**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Stable carbon isotope fractionation in the UV photolysis of CFC-11 and CFC-12" *by* A. Zuiderweg et al.

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Replies to Reviewer 1:

We thank Matthew Johnson for constructive and useful comments!

Comment 1: My main concern is that the emission spectrum of the Sb lamp is not the same as the stratospheric actinic flux spectrum. This is indicated by the observation that the photolysis rate of CFC-11 in the experiment is five times faster than that of CFC-12, while in the atmosphere the ratio of these photolysis rates is about a factor of two. As the CFC-11 absorption spectrum is shifted to longer wavelengths relative to CFC-12, this would indicate that the Sb lamp is also shifted to longer wavelengths relative to stratospheric photolysis. It is well known that isotopic fractionation is wavelength

dependent. This work shows that significant 13C enrichment exists and that it is temperature dependent, but without wavelength dependent information it is not possible to make a meaningful model of stratospheric fractionation. I advise that the discussion be extended to discuss this limitation (which will surely be addressed in future work). In addition I strongly recommend adding a figure comparing the emission spectrum of the Sb lamp with the solar UV window, together with the absorption spectra of CFC-11 and CFC-12.

Author response: The spectra of the lamp and actinic flux are indeed a valuable addition to the paper. We have added a figure (please see below as fig. 1, in revised manuscript as fig. 2) showing the normalized lamp output and actinic flux spectra at 20 and 30km (Minschwaner et al., 1993) for the UV-C region concerned. Also indicated are the upper limits of the CF_2Cl_2 and $CFCl_3$ absorption spectra in the UV region. The lamp output is indeed shifted to longer wavelengths compared to the stratospheric UV. This accounts directly for the difference in photolysis rates. However, we are unable to make an assessment as to the wavelength dependency of the fractionation that might be inherent in this reaction; this might be better addressed with the use of several lamps and/or wavelength filters in future work.

Comment 2: 33180, 20: I am curious if lamp stability may also be an issue?

Author response: Previous experiments with this same lamp to induce N_2O photolysis (Kaiser et al., 2002 and 2003) did not note instability in the lamp output; however, as this lamp is somewhat old it is possible that the power supply and/or lamp has developed intensity instability with power-on time. This would certainly explain the existence of variability in the ln(F) vs. time data, which would then not be reflected in ln(δ13C+1) vs. ln(F). We have included this discussion in the revised manuscript.

Comment 3: 33181, 11: It is not clear what the 1.5 % value represents - I cannot believe it is the quantum yield which is widely accepted to be one. If the products of photoabsorption are not two radical fragments, then what are they?? Saying that a

radical is quenched is not the same as saying it has disappeared. Quenching describes the relaxation of a hyperthermal state, such as an initially electronically, vibrationally or translationally excited radical. Quenched radicals exist. Radicals will persist until they combine with another radical giving a closed shell species, or perhaps be lost by colliding/reacting with the wall. One danger is that chlorine atoms may recombine to yield Cl_2, which would react with chlorofluoromethyl radicals reforming CFCs and a Cl atom, for example $Cl + Cl + M \rightarrow Cl_2 + M$; $CF_2Cl' + Cl_2 \rightarrow CF_2Cl_2 + Cl$. Since the question of radical fate and the extent of CFC reformation is central to the results, this issue must be resolved using a photochemical box model and included in the supplementary information.

Author response: Indeed, the quantum yield is widely accepted to be 1, and quenching is not equivalent to radical removal. This latter point has been corrected by the deletion of the passage in question. We acknowledge the risk of recombination reactions muddling the picture exists. We did some box modeling to explore the issue of recombination. In our model we calculated photo-dissociation rates using the lamp spectrum and IUPAC recommendations for the absorption cross-section for CFC-12 and Cl_2. In addition to the reactions suggested by the reviewer we assumed that CF_2Cl and Cl are lost by reactions with impurities. The problem is that reaction rate constants for many of these reactions are unknown and therefore we used upper limits for the reaction rate constants. The model results indicate that impurity levels as low as 0.4 ppb are sufficient to limit recombination to less than 5%. Therefore we conclude that recombination likely does not represent a major issue. We assume that wall reactions and reactions with gas phase impurities are responsible for removing the radicals quickly so that free Cl is at a sufficiently low level to prevent recombination from happening at a significant scale. In any case, definitive answers considering the magnitude of the isotope effect from a box model are difficult to obtain as gas phase kinetic data for the recombination reactions at relevant temperatures and pressures have not been measured to our knowledge, let alone recombination reaction 13C fractionations.

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All technical corrections have been addressed.

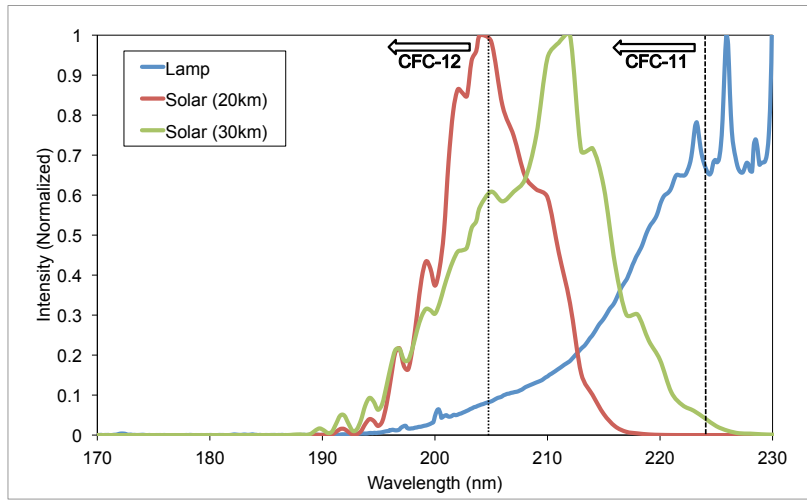Interactive comment on Atmos. Chem. Phys. Discuss., 11, 33173, 2011.

Fig. 1.

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