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Atmospheric Chemistry and Physics Discussions

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

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Response to Dr. Johnson:

> 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.

Reply: Thank you for your comments.

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.

Reply: Please see separate note about this concern. We have run photochemical model and show that S2 photolysis (and S3 and S4) is of very minor importance as a source of S. We do not observe any absorption bands characteristic to S2, demonstrating that S2 isotope self-shielding from S2 is highly unlikely during our experiments.

It is very difficult to assess the role of the photolysis of S deposited on the wall and window but it probably quickly recombined and deposited. Our cell design was such that cell wall was not exposed to direct UV light. I agree that the best way is to prevent S from reacting. Perhaps, adding ethylene is a good idea.

> 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).

Reply: The transmittance of the window material was measured, and corrected for the absorption. It was stated in 14245, line 4, "The photon flux (F0) for the Xe arc lamp was given by the manufacturer's datasheet and was corrected for measured transmittance for the window material".

> In the experiment, millimoles of OCS are photolysed, but only micromoles of sulfur are recovered. Where is the missing sulfur? Please comment.

Reply: The extent of the reaction for our experiments ranged from 74 % to 1 (f varied

from 0.26 to about 1 in Table 1). Elemental sulfur was recovered in umol quantity. The missing sulfur was still in a form of OCS.

>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.

Reply: The goal of the ZPE model was to compare it with our experimental result. It is interesting that the ZPE model does predict larger isotope effect for >285 nm, which was observed in the experiment. A paragraph is edited for clarification, and the subheading for 4.3 is changed to "comparison to the ZPE-shift model".

In order to compare our experimental results to available model of photolysis isotope effect, the ZPE-shift method of Miller and Yung (2000) was applied for OCS photolysis under the condition of the experiments. The ZPE-shift model is a simple and crude model. Laboratory cross section measurement for N2O, for example, demonstrates, the ZPE-shift model only qualitatively describes the effect of isotope substitution (Hessberg et al., 2004). In the later section, we discuss the comparison of our experimental results to a detailed model calculation using wavepacket dynamics for OCS photoexciation by Danielache et al. (2009).

>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).

Reply: Agreed. It, however, is beyond the scope of this paper to discuss alternative hypothesis of Bhattacharya experiment, and vibronic coupling could well be the explanation of the small apparent MIF observed in this experiment. A paragraph is added to discuss alternative hypotheses.

Other potential sources of MIF includes isotope self-shielding of the product S2 and symmetry-dependent fractionation during S+S2 recombination reaction, analogue to ozone recombination reaction. The S2 has structured and characteristic absorptions at 280 nm (Herman and Herman, 1963). However, such absorption bands were not observed during our experiments, suggesting that S2 isotope self-shielding is unlikely under our experimental condition. Thiozone (S3) reaction may produce ozone like MIF (Francisco et al., 2005) but the contribution of such reaction is unknown

Technical corrections:

>14235, 3: Please give a reference for the photolysis quantum yield, e.g. Rudolph and Inn, 1981.

Reply: A reference for the photolysis quantum yield, that is Rudolph and Inn (1981), is added.

>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.

Reply: The two references Griffith et al. (2000) and Rahn and Wahlen (1997) are

deleted.

>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.

Reply: Page 14238 line 1 stated, “Six replicated analyses of OCS yield 2σ standard deviations of 0.26, 0.53, and 1.05‰ for δ33S, δ34S, and δ36S, respectively”. This demonstrates that the overall procedure is repeatable at 0.5 ‰ for OCS analysis.

Additional comment is added at page 14239 line 4: The nice match between 34ε (and also f) calculated from yield and those from mass balance indicates that there is no isotopic fractionation involved in analytical procedure.

>Page 14237 line 26: The degrees sign is strange.

Reply: Yes, this is due to typeset.

>Eq. 4: F_0 should be F_0(\lambda).

Reply: Eq.4: F0(λ) is changed to F0(λ).

>Page 14244 line 2: use "number density" instead of "concentration".

Reply: “concentration” is changed to “number density”.

>Figure 1: perhaps included the actinic flux at 10 and 20 km.

Reply: Figure 1 (maybe he means Figure 2a), Figure 2 is revised to include actinic flux at 20 and 30 km.

>Figure 2c: The y-label shoud be ËĘ{34}\sigma/ËĘ{32}\sigma - 1. This also applies the caption of Fig. 2.

Reply: Corrected to 34σ/32σ-1.

>Table 3 caption: specify that the Xe lamp spectrum is used to generate the results.

Reply: The title of Table 3 is changed to – Isotope effect for OCS photolysis by Xe lamp

as a function of OCS pressure estimated from the ZPE-shift method.

References:

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nm region, J. Geophys. Res., 86, 9891–9894, 10.1029/JC086iC10p09891, 1981.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/11/C7651/2011/acpd-11-C7651-2011-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 14233, 2011.