

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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This paper describes experiments that show a significant fractionation of carbon isotopes occurring in the UV photolysis of CCl_3F and CCl_2F_2 . This is a useful study opening up new lines of investigation and should be published after revision to address the scientific issues described below.

Scientific:

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.

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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 ^{13}C 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.

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

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 $\text{Cl} + \text{Cl} + \text{M} \rightarrow \text{Cl}_2 + \text{M}$; $\text{CF}_2\text{Cl}' + \text{Cl}_2 \rightarrow \text{CF}_2\text{Cl}_2 + \text{Cl}$. 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.

Technical:

The abstract should indicate the wavelength range (e.g. 'UVC')

33174, 2: 'The chlorofluorocarbons...are stable atmospheric compounds produced at

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the earth's surface and removed in the middle stratosphere where their photolysis liberates atomic chlorine that catalytically destroys ozone.'

33176, 1: minor issue of word choice, a molecule doesn't have a delta value but rather a fixed isotopic composition. Suggest change 'molecules' to 'species'

33180, 6: please rewrite passage '..have been rejected as interference from a neighbouring peak disturbs the peak integration,..'

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

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