

***Interactive comment on “Ultraviolet absorption cross sections of carbonyl sulfide isotopologues OC<sup>32</sup>S, OC<sup>33</sup>S, OC<sup>34</sup>S and O<sup>13</sup>CS: isotopic fractionation in photolysis and atmospheric implications” by S. Hattori et al.***

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Final author comments on the paper, “Ultraviolet absorption cross sections of carbonyl sulfide isotopologues OC32S, OC33S, OC34S and O13CS: isotopic fractionation in photolysis and atmospheric implications” by Hattori et al..

We have carefully reviewed and considered the reviewer’s comments and concerns. We are grateful for the valuable comments received from Anonymous Referee #1 and Dr. Ono. We agree with both their minor and specific comments.

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Response to comments from Anonymous Referee #1, I agree with the three comments and we will revise as follows.

1) Page 20497, beginning of Section 3.4:

Reply: Rephrased this to “The positions of the vibrational peaks of the heavier isotopologues (OC33S, OC34S and O13CS) were generally red-shifted relative to the most abundant species (OC32S) cf. Fig. 3. ” and deleted second sentence to avoid possible confusion.

2) The quantities Q and d in eq. (5) should be defined.

Reply: We changed the equations and no longer use “Q” which is instead explicitly defined it in eq. (5). In addition, we slightly changed this section for clarity.

3) Eq(9): “Deviation from mass-dependent fractionation is often described using ..” A reference or, even better, a short explanation would be helpful here.

Reply: We added the sentences “Non-mass-dependent fractionation is often described as deviation from mass-dependent fractionation law using eq. (9)”.

Response to comments from Dr. Ono For general comments, see below.

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.

Reply: As referee points out, the precision of absorption cross section measurements are around 2% in the average of 195-260 nm regions. However, RSDs of high ab-

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sorption region (210 to 235nm) are less than 0.5 per mil. In addition, the precision of propagated errors of the integrated absorption cross sections are sub per mil level, and thus is lower than the RSDs of the plots. Therefore, we believe absorption cross section measurements also may be used for investigating isotope effects at per mil levels, although the precisions of IRMS method is still better. We hope the reader will see that both Lin et al. and this study represent significant steps toward this ultimate goal and that the two techniques are complimentary. We added the following three sentences to the introduction between the sentences in P. 20492 Line 10 “The ultimate goal of the different approaches is the same: to investigate sulfur isotope effect on OCS photolysis. Current theoretical methods (Danielache et al., 2009), however, are not precise enough to reconstruct the weak vibrational structures and magnitude of the absorption cross section. For laboratory experiments of OCS photolysis (Lin et al., 2011), the precision of the measurement is better than other approaches but the light source does not duplicate the stratospheric actinic flux.”

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?

Reply: Thank you for valuable comments. The heading of Section 3.1 is changed to “Error budget” to describe the overall estimation of errors. We deleted “random” at P.20494 L.24. We added the duration of the experiments as follows: “One measurement took approximately 50 minutes and three to four repetitions of measurements of

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a single OCS isotopologue, carried out in a day. After evacuation of the gas line and the cell during the night, the next isotopologue measurement was carried out. The measurements for the OCS isotopologues were carried out over a continuous series of days.” Finally, we changed Fig. A1 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<sup>-1</sup>? Consider adding error bars on y-axis.

Reply: Yes, the errors in the peak position in cm<sup>-1</sup> unit are approximately 3.7 cm<sup>-1</sup> at 235 nm and 4.5 cm<sup>-1</sup> at 212 nm region. Therefore, we added 4.5 cm<sup>-1</sup> as maximum errors in Fig. 3.

> 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.

Reply: Yes, we agree that the large variation in the ZPE isotopic fractionation constant at low and high energy is due to measurement errors. However, it is hard to quantify. We think this is worth noting and therefore added following sentences in last sentence of section 3.6 P20500 L11: “It is worth noting that the large variation in the isotopic fractionation at low and high energies may be due to measurement errors occurring at regions of low absorptivity (Fig 4 and 5), but the trend of the wavelength dependence of isotopic fractionation can be seen.”

Followings are replies for minor editorial comments from Dr. Ono:

> Page 20489, Line 8: delete “more”

Reply: Corrected.

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

Reply: Corrected to “The integrated photolysis rate of each isotopologue at 20 km in

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which OCS photolysis dominantly occurs was calculated.”.

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

Reply: Added Krouse and Grinenko, 1991 here.

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

Reply: Deleted “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?

Reply: Moved this sentences to section 2.2 “Spectroscopy”. We do not expect that temperature may produce such a large effect of 50 per mil. According to Boltzmann’s equation the population of vibrationally excited states is much more sensitive to temperature than is the population of the ground state. This effect is amplified in the UV absorption spectrum because the vibrationally excited states have larger absorption intensities per molecule than does the ground state; as shown in Danielache et al. (2009) the transition dipole moment changes with molecular geometry. Hot band absorptions from the excited states are located on the low energy side of the absorption maximum; therefore the absorption on the high energy side is not a sensitive function of temperature. Therefore we do not expect significant temperature effects in the fractionation spectrum of OCS. We note that temperature causes the fractionation spectrum of nitrous oxide in the hot band region to change by about 20 per mil as temperature decreases from 288 to 233 K (von Hessberg et al. 2004); however no significant change is seen in nitrous oxide on the high energy side. A conservative estimate is that a change from surface to stratospheric. Temperature would change the fractionation by

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at most 5 per mil.

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

Reply: Added. This is very valuable comment. Thank you very much.

> 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 (?)

Reply: Corrected. S is natural abundance, we therefore calculated and consider natural abundance of isotopes (see Appendix A).

> p. 20494, line 1, can you also state resolution in cm<sup>-1</sup>?

Reply: Yes, we can but the resolution in cm<sup>-1</sup> is not constant number. We added “data were recorded at 0.02 nm (2.96 to 5.26 cm<sup>-1</sup>)”.

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

Reply: We added Section 2.3 “Notation”, and 1st paragraph of the section 3.1 is moved to section 2.2.

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

Reply: Changed.

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

Reply: Corrected.

> Page 20496, line 13, define “change”

Reply: Thank you, we have changed the text to read, “It is noteworthy that the largest changes in integrated intensity, width of absorption envelope and shift in position of vibrational structure was seen for <sup>13</sup>C...”

> I noted that mass shift for C-13 (13/12-1) and S-34 (34/32-1) is 8 and 6 percent

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respectively. Sigma-max position is identical for 34S and 13C substitution.

Reply: Yes, this is good point. It may be due to a cancellation effect from both blue-shift and red-shift, but it is hard to say clearly at this moment.

> 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.

Reply: We can use identical definition for sulfur isotopes, but cannot for carbon because of difference in denominator (see Appendix A). We corrected equation 6-7 and 11-12 using some indices.

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

Reply: In this passage we are discussing overall behavior as shown in the figures and the reader can refer to them to see precisely what "close to zero" means. We do not feel that more detail is necessary.

> Page 20502, Line 14, "calculated" -> "estimated"

Reply: We changed "calculated" in P20502 L9 to "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.

Reply: Deleted.

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

Reply: Corrected.

We would like to again thank the referees for taking time to carefully review our manuscript and thereby help improve it.

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Sincerely,

Shohei Hattori, Johan Albrecht Schmidt and Matthew Stanley Johnson

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

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