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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “Abundances, emissions, and loss processes of the long-lived and potent greenhouse gas octafluorooxolane (octafluorotetrahydrofuran, *c*-C_4F_8O) in the atmosphere” *by* Martin K. Vollmer et al.

Anonymous Referee #1

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This paper presents atmospheric measurements of C4F8O along with laboratory studies of its IR spectrum and loss processes via photolysis and reaction with O(1D). The conclusion is that C4F8O is very long lived (> 3000 y) and has a GWP100 of the order of 12000.

Whereas the laboratory studies of the IR spectrum appear to be of high quality, the investigation of the UV spectrum and the reaction with O(1D) are rather disappointing. It is not clear if C4F8O absorbs in the 200-225 nm investigated (the authors do not present a Figure) and the O(1D) reaction appears to have been carried out with

a reference reactant that reacts too rapidly with O(1D) to get a good number for the rate coefficient. The most disturbing aspect is that the authors calculate that Lyman-alpha absorption may actually dominate the atmospheric loss of C4F8O, but only an unfounded guesstimate of the cross-section is made. A measurement of the VUV spectrum of C4F8O would significantly improve the laboratory studies and the manuscript as a whole. In addition, no mention is made of loss via hydrolysis (ocean) or reaction on particles. If such loss processes can indeed be neglected, the authors should provide physical constants (e.g. solubility / hydrolysis rate constants from the literature) that support this. These issues should be addressed in a revised version, as should the comments below:

Acronyms: use of acronyms is fine if it improves readability. The term ABN appears only three times in the manuscript (the first time being its definition). I would encourage use of the full name Aurora Basin North (as used in Figure 1).

P6L29 Some of the terms (A, I, L) need to be italicised as in the equation they refer to.

P6P6 Estimated accuracy of 1 %. Please state how this value is calculated.

P7L15 What was the effective spectral resolution of the MC/CCD ?

P7L24 The chemical element O should not by italicised

P8L4 Why not use the terms k1a and k2a to define the rate coefficients for reactions 1a and 2a. Also in equation (II) ?

P8L3 replace “at times t0 and t” with “at times zero and t”.

P8L11 The chemicals element (O) should not be italicised

P8L19 is the “dark” loss of C4F8O measured in the presence of O3 ?

P8L23 Figure 2 is mentioned before Figure 1. The numbering of the Figures needs adjusting.

P8L28 Equation (I) describes absorption at any discrete wavelength, ïĄň and not over a range of wavelengths as the integrated band strength is calculated.

P8L28 The uncertainty estimates need attention. How do the individual uncertainties of combine to result in 3% ? How about the 1 % uncertainty quoted previously for the dilution in He ?

P9L3 cross sectionS decreasing monotonically. . ..

P9L7 An upper limit for the absorption cross section is presented. Please add a Figure (Supp. Inf) to clarify how this value was obtained.

P9L16 The problem with this measurements of the relative rate coefficient is that while measureable amounts (up to 10 %) of CHF3 are removed, the changes in the C4F8O concentration are too low to measure reliably. Could this have been improved by a better choice of reference compound (i.e. one that reacts more slowly with O(1D) ? Why was the experiment stopped after only 10% of CHF3 was depleted ? Which absorption bands of C4F8O and CHF3 were used to derive the fractional losses ? Unless there are good arguments against, the authors should consider doing further experiments to nail down this number. Alternatively, they might consider using the correlation between ionisation potential and O(1D) rate coefficient that is frequently used to estimate the latter.

P9L24 The authors state that reaction with OH will not represent a loss of C4F8O in the atmosphere. I agree, but the authors should state why this is most likely to be the case. Will a perfluorinated furan react with OH like other fully fluorinated organics ? What upper limit to the OH-rate coefficient would be necessary for OH reaction to compete with O(1D) induced losses ?

P10L3 The authors state that is reasonable to assume a Lyman-alpha cross-section of about 1x 10-17 as it is “roughly consistent“ with highly fluorinated compounds. As the authors go on to conclude that this process has the shortest associated lifetime,

I find this unacceptably vague. What is the physical basis for assuming that a fluorinated furan will absorb at 121.6 nm with the same cross section as non-heterocyclic, perfluorinated gases ? Measurement of the cross section at this wavelength is not impossible. The NOAA lab certainly has VUV capability (e.g. for 185 nm measurements using Hg-lines) which could be extended to 121.6 nm. Surely even a rough experiment is better than a precarious assumption.

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