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Carbonyl sulfide photolysis in the stratosphere: Fractionation of C and S isotopes

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A first principles model of the photolysis of OCS was constructed to provide insight into the loss of stratospheric OCS and it's role as a source of stratospheric sulfate aerosol. The model derived UV absorption cross sections for OCS, $OC^{33}S$, $OC^{34}S$, $OC^{36}S$ and $O^{13}CS$ using the time-depedent quantum mechanical formalism and recent potential energy surfaces for the lowest four singlet and lowest four triplet electronic states, and provides a detailed description of OCS photolysis including isotopic fractionation and its temperature dependence. There is clear evidence that the photolysis qualtum yield is unity at all wavelengths and for all isotopologues. The model was benchmarked against our recent experimental cross section measurements for $^{32,33,34}S$ and $^{12,13}C$ OCS, showing excellent agreement. Photolysis leads to only a small enrichment of ^{34}S in the remaining pool of OCS. A simple stratospheric model shows that stratospheric removal slightly favors light OCS in constrast to the findings of Leung et al. (2002). These results show, based on isotopic considerations, that OCS is an acceptable source of background stratosperic sulfate aerosol in agreement with a recent model study of Bruhl et al. (2012). The ^{13}C isotopic fractionation due to photolysis of OCS is significant and will leave a strong signal in the pool of remaining OCS making it a candidate for tracing using the ACE-FTS and MIPAS data sets.