



## **High Precision Spectroscopy of $^{32}\text{S}$ , $^{33}\text{S}$ and $^{34}\text{S}$ Sulfur Dioxide:**

### **Ultraviolet Absorption Cross Sections and Fractionation Constants**

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Many questions have been raised concerning the hypothesized role of photolysis of  $\text{SO}_2$  in the Archaean and modern atmosphere in producing mass independent fractionation found in the geological and ice-core records. We report the first measurement of the ultraviolet absorption cross sections of  $^{32}\text{SO}_2$ ,  $^{33}\text{SO}_2$  and  $^{34}\text{SO}_2$ , recorded using a Bruker vacuum Fourier-transform spectrometer from 52,500 to 30,300  $\text{cm}^{-1}$  (190 to 330 nm) at 293 K with a resolution of 25  $\text{cm}^{-1}$ . The  $^{33}\text{SO}_2$  sample was produced by the combustion of isotopically enriched  $^{33}\text{S}$  while the  $^{34}\text{SO}_2$  and natural abundance samples were obtained from commercial manufacturers. The spectrum of the natural abundance sample is in agreement with previously published spectra. The spectra of the isotopically pure species were calculated based on the isotopic composition of the samples used for the measurements. The  $^{32}\text{SO}_2$ ,  $^{33}\text{SO}_2$  and  $^{34}\text{SO}_2$  absorption spectra show rich vibrational structure and the positions and widths of the peaks change with isotopic substitution in a complex fashion.

The results imply that large wavelength-dependent and broadband isotopic fractionations are associated with the UV photolysis of  $\text{SO}_2$ . The analysis of the spectra show

that the broadband photolytic mass independent fractionation factors are mainly due to the change in absorption cross section and not from the red shifting of the vibrational structure of the heavier isotopologues.