Replies to Review #1 for

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.
By Anonymous Referee #1 (Received and published: 16 October 2018)

Replies to the reviewer comments are added in blue color following each comment, and the revised text is in green.
We thank the reviewer for his/her input. We believe that with the suggested changes to these valuable comments, the manuscript will improve.

Reviewer Comment: 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:

Reply: We address the individual concerns below where most of them are mentioned in a more specific form. With regard to losses other than atmospheric, we refer to the replies to reviewer 2, who has commented on similar issues. Note that research on this compound is extremely sparse, e.g. we have not found reasonable peer-reviewed solubility data, to further investigate other potential sink. This is also clearly out of the scope of this study.

Reviewer Comment: 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).

Reply: We agree with this suggestion and suggest to use the full name for Aurora Basin North in the main text. However, in the supplement, the term ‘Aurora Basin North’ appears many times, consequently we suggest to use the abbreviated form (ABN) there.

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

Reply: This is now fixed, also with regard to equation II.

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

Reply: This probably refers to P7L6, not P6L6. The estimated accuracy is based on the estimated uncertainty of the pressure measurements used in the preparation of the standard gas mixtures. These include the uncertainty in the sample pressure, the total mixture pressure, and the linearity of the pressure gauge (estimated to be 0.2%). On the basis of these estimates, we report an estimated accuracy of around 1%.
We suggest to revise the sentence on P7L5 "The dilute mixtures of *c*-C_4F_8O in a He (UHP, 99.999 %) bath gas was prepared manometrically in a 12 L Pyrex bulb with an estimated accuracy of 1 %." by "The dilute mixtures of *c*-C_4F_8O in a He (UHP, 99.999 %) bath gas were prepared manometrically in a 12 L Pyrex bulb with an estimated accuracy of 1%, as derived from the accuracy of the pressure measurements. The pressure measurement uncertainty includes the uncertainty in the sample pressure, the total mixture pressure, and the linearity of the pressure gauge (estimated to be 0.2%)."

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

Reply: The resolution of the UV spectrometer was ~1 nm.
Actions Taken: P7L16, the sentence "…using a 0.5 m spectrometer equipped with a charge-coupled device (CCD) detector." will be replaced by "… using a 0.5 m spectrometer (1 nm resolution) equipped with a charge-coupled device (CCD) detector."

Reviewer Comment: P7L24 The chemical element O should not by italicised.

Reply: This is now fixed.

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

Reply: Yes, k_{1a} and k_{2a} are the reactive rate coefficients for the reaction of O(^{1}D) with *c*-C_4F_8O and CHF_3, respectively. In the Equation (II), $k_{c\text{-}C4F8O}$ and k_{CHF3} are suggested as replacements for k_{1a} and k_{2a}, respectively.

Reviewer Comment: P8L3 replace "at times t0 and t" with "at times zero and t".

Reply: Done, it now reads 'at times zero (t_0) and t.

Reviewer Comment: P8L11 The chemicals element (O) should not be italicised

Reply: This is now fixed.

Reviewer Comment: P8L19 is the "dark" loss of C4F8O measured in the presence of O3 ?

Reply: Yes, under these experimental conditions, the loss of *c*-C_4F_8O in the absence of O(^{1}D) production implies the dark loss of *c*-C_4F_8O under identical experimental conditions.
Actions Taken: The sentence "Experiments performed separately demonstrated that there was no significant loss of *c*-C_4F_8O or CHF_3 in the absence of O(^{1}D) production." will be replaced by "Experiments performed separately demonstrated that there was no significant loss of *c*-C_4F_8O or CHF_3 under identical conditions in the absence of photolysis."

Reviewer Comment: P8L23 Figure 2 is mentioned before Figure 1. The numbering of the Figures needs adjusting.
Reply: This is now fixed, first-mentioned figure (IR spectrum) is now Figure 1.

Reviewer Comment: P8L28 Equation (I) describes absorption at any discrete wavelength, ï¿Aˇn and not over a range of wavelengths as the integrated band strength is calculated.

Reply: The reviewer is correct, and the revision is suggested for P8L27 by replacing the sentence “Absorption spectra were quantified using Beer’s law” by “Absorption spectra, A(v) (base e), (or integrated band strengths) were quantified using Beer’s law”

Reviewer Comment: 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 ?

Reply: The absolute uncertainty of the total integrated band strength was based on the root mean square analysis including the estimated uncertainties of the measured absorbance (±0.5%), the optical pathlength (±0.5%) and the concentration (±1%). The uncertainty of the concentration is directly related to the pressure uncertainty where a value of ±1% has been used for the calculation. This resulted to a total uncertainty of 2.1%. We assigned a conservative uncertainty of 3%. We suggest to leave the text unaltered and not include such detail of how the estimate was derived.

Reviewer Comment: P9L3 cross sectionS decreasing monotonically

Reply: This is now fixed, the word is pluralized.

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

Reply: The following figure will be added in the Supplement. At the end of P9L4, the sentence “(An example of the measured UV spectrum of the *c*-C_4F_8O sample is shown in the Supplement)” will be added.

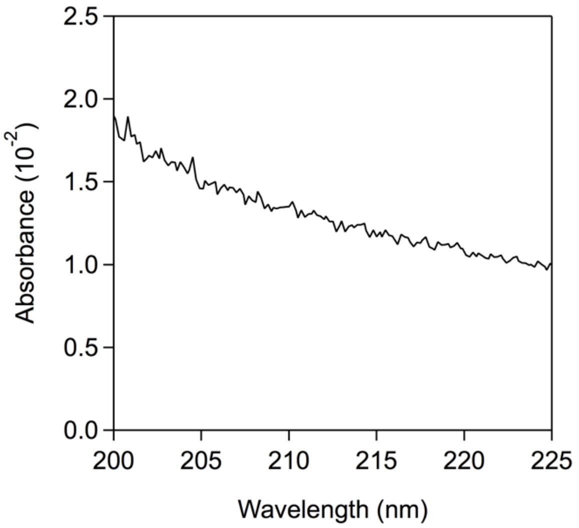

Figure S2. Measured 296 K gas-phase UV spectrum of the octafluorotetrahydrofuran (*c*-C_4F_8O) sample used in this study. The *c*-C_4F_8O concentration was 2.16□ x10^{19} molecule cm^{-3}. Assuming no absorption from possible sample impurities, the *c*-C_4F_8O absorption cross section at 210 nm was found to be 6.25 x 10^{-24} cm^2 $molecule^{-1}$. As discussed in Section 3.2, such a low cross section is susceptible to overestimation due to the presence of impurities in the *c*-C_4F_8O sample. Therefore, this spectrum was considered as an upper-limit in our lifetime analysis.

Reviewer Comment: 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.

Reply: Regarding the $O(^1D)$ reaction, presently there is not a more reliable reference compound to be used. Note that it is extremely difficult to accurately measure small $O(^1D)$ rate coefficients. It is also worth noting that an improved measure of the $O(^1D)$ reactive rate coefficient for the furan reaction would not significantly alter our conclusions regarding the atmospheric loss of the furan. In this work, a conservative upper-limit rate coefficient was reported that can be refined in the future, if warranted.

Regarding the extent of reaction: The 248 nm photolysis of ozone was used as a source of $O(^1D)$ in the photochemical reactor. The introduction of ozone to the reactor was accompanied by an addition of molecular oxygen. After multiple ozone additions, the reaction of $O(^1D)$ by O_2 can dominate the $O(^1D)$ loss, making the $O(^1D)$ + furan and $O(^1D)$ + CHF_3 reactions less significant.

Regarding the absorption bands: The absorption bands used in this study were 1120-1000 and 1180-1120 cm^{-1} for *c*-C_4F_8O and CHF_3, respectively.

Regarding further laboratory studies of the $O(^1D)$ reaction: Based on our experimental data and analysis, the $O(^1D)$ reaction will have a minor impact on the furan global atmospheric lifetime. Therefore, at our current level of understanding of the atmospheric chemistry and modeling (i.e., lifetime determination for persistent compounds) further refinement of the $O(^1D)$ rate coefficient is not warranted at this time.

The sentence "the precision of the infrared spectral subtractions are the primary sources of uncertainty in the measurements." will be replaced by "the precision of the infrared spectral subtractions are the primary sources of uncertainty in the measurements. The low conversion of the *c*-C_4F_8O and CHF_3 achieved in these experiments was primarily due to the build up of O_2 associated with the addition of ozone to the reactor, making the loss of $O(^1D)$ by reaction with O_2 more significant than its reaction with *c*-C_4F_8O and CHF_3. The absorption bands used in this study were 1120-1000 and 1180-1120 cm^{-1} for *c*-C_4F_8O and CHF_3, respectively."

P9L16, at the end of the paragraph of the Section 3.3, the sentence "Given the small $O(^1D)$ rate coefficient for the reaction between $O(^1D)$ and *c*-C_4F_8O, a refinement of the measured $O(^1D)$ reactive rate coefficient will have a negligible impact to the total atmospheric loss of *c*-C_4F_8O." is suggested to be added.

Reviewer Comment: 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?

Reply: As stated, the loss of *c*-C_4F_8O by reaction with OH radicals is most likely a negligible process. Due to laboratory challenges, it is not possible to measure values approaching 1×10^{-17} cm^3 $molecule^{-1}$ s^{-1} (equivalent to 3000 years lifetime). We estimate that our laboratory measurements would, at best, yield a rate constant upper-limit of $\sim 1 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}, which would be a gross overestimate of the true rate constant. Reporting such a rate constant would be very misleading and possibly misinterpreted by the community. We did not attempt to conduct OH reactivity measurements of this compound for these reasons. The expected low-reactivity of the furan is supported by its low O(1D) reactivity. To compete with O(1D) induced losses, the OH rate coefficient would be equivalent to >1 x 10^{-18} cm^3 $molecule^{-1}$ s^{-1}.

Actions Taken: P9L22, the sentence "The loss of *c*-C_4F_8O via reaction with the OH radical is assumed to make a negligible contribution to the global lifetime and consequently we ignore the last term in Equation 4." is planned to be replaced by "The loss of c-C_4F_8O via the reaction with the OH radical is assumed to make a negligible contribution to the global lifetime in our analysis. the OH rate coefficient would need to be ~1 x 10^{-17} cm^3 $molecule^{-1}$ s^{-1} (equivalent to a 3000 year lifetime) to make a significant global lifetime contribution. Such a low rate coefficient represents a significant challenge to current rate coefficient measurement methods. Additionally, an expected OH low-reactivity of the furan is supported by its low $O(^1D)$ reactivity measured in this work. Additional laboratory studies that are beyond the scope of the present work would be needed to quantify the OH reaction."

Reviewer Comment: 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.

Reply: The Lyman-alpha absorption cross section was not measured as part of the present study. We are implying that it should be measured in future studies, which would refine our analysis. In the absence of experimental data, we surveyed available cross section data for highly fluorinated compounds and found that a cross section of 1 x 10^{-17} cm^2 $molecule^{-1}$ would represent a reasonable cross section upper-limit. Using this cross section value in our lifetime analysis provides a Lyman-alpha photolysis lifetime of ~4500 years. Assuming a smaller or greater cross section would yield slightly longer or shorter lifetimes, although the relationship is not linear due to the dependence on the transport time to the mesosphere. Therefore, in the absence of experimental data, we believe our assumed cross section and lifetime is reasonable. Laboratory studies to measure VUV cross sections would help refine our analysis but not alter the primary conclusion from this work that the atmospheric lifetime of the furan is extremely long. Note that measuring VUV spectra in the laboratory is significantly different than measuring 185 nm cross sections and requires specialized equipment.

Actions Taken: P10L2, the sentences "It is reasonable to assume a Lyman-α cross section of 10^{-17} cm^2 $molecule^{-1}$ for *c*-C_4F_8O which would be roughly consistent with values for highly fluorinated compounds (SPARC, 2013). The estimated lifetime due to Lyman-□α photolysis, $\tau_{Lyman-\alpha}$, is then ~ 4500 years (a smaller Lyman-α cross section would lead to a longer lifetime)." will be replaced by "The scope of the present study did not include a measurement of the Lyman-α cross section. It is however reasonable to assume a Lyman-α cross section of 10^{-17} cm^2 $molecule^{-1}$ for *c*-C_4F_8O which is in the range of values for highly fluorinated compounds, (0.035 - 10) x 10^{-17} cm^2 $molecule^{-1}$ (SPARC, 2013). Therefore, in the absence of experimental data, we consider the Lyman-α cross section, 1x10^{-17} cm^2 $molecule^{-1}$, used in our lifetime analysis as a reasonable estimate. Note that a smaller (larger) Lyman-α cross section would lead to a longer (shorter) photolysis lifetime, although the lifetime dependence on the cross section value is not linear due to the lifetime dependence on the transport time to the mesosphere."