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Ultraviolet absorption cross sections of isotopically substituted carbonyl sulfide species: Theory, experiment and modeling

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We report measurements of the ultraviolet absorption cross sections of OC32S, OC33S, OC34S and O13CS from 195 to 260 nm. The OCS isotopologues were synthesized from isotopically-enriched elemental sulfur by reaction with carbon monoxide. The measured cross section of OC32S is consistent with literature spectra recorded using natural abundance samples. Relative to the spectrum of the most abundant isotopologue, substitution of heavier rare isotopes has two effects. In addition the isotopologue absorption cross sections were calculated from first principles; theory and experiment are in remarkably good agreement. Sulfur isotopic fractionation constants (33ε, 34ε) as a function of wavelength are not highly structured, and tend to be close to zero on average on the high energy side and negative on the low energy side. The integrated photolysis rate of each isotopologue at 20 km, the approximate altitude at which most OCS photolysis occurs, was calculated. Sulfur isotopic fractionation constants at 20 km altitude are ([U+FF0D] 3.7 ± 4.5)‰ and (1.1 ± 4.2)‰ for 33ε and 34ε, respectively, which is inconsistent with the previously estimated large fractionation of over 73‰ in 34ε. This demonstrates that OCS photolysis does not produce sulfur isotopic fractionation of more than ca. 5‰ suggesting OCS may indeed be a significant source of background stratospheric sulfate aerosols. In addition to measurement of absorption cross section, we report preliminary results of theoretical calculations of absorption cross sections of OCS isotopologues.