We thank the referees for their valuable time spent in reviewing our manuscript and the constructive comments. We will address each of these comments in the revised manuscript as outlined in detail below. Note that the revisions to the manuscript do not alter the results from the laboratory studies or the overall conclusions of this work.

In addition to the referee comments it was pointed out to us off-line that the NF_3 atmospheric abundance given in our Table 1, as taken from WMO (2011), is in error. We have revised the value and added a reference to Arnold et al. (2012), which reports the corrected abundance. In addition, we have added the year of the observations, which is an important consideration, that was overlooked in our original manuscript.

The referee comments are repeated here along with our response and actions taken.

Reviewer #1: (Dr. T J Dillon)
Specific comments
(1) Section 2.1, regarding the use of 248 nm laser photolysis throughout. Do any of the reactant molecules absorb photons at this wavelength?

Response: NF_3, N_2O, and CF_3Cl have weak UV absorption at 248 nm, while the other compounds can be considered non-absorbing at this wavelength. As part of this work, background experiments were performed for each compound to verify that photolytic losses were negligible, <0.4% (see page 7, line 25).

Action: The following text was added to page 7 "NF_3, N_2O, and CF_3Cl have weak absorption at 248 nm, while the other reactants have no reported absorption at 248 nm (Sander et al., 2011)."

(2) Section 2.2. On page 24020 the description of k_rise is a little confusing; it reads as if reaction 11 is O(1D) + O3, and therefore as if reaction with butane is not important. It may be better to state that k_rise is dominated by reaction 11 (with butane), with a small contribution from reaction 12 (with O3). The importance of the butane reaction is easy to overlook as in Figure 1 the y-axis plots k_rise – k_0. Were the measurements of k_0 consistent with [butane] and literature k-values for O(1D) + butane?

Response: The equation numbering in the text was revised and instead of quoting the reaction number an explicit reference to "the n-butane reaction" is now used in the text. Measurements of the rate coefficient for the O(1D) + n-butane reaction were performed and found to be consistent with literature values as given on page 10-11.

Action: The following text was added to the description of the OH profile on page 10 "k'_{Rise} is determined by the total loss of $O(^1D)$, which <u>includes significant reaction</u> with *n*-butane, reaction with O_3 ..."

(3) Section 3.1, results for O(1D) + NF3. The value obtained is stated in the text & table 2 to be (2.55 +/- 0.2)x10-11 cm3 molecule-1 s-1, whereas in table 3 this is listed as (2.55 +/- 0.38)x10-11 cm3 molecule-1 s-1. Does the inclusion of systematic error estimates account for this discrepancy? Please clarify in the text (perhaps in section 3.5). As stated in the text, there is reasonable agreement between the three recent determinations of k_total (2.0, 2.35 & 2.55 x10-11 cm3 molecule-1 s-1); all are significantly larger than the first determination from Sorokin et al.

Response: Yes, the greater value is due to including estimated systematic error. Footnote a in Table 3 states that the values quoted in the table include estimated systematic errors.

Action: None

The relative rate determinations of k from this work (all around 2.2x10-11 cm3 molecule-1 s-1) also fall within this range of recently reported k-values. Since the relative rate results are only sensitive to reactive product channels, it seems to me that the results from this work underpin the conclusions of both Zhao et al. and Dillon et al., who both report a near-unity yield of reactive products. This result is particularly robust since all used very different methods to probe the product distribution.

Response: Yes, there is a high level of agreement among the available kinetic data for the $O(^1D) + NF_3$ reaction.

The final paragraph of section 3.1 is therefore slightly misleading, emphasising differences between the reactive product yield reported here (0.87 +/- 0.13) and that from Zhao (0.99). First, there is no great difference given the reported uncertainties. Second, use of only the k-total value from this work (the largest reported) to calculate product yields may skew the data. Perhaps it would be more sensible to use an average of the three recent k_total values (= 2.3x10-11 cm3 molecule-1 s-1) to calculate a yield of reactive products from the relative rate data in this work (2.21 / 2.3 = 0.96).

The only reason to rely solely upon the k_total from this work would be if systematic errors present in both the absolute and relative-rate determinations were to cancel-out. This does not appear to be the case. The apparent agreement between the product yield calculated in this work, and that of Sorokin offers false reassurance, as it was subsequently demonstrated that the FO monitored by Sorokin is not a primary product of O(1D) + NF3 (see Dillon et al., 2011).

Response: This comment raises an important point regarding comparing the present work with previous studies that needs further clarification in the revised manuscript. In our paper, we have quoted the reactive yield that would be calculated using our experimental measurements of k(Total) and k(Reactive). The reactive yields reported in Table 3 for each study are the values that would be obtained using their reported values of k(Total) and k(Reactive) were possible. What we need to clarify, however, is that it is the reactive rate coefficient that is the critically important result from this work, not the reactive yield. That is, it is the reactive rate coefficient, which was directly measured in our work, that determines the compounds atmospheric lifetime. So taking an average of the previously reported values is not necessary and in itself somewhat misleading.

Action: The text on page 12 has been revised to clarify this issue: “The available literature data for the $O(^1D) + NF_3$ reaction is summarized in Table 3. The reactive branching ratios determined in the various studies are included in Table 3 for comparison purposes. The present work and the previous studies clearly indicate that the reaction has a high reactive branching yield. Using the data obtained in our work gives a reactive branching ratio of 0.87 ± 0.13, while the Sorokin et al. (1998) study reports 0.83 ± 0.25 and Zhao et al. (2010) reports 0.99 +0.01/-0.04. Note that the reactive rate coefficient reported in this work is independent of the total rate coefficient and should be used in atmospheric model calculations, while a calculated reactive branching ratio would be dependent on the value chosen for total rate coefficient.”. The discussion of reactive branching ratio values in the conclusions section of our original manuscript has been removed to avoid unnecessary confusion.

(4) Section 3.6. I strongly suggest you mention the new measurements of IR band strengths for NF3 in the abstract. Otherwise this important result may get lost when future calculations of lifetime, GWP etc. are conducted.

Response: Agreed.

Action: The following was added to the end of the abstract “As part of this work, infrared absorption bands strengths for NF_3 and SF_5CF_3 were measured and found to be in good agreement with recently reported values.”

(5) In section 4, conclusions, regarding the O(1D) + perfluorocarbons it is stated that "The improved upper-limit reactive rate coefficients result in longer calculated atmospheric lifetimes and greater global warming potentials for these persistent greenhouse gases (WMO, 2011) than those obtained using the currently recommended rate coefficient data (Sander et al., 2011)." Could you try to quantify this statement? If reaction with O(1D) is the principal loss process for these compounds then any change in k will impact on lifetime calculations. Calculated lifetimes and GWPs for these compounds must surely be more dependent upon VUV photolysis rates than any upper-limits for O(1D) reaction rates.

Response: We have made a generally true, but qualitative statement in the conclusions. As the O(1D) rate coefficient upper-limits decrease, as established in this work, other loss process will contribute more to the compounds atmospheric loss. O(1D) reactive loss is not expected to be the principal loss process for these compounds. Quantifying the relative significance of the relative atmospheric loss processes, including VUV photolysis, requires the use 2D or 3D models that accurately account for stratospheric transport and circulation, which is beyond the scope of this study. We do, however, recommend in our conclusion section that the kinetic data presented in this work be used in future model calculations.

Action: None

Reviewer #2: (Dr. M S Johnson)

Scientific comments:

(1)+(2) The infrared reference spectra will be valuable to other workers in the field and should be published, perhaps as supplementary data files and/or in an archive such as the Eurochamp database of IR spectra from reaction chamber experiments, http://euphore.es/FTIRReferences2/ (All gases, but in particular NF3.) A better description of the infrared fitting should be given. On page 5 section 2.1 please provide more information, e.g. model and resolution of spectrometer. What was the absorption path length? What spectral windows were used for each compound? Are there problems with overlapping absorptions in the bands used for fits? On page 9 one reads that concentrations were measured 'online'. How was the fitting done and what were the errors on the fit? It is very likely that these compounds have overlapping absorptions and these correlations could result in errors. If fits were made in regions of absorption by atmospheric CO2 or H2O (was it a vacuum instrument?), this could introduce error. If fits were done in regions with overlapping O3 absorption, and [O3] changes during the course of an experiment, this could bias the results. I would like the authors to include a figure showing the experimental infrared data, the synthetic fit and the residual for a complex reaction mixture towards the end of an experimental series. This will allow the reader to see if there are species e.g. reaction products, that are not fit effectively, that remain in the residual and influence the fitting function. What detector was used in the infrared spectrometer and is it linear? Is there non-Lambert-Beer behavior?

Response: (a) Details of FTIR measurements (resolution, path length etc.) are provided in page 6, line 26-28. The fact that KBr windows were used has been added to the text. Isolated bands were used in almost all cases and spectral interference was negligible. We have put together a table and figures that give the bands (wavenumber regions) used in the data analysis and show the infrared spectra for each compound. This material will be included in a supplement file. Spectra were not "fit", but the band integrated areas measured and used to determine concentrations. Beer's law was tested and obeyed for NF_3 and SF_5CF_3 as stated on page 17.

Action: A supplementary file will be submitted with the revised manuscript. The following text has been add to page 6: “A summary of the infrared spectra for the compounds included in this study is given in the Supplementary Material.”.

(3) The pressure changes significantly during the course of an experiment. Does this change the experimental spectra relative to the presumably low pressure reference spectra via pressure broadening - is this effect seen in the residual?

Response: Pressure broadening was not a factor over the pressure range ~180 to 500 Torr He for all the compounds except N_2O. As a result, experiments with N_2O were also performed at higher pressures, 500 and 600 Torr, as a test of possible systematic error as stated in the text on page 7. None were found.

Action: None

(4) There is good logic in measuring the reaction rate of CHF3 accurately and then using this as the standard for further rate determinations. However, uniquely amont the 7 species studied, this one molecule is vulnerable to attack by the OH radical. Therefore I would like additional information concerning the error that OH radical reaction may introduce. First of all, what is the background concentration of H2O in the reactor, based on the FTIR data? All systems will have some water. This work obtains a slightly faster CHF3 reaction rate than the previous study by Force and Wiesenfeld. Could this be due to OH in the system? One argument is given regarding the rate of reaction of OH with O3 vs. OH with CHF3 (page 16), but a better approach would be to use a box model, incorporating H2O and CHF3 concentrations to calculate the rate of production of OH and its concentration, and the fraction of CHF3 lost to OH vs O1D.

Response: **(a)** No direct measurement of the background H_2O impurity level was possible using the FTIR measurements. On the basis of an estimated H_2O concentration alone, a box model calculation would not necessarily provide a definitive result. However, under the conditions of our experiments, OH, if formed at all, would predominately react with the O_3 present in the system as described on page 16. The sensitivity to the possibility of OH formation and its contribution to loss of CHF_3 was tested, as noted in the text, by measurements of the rate coefficients with variations in the O_3 concentration, which would alter the relative efficiency of OH radical savaging between O_3 and CHF_3. The rate coefficients were found to be independent over the range in O_3 concentrations used (a factor of 2 variation). **(b)** The Force and Wiesenfeld reported rate coefficient is highly uncertain, ±70% (see Table 3), so a comparison of the presently measured rate coefficient, ±15%, is not necessarily meaningful, although the reported absolute values agree well within the reported uncertainty limits (the reported values differ by 20%).

Action: None

(5) The experiments were carried out at ’room temperature’, ’296 K’, and the error in this is ’<1%’. Was the temperature of the reaction cell measured directly (if so then please state how), and what was the variance, or was the temperature taken from the room’s thermostat? Did the teflon membrane pump (and photolysis laser) heat the sample during the course of an experiment?

Response: The gas temperature in the reactor was measured using a thermocouple in direct contact with the reaction mixture. The estimated uncertainty in the temperature reflects the day-to-day variations in the ambient temperature of the room. The reactions studied have weak, if any, dependence on temperature, so this level of uncertainty in the temperature is inconsequential. The gas temperature was unaffected by the photolysis laser or operation of the circulating pump.

Action: The text in the experimental section on page 10 has been revised to "All measurements were performed at ~296 K with temperatures measured using a thermocouple in direct contact with the reactors gas mixture."

(6) Are any of the compounds known to absorb at 248 nm?

Response: NF_3, CF_3Cl, and N_2O have weak UV absorption at 248 nm, while the other compounds can be considered non-absorbing at this wavelength. As part of this work, background experiments were performed for each compound to verify that photolytic losses were negligible, <0.4% (see page 7, line 25).

Action: The following text was added to page 7 "NF_3, N_2O, and CF_3Cl have weak absorption at 248 nm, while the other reactants have no reported absorption at 248 nm (Sander et al., 2011)."

(7) It is interesting that a series of compounds were used as references to determine the CHF3 reaction rate. Please list each of these determinations individually - it may help identify outliers which could be the subject of subsequent studies.

Response: In our CHF_3 measurements, NF_3 was used as the sole reference compound as reported in Table 2.

Action: None

Technical comments:

Page 5, 4th line from bottom, something is redundant in 'reactant reactive'?

Deleted "reactant"

Page 6, first line, change 'where' to 'were'

Corrected

Page 7, sentence just above section 2.2, it is unclear if the NF3/N2O experiment was done as a blank (no O3), or as a regular experiment.

This was a regular experiment. Text revised to "In addition, NF3 rate coefficient measurements with N2O as the reference compound were performed…"

page 10, 7 lines from end, remove 'the' in 'P2O5 traps as used in 'the our SF5CF3 measurements.'

Done

References:

Burks et al., check O term symbol, extra '2'.

The "2" is correct.

Ivy et al., spelling of 'histories'

Corrected

Zhao et al., change 'O(3P)' to 'O(1D)'.

Corrected