**Atmospheric
Chemistry
and Physics
Discussions**

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

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This is an interesting paper that deserves to be published after minor corrections and clarifications The manuscript tries to answer three different questions, namely the isotopic fraction factor of OCS photodissociation, the source of the sulfate aerosols in the stratosphere, and add another piece of the puzzle in the long run to isolate the causes of the sulfur isotope anomaly found in sedimentary Archean rocks and volcanic stratospheric sulfur compounds . Audience thus surpasses just the regular isotope field. The MS is serious, clear, well organized and presented. I don't see any major flaws, errors, wrong presentation, improper reference/citation or mistakes that could prevent its publication.

Few general comments: I think the authors are overestimating the accuracy of

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the "blue" shift or the TS calculation. These are the biggest uncertainties in their manuscript and their interpretations and conclusions should take this into account, especially for the source of SSA. Author should re consider their interpretation/conclusion in the light of this comment and keep these uncertainties in mind when rephrasing. For the change in the shape of broad cross section by isotopic substitution, author can read Ndengué, et al. (2010), Absorption Cross Section of Ozone Isotopologues Calculated with the Multiconfiguration Time-Dependent Hartree (MCTDH) Method: I. The Hartley and Huggins BandsâĂŽ The Journal of Physical Chemistry A, 114(36), 9855-9863, doi: 10.1021/jp103266m where effect of substitution is detailed. One way to reduce their uncertainties will be to find a way to scavenge S before it can further reacts with OCS. Did they try to use O2 ? As long as SO2 formed is kept negligible its should be fine, even if it is not the case, as long as no S exchange occurs between OCS and S/SO/SO2, following just OCS should be enough to deduce the fractionation factor. The last general comment concerns the UV range they have tested. Looking at the Farquhar's experiment on SO2, I'm wondering if a huge and large effect will not appear during OCS photolysis but not in the weak absorption band but the strong band that exists deeper in the UV, lower than 180 nm, exactly as SO2 which did not display a strong S-MIF with the Xe lamp but a huge one at shorter UV.

Below my minor comments/questions that I will like to be answered by the authors.

Page 14234 line7: I don't like the term "isotope effect", the usual term is "isotope fractionation constant" which point to a value, effect is more general and process oriented.

Page 14234 line18: How the 10 ‰ is calculated? Difference in slope (linear to go faster) is 0.019, to get a difference of 10 ‰ in cap33, you need 500 ‰ fractionation in del34. Seems too much

Page 14235 line 14: change "carbon dioxide" to greenhouse gases Page 14235 line 15: change "volcanic SO2" to SO2 (natural and anthropogenic) Page 14235 line 25: missing "and" between del34 and "the UV"

Page 14237 line 1: Say how this lamp compare to Sun especially in the UV range of interest, and even if the figure 2 displays it. Page 14237 line 3: Say if these flux are measured or given by the manufacturer Page 14237 line 11: Is this column suitable for SO2 separation? OCS contains no SO2? This is important for the rest of the MS (see below) Page 14237 line 15: Do the authors have any idea how S deposition on the window can affect the photolysis rate? Page 14237 line 16-18: It is not OCS neither ZnS that precipitated but S Page 14237 line 20: Is this procedure quantitative to recover all S reservoirs? Nowhere data are provided to prove that no fractionations are associated with the extraction procedure.

Page 14238 line 1: Six replicates of OCS. Be more precise. If it is six times the measurement of the same OCS bulb, I wonder if the SD calculated here can be applied to the normal set up Page 14238 line 8: remove x 1000 in the expression

Page 14239 line 9: As it is explained later, what is important is the quenching effect not the addition of N2 in the cell, change "addition of N2 has.."

Page 14240 line 8: change "the factor $\frac{1}{2}$" to "the statistical weight" or something equivalent Page 14240 line 9: I don't really see why steady state condition for S will not produce an isotopic fractionation during the reaction. What you can assume is that during SSC S is at isotopic equilibrium (i.e. S follows the evolution of the source with a constant fractionation)) but the overall fractionation depends on all possible combinations; OC32S + 34S, OC34S + 32S vs OC32S + 32S, any reaction forming 34S32S contributes to the overall fractionation

Page 14241 line 11: I found $\frac{1}{4}$ and not 1/5 (0.75 x 5 10(-11)/15 10(-11))

Page 14246 line 23: There is no SO2 in the cell at the beginning or end of experiment that could explain the 0,538 exponent, for instance?

Page 14247 line 20: Only the first weak UV absorption band is studied here. What if the OCS displays the same behavior as SO2 photolysis? Almost no effect on the weak

band and a very strong S-MIF in the strong absorption band at deeper UV? It is too premature to claim that during OSC photolysis and subsequent reactions the process is MD, as explained by authors in the paragraph that follows. So here precise the UV domain concerned by the MDF.

Reference page 14251 line 18: Give the DOI of the Lu et al. reference.

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