

Interactive comment on “Multiple-sulfur isotope effects during photolysis of carbonyl sulfide” by Y. Lin et al.

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Final Author comments on the acpd-11-14233-2011, “Multiple-sulfur isotope effects during photolysis of carbonyl sulfide” by Ying Lin, Min Sub Sim, and Shuhe Ono

We have carefully reviewed and considered all reviewer's comments and concerns. Summary of the replies to major comments are listed below. Replies for other minor comments are supplied in separate files.

Overall The goal of the work is to verify the claim made Leung et al. (2002) and Collussi et al. (2004) about the large (>70 ‰ isotope effects during the UV photolysis of OCS. Our work clearly demonstrates that the OCS photolysis produces less than 10‰ isotope fractionation (in $^{34}\text{S}/^{32}\text{S}$ ratios), and questions this earlier claim of very large

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isotope effect. The ZPE-shift model was presented simply to compare the results, and the above conclusion does not rely on the ZPE-shift model. Reviewers (Joel Savarino and Matt Johnson) suggest trapping S as it forms (by O₂ or potentially ethylene). Such an experiment would be ideal for determining the isotope effects at a few per mil level (rather than a percent level). This is clearly a next step but it is beyond the goal of this study because we have achieved determining the isotope effect at 10 per mil level. After the submission of this manuscript, Hattori et al. submitted the UV cross-section measurements of all four S isotopologues of OCS (ACPD, 11, 20487–20520). The result of their work agrees perfectly with our conclusion that large isotope fractionation is not expected for OCS photolysis. While the cross-section measurement provides the isotope fractionation as a function of wavelength, the precision of absorption measurement is on the order of a few percent (Hattori et al., 2011, Fig. A1 and p. 20495 line 8). The approach taken in this study can constrain the isotope effect at sub-per mil level but the downside is the secondary reactions that may complicate the interpretation and limit the accuracy. Two techniques are complimentary, and should be exercised in parallel. This is exactly what happened for the photolysis isotope effect for N₂O. Results from theory, spectroscopy and photochemical experiments are now converging for N₂O. We expect similar approach could be followed for OCS toward the goal of using sulfur isotope ratios to constrain the origin and fate of stratospheric sulfate aerosols, which has a major impact on the radiation budget of the Earth. I hope the readers will see that this study represents a significant step toward this ultimate goal.

Reply for specific major comments by reviewers

Photochemistry of S₂ as an additional source of S (Johnson, Danielache) Matt Johnston concerned about the chemistry follows sulfur abstraction reaction. In particular, can S₂ be a source of S in addition to OCS photolysis? We have not observed characteristic S₂ absorption at around 280 nm during the experiments, placing an upper limit for S₂ number density (< 10¹⁵ molecules/cm³). We have made a photochemical model calculation following Matt Johnson's suggestion. Using rate constants for vari-

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ous recombination reactions tabulated in Ueno et al. (2009), our model suggests that S2 would rather quickly recombine to S4, and S2 photolysis is expected to be a minor sink for S2, and very minor source for S. Detail of the calculation is summarized in a separate note.

Concern about the ZPE-shift model (Savarino, Johnson) The goal of ZPE model is to compare it with our experimental result, and our conclusion does not rely on the ZPE-model. The ZPE model predicts larger isotope fractionation for >285 nm, consistent with the measurement. A paragraph will be edited for clarification, and the subheading for 4.3 can be changed to “comparison to the ZPE-shift model”.

Precision and accuracy of the measurements (Savarino, Johnson) Page 14238 line 1 states, “Six replicated analyses of OCS yield 2σ standard deviations of 0.26, 0.53, and 1.05‰ for $\delta^{33}\text{S}$, $\delta^{34}\text{S}$, and $\delta^{36}\text{S}$, respectively”. This demonstrates that the overall procedure is repeatable at 0.5 ‰ for OCS analysis. Reduction of elemental sulfur is a rather established technique, and tested for quantitative recovery. Furthermore, the overall agreement for isotope mass-balance (Table 1) suggests no significant isotope fractionation during the procedure.

Origin of potential mass-independent fractionation (Savarino, Johnson) Matt Johnston raised a question about the vibronic coupling as a source of MIF. We fully agree this. It, however, is beyond the scope of this paper to discuss alternative hypothesis of Bhattacharya experiment. Observed apparent MIF (or fractionation that does not follow canonical mass fractionation law) could well be explained by an alternative hypothesis, such as self-shielding (although S2 self-shielding isn't very likely) or symmetry effect in S recombination reactions. A paragraph will be added to discuss these alternative hypotheses.

Replies for minor comments are provided in separate files.

Best wishes,

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Ying Lin and Shuhei Ono August 10, 2011

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 14233, 2011.

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