Atmos. Chem. Phys. Discuss., 11, C5929–C5932, 2011
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Atmospheric
Chemistry
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Discussions

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

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Received and published: 4 July 2011

Review of Multiple-sulfur isotope effects during photolysis of carbonyl sulfide Y. Lin, M. S. Sim and S. Ono ACPD 11, 14233 - 14258, 2011

General Comments: This paper describes laboratory experiments and their interpretation using an assumed reaction mechanism and transition state theory to derive the isotopic fractionation occurring in the UV photolysis of carbonyl sulfide. The results are very relevant to the larger goal of determining the non-volcanic source of stratospheric sulfate aerosol, and are also relevant to work with sulfur in the Archean atmosphere. While the experiments and analysis are well done there are some scientific issues described below that must be addressed prior to publication.

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Specific Comments: It is a major concern that the photolysis of S2 is not included in the model. The model starts with the photolysis of OCS: OCS + hv –> CO + S followed by S + OCS –> CO + S2 Unfortunately, there seems to be a very good chance that S2 (and Sn) could be photolysed, recycling S atoms S2 + hv –> 2S This mechanism could be the dominant process removing OCS from the experiment. The Schumann-Runge system of O2 is well known and has a peak absorption cross section of >3E-17 cmˆ2, a hundred times larger than that of OCS. Although there are no good measurements of the absorption cross section of S2, it is known that the analogous transition in O2 is shifted to the 240 to 360 nm region in S2 (e.g. Okabe). There is no way in the present experiment to tell the relative roles of the two OCS loss processes. Additional experiments should be performed to test this, for example experiments could be done in the presence of an excess of a compound that will remove S atoms from the system, and be photolysed slowly enough that it is not itself a source of S atoms. An additional issue is that the yellow polysulfur residue formed on the walls of the cell is very easily photolysed by UV light (Eckert and Steudel, 2003), providing another source of S atoms that may react with OCS. It may be useful to construct a box model of the chemistry in the reactor, using e.g. Kintecus, to determine the relative roles of OCS loss processes. Once the model includes S2 photolysis, a test could be made to see if the steady state S2 concentration is in a range that would give rise to self-shielding effects since it has a highly structured spectrum. In addition, S, S2 and Sn will _slowly_ diffuse to the walls and be lost, this should be added to the model. Note, see Billmers and Smith 1991 for absorption of S3 and S4.

14237, 2: It would be very useful to have a measurement of the spectrum of the photolysis lamp + window, so that in the future a calculation can be made of the fractionation in the experiment using isotopologue-specific cross sections. Is there such a measurement? The next best thing would be to combine the manufacturer's lamp spectrum with the absorption spectrum of the window (Figure 2A only shows the lamp).

In the experiment, millimoles of OCS are photolysed, but only micromoles of sulfur are

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recovered. Where is the missing sulfur? Please comment.

Please note that while the ZPE theory is easy to use, it is not correct. Large differences between experiment and ZPE theory are known for e.g. H2O/HDO, HCl/DCl and the N2O isotopologues and isotopomers. Perhaps it is good to within a factor of two, but it is far from exact.

14246, section 4.4: There is a simple mechanism, apart from near resonant vibronic coupling between singlet and triplet states, that can explain the mass independent fractionation seen in the CO2 photolysis experiments of Bhattacharya et al (2000). The CO2 absorption spectrum has vibrational structure and the positions of these peaks will change with isotopic substitution. Their experiment used a narrow line photolysis source, and so it is very likely that the different CO2 species in their experiment experienced different rates of photoexcitation that could easily give rise to MIF. In addition to this, there may or may not be an additional MIF in the photolysis process - we simply do not know. Instead of having the argument rest on a speculative interpretation of an experimental observation, I would suggest instead making an analogy to the photolysis of nitrous oxide. It is a good analogy because it is a linear 16 valence electron three atom molecule like OCS with roughly similar potential energy surfaces, spectroscopy and photodissociation dynamics. As shown in Schmidt et al. 2011, broad-band NNO photolysis will give mass-dependent fractionation. And, as shown in this paper, it is easy to find a narrow band photolysis wavelength that will give mass independent fractionation even when broadband photolysis does not (cf. Figure 5).

Technical Corrections: 14235, 3: Please give a reference for the photolysis quantum yield, e.g. Rudolph and Inn, 1981. 14235, 11: The two references Griffith et al., 2000 and Rahn and Wahlen, 1997 do not appear relevant here as they are concerned with N2O. In sec. 2 the authors describe their analysis procedure. Does this procedure give rise isotopic fractionation? Maybe the authors can add a line or 2 commenting on this. page 14237 line 26: The degrees sign is strange eq. 4: F_0 should be F_0(\lambda) page 14244 line 2: use "number density" instead of "concentration".

Figure 1: perhaps included the actinic flux at 10 and 20 km. Figure 2c: The y-label shoud be ˆ{34}\sigma/ˆ{32}\sigma - 1. This also applies the caption of Fig. 2. Table 3 caption: specify that the Xe lamp spectrum is used to generate the results.

References:

Billmers, R. I. and A. L. Smith, Ultraviolet-visible absorption spectra of equilibrium sulfur vapor: Molar absorptivity spectra of S3 and S4, J. Phys. Chem 95, 4242 - 4245, 1991. Eckert, B. and Steudel, R., Molecular spectra of sulfur molecules and solid sulfur allotropes, Top Curr Chem 231:31-98, 2003. Okabe, H., Photochemistry of Small Molecules, Wiley, 1978. Rudolph, R. N., and Inn, E. C. Y.: OCS Photolysis and Absorption in the 200- to 300-nm Region, J. Geophys. Res., 86, 9891-9894, 10.1029/JC086iC10p09891, 1981. Schmidt, J. A, M. S. Johnson, and R. Schinke, Isotope effects in N2O photolysis from first principles, Atmos. Chem. Phys. Discuss., 11, 16075-16105, doi:10.5194/acpd-11-16075-2011, 2011.

Sincerely, Matthew S. Johnson and J. A. Schmidt Department of Chemistry University of Copenhagen, Denmark

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