

## ***Interactive comment on “On the isotopic fingerprint exerted on carbonyl sulfide by the stratosphere” by J. A. Schmidt et al.***

**J. A. Schmidt et al.**

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Dear Editor and Referees,

We would like to thank Prof. Ono and Prof. Lyons for carefully reviewing our contribution. We are very grateful for the valuable comments and suggestions they provided which have helped us improve our manuscript. We tried to answer all the questions posted and implement all the suggested changes. Please see the detailed reply below.

We have also done a few additional changes to manuscript which are also described below.

In response to a comment by Referee #1 we wish to change the title of the paper to: “OCS photolytic isotope effects from first principles: sulfur and carbon isotopes,

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temperature dependence and implications for the stratosphere”.

We would also like to change the order in the list of authors so that Matthew S. Johnson becomes second author, i.e.: “J. A. Schmidt, M. S. Johnson, S. Hattori, N. Yoshida, S. Nanbu, and R. Schinke”.

We hope it is possible to accommodate these changes.

On behalf of all the authors:

Sincerely,

Johan Albrecht Schmidt

## 1 Detailed reply:

### 1.1 Referee #1 (S. Ono):

**Referee #1 writes:** *Title: I noted that the title is not very informative. Perhaps, the largest contribution from the work is to derive accurate temperature dependence of the isotope fractionation factor. This would help more accurate modeling. I would suggest changing the title, accordingly. This should be helpful to make contrast to the previous works by Jorgensen, Danielache, Hattori, et al.,*

**Our reply:** Thank you. We have changed to the title so it now reads: “OCS photolytic isotope effects from first principles: Sulfur and carbon isotopes, temperature dependence and implications for the stratosphere”. We believe that the new title gives a better description of the contents of the paper.

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**Referee #1 writes:** *Abstract: I would make it clear that this work is to extend previous ab-initio model approach to isotopologues.*

**Our reply:** We have changed the second sentence of the abstract so it now reads: "UV absorption cross sections for OCS, OC<sup>33</sup>S, OC<sup>34</sup>S, OC<sup>36</sup>S and O<sup>13</sup>CS are calculated using the time-depedent quantum mechanical formalism and a recently developed ab-initio model for the photodissociation of OCS which takes into account the lowest four singlet and lowest four triplet electronic states."

**Referee #1 writes:** *Line 8, Page 25340, "The 13C fractionation in the stratosphere is also negative but ... to be detected and traced using the ACE-FTS or MIPAS data sets ..." This is an excellent prediction. What is presented in Figure 5, though, is epsilon values. I am wondering if you can make a simple model including transport to estimate what you would expect for O13CS/O12CS ratios of stratospheric OCS.*

**Our reply:** This is an excellent suggestion. In fact, we currently plan on using the presented theoretical cross sections in a more sophisticated model that includes vertical transport and covers a broader range of altitudes. However, such chemical transport modeling is beyond the scope of the present study and will be presented elsewhere.

**Referee #1 writes:** *Line 11 - 22, p. 25339. Potential of MIF like feature is interesting but the number of photons b/w 205-212 nm would be very small below 20 km so that the photolysis rate is very small?*

**Our reply:** Yes that is correct, the photolysis rate at 16 km is in order of magnitude smaller than the photolysis rate at 20 km.

**Referee #1 writes:** *line 14, 25332, "very large" -> add number to compare how large*

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*it is.. line 2, p. 25337, In a strict sense, the model used empirical shifting of 200 cm-1 for A-state. It is not completely ab-initio. line 1, p. 25338, "linearity" -> linear geometry line 16, p. 25340, "marginal" -> xx permit for 34S/32S.*

**Our reply:** Concerning p. 25332: We have changed the sentence so it now reads: "The concentration profiles showed a very large  $^{34}\text{S}$  depletion in the stratosphere (down to  $-400\text{‰}$  and highly variable)". Concerning p. 25337: That is correct. Strictly speaking the model is not completely ab-initio as it includes an offset whose magnitude was determined by comparison to experiment. We have added the following sentence to p. 25337: "The magnitude of the shift was determined by comparison to experimental cross sections, and the calculations are therefore not strictly ab-initio." Concerning p. 25338: We have changed the sentence so it reads: "... becomes more localized around  $\gamma = 0^\circ$  (i.e. linear geometry) where the TDM is small ...". Concerning p. 25340: It is difficult to give a single number because the fractionation varies with wavelength and temperature.

1.2 Referee #2 (J. Lyons):

**Referee #2 writes:** *Line 127 – Justify setting quantum yields to unity. Is there any data on quantum yields in this wavelength region? Isotopic differences in yields can lead to large isotope effects, as I'm sure the authors know.*

**Our reply:** We have expanded the section so it now reads: "The yield of dissociation,  $\varphi(\lambda)$ , is set to unity which is justified by the calculations because: (i) excitation of the A and the B state (which give the main contribution to the cross section) facilitates very rapid dissociation (the dissociation lifetime is less than 100 fs) and the quantum yield is therefore unity for these states. This is also supported by experimental observations by Zhao et al. (1995) who found the yield of dissociation to be unity at 248 nm (were only the A and B state contribute). (ii) predissociation from the C and c states

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(which is responsible for the super-imposed structure in the cross section) is relatively fast. Our preliminary study of the c state predissociation mechanism indicates that spin-orbit interaction with the A state gives the c state a lifetime on the order of  $\sim 0.3$  ps which is much shorter than the fluorescence lifetime and the collisional lifetime in the atmosphere. The C state couples non-adiabatically via the kinetic energy operator with the B state (forming an avoided crossing around linearity); this type of coupling is typically stronger than spin-orbit coupling and as a result the lifetime of the C state is likely less than the c state lifetime. ". We have also added the following sentence to the abstract: "The photodissociation dynamics provide strong evidence that the photolysis quantum yield is unity at all wavelengths for atmospheric UV excitation, for all isotopologues."

**Referee #2 writes:** *Line 135 – give standard for  $^{13}\text{C}$ , presumably PDB.*

**Our reply:** Yes that is correct. We have changed the sentence so it reads: "A relative isotope ratio difference for carbon-13 ( $\delta^{13}\text{C}$ ) is defined in a similar way with Vienna Pee Dee Belemnite (VPDB) being the recommend reference. "

**Referee #2 writes:** *Line 156 – Why attribute the need for a 30% increase in cross section to inaccuracies in transition dipole moments? What is the evidence for this being the source of the error, and what can be done to improve it?*

**Our reply:** The integrated cross section (or the overall magnitude) depends only on the integrated transition dipole moments multiplied by the initial vibrational wavefunction. The quality of the vibrational wavefunctions can be gauged from the predicted vibrational energies and equilibrium geometries, which are found to be in good agreement with experimental values. It is therefore much more likely that the underestimation of the total cross section is due an underestimation of one or more of the transition dipole moments. The cross section is proportional to the square of the

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transition dipole moment. A 14% underestimation of the transition dipole moments will therefore produce a cross section that is 30% too small. Since submitting the original manuscript to ACPD we have done a deeper analysis of the transition dipole moments. We found that the inclusion of higher excited states in the ab-initio calculations is necessary, since these states perturb the transition dipole moments of the lower states, the main effect being that excitation of the B state is more intense than was initially indicated. We have constructed a new set of transition dipole functions and redone all quantum calculations. The new transition dipole function reshuffles the contribution from the different electronic states and has almost no effect on the total cross section. The new total cross section is slightly larger than the old, improving the agreement with experimental results. The new fractionation constants are very similar to those calculated with the old transition dipole functions. The biggest difference between the old and new results is seen for the carbon-13 fractionation constant at wavelengths shorter than 200 nm. The new results suggests that carbon-13 fractionation is less severe which also makes carbon-13 fractionation in the lower stratosphere less severe. The new transition dipole moments are consistent with experimentally observed angular distributions while the old transition dipole moments are not.

**Referee #2 writes:** *Line 220-224 – Please discuss the Leung et al. 2002 and Colussi et al 2004 results in more detail, and in comparison with Lin et al. 2011 and Hattori et al. 2011. Colussi et al. differs dramatically from the latter two, but are the experiments directly comparable? Do the Lin et al. 2011 and Hattori et al. 2011 results imply isotopic quantum yields that are  $\sim$  unity, thus removing concerns about differences in isotopic yields?*

**Our reply:** As we note (p. 24332, l. 19) the experiments of Lin et al. (2011) and Hattori et al. (2011) contradict the results of Colussi et al. (2004). The present work agrees with Lin and Hattori. As we have argued above, the photolysis quantum yield is very likely unity. Yes, the spectra obtained by Hattori and Colussi can be directly

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compared, available evidence strongly suggests Colussi is in error.

**Referee #2 writes:** *Table 2 – The stratospheric model is very weak. This is of course not the emphasis of the paper, but a vertical profile of expected isotopic values for OCS would be a nice addition*

**Our reply:** We are planning a more sophisticated transport model study of OCS, which will be published elsewhere. We do agree that it would be useful to extend the presented model to cover a broader range of altitudes. We have therefore updated Table 2 to include data up to an altitude of 36 km.

## 2 Additional changes:

In additions have a number smaller changes to the wording in the manuscript and added few additional sentences and references.

We have extended Figs. 4 and 5.

We have corrected a typo in Table 2: The values for  $^{13}\epsilon_{\text{OH}}$  were incorrect.

Finally we have removed point (IV) in the conclusion.

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 25329, 2012.

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