Atmos. Chem. Phys. Discuss., 11, C8858–C8861, 2011
www.atmos-chem-phys-discuss.net/11/C8858/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ultraviolet absorption cross sections of carbonyl sulfide isotopologues $OC^{32}S$, $OC^{33}S$, $OC^{34}S$ and $O^{13}CS$: isotopic fractionation in photolysis and atmospheric implications" *by* S. Hattori et al.

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Received and published: 12 September 2011

In this study, Hattori et al., revisit the isotopologue dependent cross section for carbonyl sulfide. Here, previous study suggested very large (>60 per mil) isotope fractionation compared to OC34S versus OC32S. The authors synthesized OCS, carefully purified and measured their UV cross sections. This new study does not reproduce the previous claim of large isotope shift. Its implication is discussed. The study represent extremely thorough experimental approach and to push the limit of instrumental precision. This would be an ideal case study for following and on-going measurements of isotopologue

specific cross sections of other gases (e.g., SO2), and their application in atmospheric chemistry and physics. I do not see any flaw in the work. I would suggest following would help clarify and improve the quality of the manuscript.

1. While this work clearly demonstrates large (tens of per mil level) isotope effects are not expected for OCS photolysis, it may not be used to test the isotope effect at per mil level since the precision is on the order of a percent. The cross section measurements are very important, however, because they provide different kinds of information compared to laboratory photolysis reactions (which tends to be messy) or theoretical calculations. Authors may add a sentence or two in the introduction to compare this study to other works (Lin et al., and Danielache et al.), and discuss pros and cons for these different approaches.

2. The manuscript roughly divides errors to random and systematic. (p. 20494, line 23). Authors may consider changing the term "random" to a more descriptive word (e.g., temperature dependence is not totally random), and consider devoting one section for error estimates, since it is critical to this study, and readers may be interested in this. Random error may be due to temperature, and spectrometer stability, then it may be worth noting duration for the experiments (how long does it take to make one cycle of analysis?, did you measure OC32S many times, then switched to 34S? or did you measure 32S and 34S alternately?) I cannot see the errors from Fig A.1 for the most critical region (210-230 nm). Consider changing the axis. Perhaps, you can make it in log scale for Y axis?

3. Figure 3, The measurement resolution is 0.02 nm. Thus, errors in peak position would be on the order of 5 cm-1? Consider adding error bars on y-axis.

Fig 4, the large variation in the isotope fractionation constant for ZPE model at low and high energy ends are probably due to measurement errors. I am not sure what you can do but I found this is a bit misleading as this is due to measurement error not due to ZPE model. The same applies for Fig. 5.

Some minor editorial comments:

Page 20489, Line 8: delete “more”

Line 12, rephrase the sentence starts with “Since OCS photolysis . . .“

20490, Line 20, Johnson et al., is not the only ref.. Add more reference, and e.g.,

Line 23, add more reference to Krouse and Grienko, 1991, or delete of “biogeochemical and geological”

p. 20492: Line 1: “Room temperature measurements are . . .“ This sentence and the one preceding about the temperature effect may better be in experiments or discussion section rather than in introduction. Question is that temperature may not produce 50 per mil effect but may well produce a few permil effect? Can you make any quantitative assessment, here?

Line 13, add “to isolate the effect of 13C, 18O and 17O isotope substitution”.

P 20493, Line 10, reword “rising” to ramped or increased Line 11, waiting 2 min -> held at 473 K for 2 min. Line 22, thus, S is in natural abundance (?)

p. 20494, line 1, can you also state resolution in cm-1?

Section 3.1., some material here may be better suited for experimental section, also consider adding “notation” section to clean up later discussion.

Section 3.2, consider changing subheading to “comparison with previous study”

p. 20495, line 3, cell densities -> OCS number density in the cell. or simply pressure

Page 20496, line 13, define “change”

I noted that mass shift for C-13 (13/12-1) and S-34 (34/32-1) is 8 and 6 percent respectively. Sigma-max position is identical for 34S and 13C substitution.

p. 2049 line 9, equation 6-9 and 11-15 use identical symbols and define different

quantity, and are not consistent with equation 16. i.e., Equation 16 use “i” for 33, 34 but 6-8 are not.

p. 20500, line 13, “close to zero” is very subjective word. This appears through out the text.

Page 20502, Line 14, “calculated” -> “estimated”

Line 20, “and the OCS + O(3P) reaction is. . .”. This is an unpublished result, and may not be critically needed for this paper. I would delete this sentence. You could just say, experiments are on-going, though.

p. 20505, l, 18, reword, “is an acceptable source”.. e.g., “can be the major source of”

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 20487, 2011.