³³S and ³⁴S samples are in agreement with previously published spectra. We conclude that the main source of error is the standard deviation of the measurements themselves while the root-mean-square of other sources of error is in average 20%. The spectra of the isotopically pure species were corrected based on the isotopic composition of the samples used for the measurements. The absorption spectra show rich vibrational structure and the positions and widths of the peaks change with isotopic substitution in a complex fashion.

We present here the application of the first direct laboratory studies of the absorption cross sections of the ³²SO₂, ³³SO₂, ³⁴SO₂ and ³⁶SO₂ isotopologues. These data, together with extrapolated spectra by red shifting are used to derive the photolytic fractionation factors and the mass independent anomaly at different levels of present atmospheric levels (PAL) of oxygen. By comparison of the employed data sets it is discussed the origin of the mass independency factor during the photolysis in the presence of oxygen. Our results show that the mass independency is a combination of red shifting of the heavier isotopes and the change in the absorption cross section which is independent of the isotopomers. The obtained results give a new insight of the possibilities of mass independent fractionations observed in archean rock samples or stratospheric aerosols.

Keywords: SO₂, Sulfur isotopes