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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Rate coefficients for the reaction of $O(^1D)$ with the atmospherically long-lived greenhouse gases NF_3, SF_5CF_3, CHF_3, C_2F_6, c-C_4F_8, n-C_5F_{12}, and n-C_6F_{14}" *by* M. Baasandorj et al.

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This is a comprehensive study of an important set of atmospheric molecules that is a valuable contribution to the field. I recommend publication after addressing some minor questions and technical points listed below. The paper is very well written, it is a pleasure to read. The figures and tables are excellent as are the construction and the references. The many things that are done well in this paper are not commented below.

Scientific comments:

1. 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.)

2. 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?

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?

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.

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?

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

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.

Technical comments:

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

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

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.

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

References:

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

Ivy et al., spelling of 'histories'

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

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 24011, 2012.