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Atmospheric Chemistry and Physics Discussions

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

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Review of Schmidt et al., "On the isotopic fingerprint exerted on carbonyl sulfide by the stratosphere"

In this paper, Schmidt et al. present UV cross sections for major sulfur and carbon isotopologues of carbonyl sulfides using first principles. The result confirms previous experimental cross section measurements by Hattori et al., and photochemical study by Lin et al., showing relatively small isotope effects resulting from UV photolysis. Given the available data for SSA and OCS isotope compositions, it is concluded that OCS can be the major source of stratospheric sulfate aerosols, which has significant effects on the radiation budget.

The study is largely based upon the previous work by the group. In two publications in Journal of Chemical Physics, the group presented theoretical cross section for OCS, and this work in ACP extend the study to isotopologues of OCS, and its implication to the stratospheric sulfur cycle. This is quite useful for ACP community because now we can make quite accurate estimate of what isotopic product of OCS photolysis would be, and then make some quantitative estimates on how much fraction OCS photolysis could contribute to SSA. The fractionation factor for sulfur is a bit small to be a distinctive signature, but for carbon isotopes it could make significant contribution to 13C/12C ratios of the remaining OCS. This is somewhat similar to the central position 15N of N2O.

My relatively minor comments are:

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.,

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

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.

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?

ACPD

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Very minor comments are:

line 14, 25332, "very large" -> add number to compare how large 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.

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