

## ***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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Responses to Reviewer 2:

We thank Jochen Rudolph for constructive and useful comments!

Comment 1: Specifically, the isotope fractionation is treated and discussed similarly to the kinetic isotope effect of a chemical reaction. In a formal way a photolysis rate can be described as a first order chemical reaction, using J-values instead of rate constants. However, there is a fundamental difference. J-values will heavily depend on the actinic flux intensity and spectrum and therefore vary with geographical location, time of day, season, altitude, and so on. For laboratory experiments J-values will depend on the light source used. There is effectively no information on the light source, except

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the manufacturer and that it has a continuous emission spectrum from 190-225 nm. This is vague and the information is not even sufficient to get information from the supplier since there is a wide range of very different types of Sb-lamps (what is typically called Sb-lamps are lamps used for AAS, which have a line spectrum, I assume that is not what is meant here). The authors mention that the lamp spectrum and the solar actinic flux spectrum do not match, which may explain the difference in photolysis rate ratio (CFC-11:CFC-12) between the laboratory measurements presented here and the atmosphere. Unfortunately there is no discussion of how this may impact isotope fractionation. It would be extremely useful for the reader if not only an emission spectrum for the light source, but also absorption spectra for CFC as well as typical actinic flux spectra for relevant altitudes were provided.

Author response: A figure including the spectra has indeed been added (Fig. 1, below, as fig. 2 in revised manuscript) for the lamp concerned, which was a custom built model from Heraeus. As mentioned in the response to a similar question posed by reviewer 1, the lamp is shifted to longer wavelengths and therefore accounts for the behavior we see with regards to photolysis rate differences. We do not have a means at hand for assessing the possible wavelength dependence of the fractionation, and this limitation has been mentioned in the text.

Comment 2: Some details: When looking at Figure 3, there are a few things that surprise me. First of all, the regression lines all converge to the “zero reaction time” point nearly as if they have been forced through this point. Furthermore, for some of the regression lines this one data point seems to have a substantial influence on the slope. There is not much explanation of specifics of the linear regression analysis used to derive the isotope effects.

Author response: We thank the referee for pointing out this inconsistency. In the revised version (Fig.2 below, fig. 4 in revised manuscript) we treat the pre-exposure point exactly the same way as the other points and we also do not force the fit through zero. As a result, the obtained values for the isotope fractionation and the photo-dissociation

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rate change, but the changes are small.

Comment 3: As far as I understand, the concentration (or mass) at exposure time zero was not actually measured, but calculated based on the procedure used to create the reaction mixtures. There is not much explanation let alone discussion of the uncertainty and accuracy of this process and resulting uncertainty and potential bias for isotope effects. Furthermore there is very little information about accuracy of concentration measurements. Since the concentration for the “zero exposure time” data points are determined by a methodology different from that used for the exposure experiments, combining them into one set requires an evaluation of the accuracy of both methods, not just of their reproducibility. Otherwise combining the data may create biased results. This can be avoided by excluding the “zero exposure time” data point from the regression analysis. It may increase the uncertainty of the isotope effects determined from regression, but this still would be much better than seemingly more accurate results which may be subject to bias of unknown magnitude.

Author response: We trust that these concerns no longer apply because we removed the inconsistency regarding the zero-exposure point. The CFC mixture has been prepared with an accuracy of +/- 10 %. However, all measurements were done with the same mixture and therefore we do not expect an additional uncertainty for the isotope fractionation from this.

Comment 4: Page/Line 33181/10-21: The discussion of the possible influence of recombination on loss rates and isotope effects needs more clarity. The experiments of Folcher and Braun were conducted with a CO<sub>2</sub> Laser at wavelength of 9.6  $\mu\text{m}$  and 10.6  $\mu\text{m}$ . I do not understand how these results were used to evaluate radical yields, quenching and recombination efficiency for photolysis experiments in the UV-range. UV-photolysis will yield radicals (dissociation products). Furthermore I am not sure I understand how quenching of excited states could result in loss of CFCs, which is what is measured here. The potential fate of the radicals could be radical-radical combination (including, but not necessarily limited to reformation of the reactant) or reaction

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with impurities. The Rayleigh plot will only show the net effect, its linearity therefore does not allow identifying or excluding specific processes since radical reactions will be very fast compared to the duration of the presented experiments. It also needs to be discussed to which extent a temperature dependence of radical recombination rates may affect the observed temperature dependence of the isotope effects.

Author response: The relevant section has been removed from the manuscript as the reaction setup in this work is significantly different and - as both reviewers pointed out correctly - the Folcher and Brown results do not provide evidence against potential recombination. Further, quenching does not imply removal of radicals; this has been corrected by the deletion. We acknowledge recombination of CFC-11 and CFC12 may potentially bias our observations. However, we have undertaken box modeling and found that recombination, impurity levels of 0.4 ppb are sufficient to largely suppress recombination (also see reply to comment 3, reviewer 1). Therefore we think that recombination does not constitute a significant problem. Besides making this point, we refrain from discussing temperature and other potential effects of recombination, because gas phase kinetic data for the recombination reactions at relevant temperatures and pressures have not been measured to our knowledge, let alone recombination reaction <sup>13</sup>C fractionations.

Comment 5: 33180/15: better “Photolysis rates” instead of “Reaction rates”. 33181/26: This needs more explanation. The meaning and usefulness of a sample calculation for 34 km altitude which needs to be corrected for transport may not be obvious for readers who are not familiar with the cited publications.

Author response: Noted, and has been added.

Comment 6: 33182/25: It would be very useful to provide some estimate (with caveats regarding uncertainties) at which rate the average CFC isotope ratio is expected to change. This is essential to decide which timescales need to be covered by atmospheric (including archives or ice cores) observations and what kind of accuracy and

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reproducibility needs to be achieved in the measurements.

Author response: Our paper on CFC-12  $\delta^{13}\text{C}$  depletion detected in firn air from Greenland has been submitted to ACPD that addresses exactly this point. As an example, with assumptions of an atmospheric lifetime of 100 years, an  $\varepsilon$  of  $-35\text{‰}$  and 0 mol/yr emission of CFC-12, a constant enrichment of the atmospheric reservoir due to photolysis of  $0.28\text{‰yr}$  should be expected. This paper is not yet in open discussion but should be soon.

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

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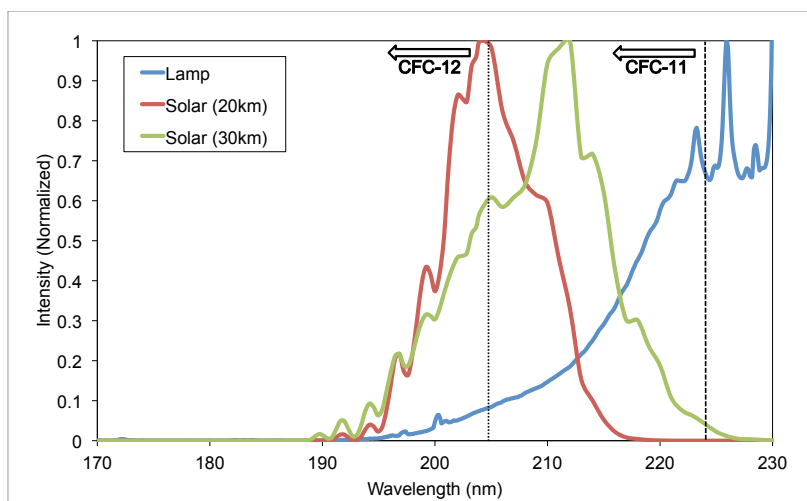


Fig. 1.

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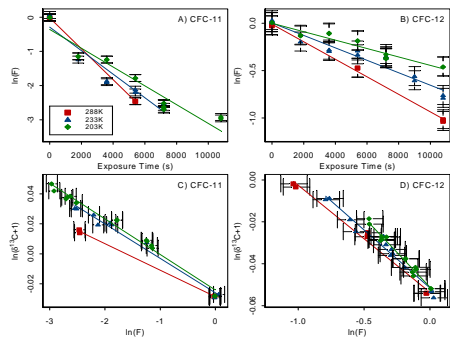


Fig. 2.

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