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# Atmospheric lifetimes and global warming potentials of atmospherically persistent $N(C_xF_{2x+1})$ , $x = 2-4$ , perfluoroamines

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2 **Atmospheric lifetimes and global warming potentials of**  
3 **atmospherically persistent  $N(C_xF_{2x+1})_3$ ,  $x = 2-4$ , perfluoroamines**  
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6

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31 **Abstract**

32 Laboratory studies of the gas-phase O(<sup>1</sup>D) reaction and UV photolysis for N(C<sub>x</sub>F<sub>2x+1</sub>)<sub>3</sub>,  
33 x=2–4) and an evaluation of their atmospheric lifetimes and global warming potentials (GWPs)  
34 is reported. The O(<sup>1</sup>D) + PFA reactive rate coefficient was measured to be (10<sup>-12</sup> cm<sup>3</sup>molecule<sup>-1</sup>  
35 s<sup>-1</sup>) 1.10±0.10, 1.36±0.10, and 1.69±0.11 and the UV photodissociation yield, σ(λ) × Φ(λ), at  
36 193 nm was measured to be (10<sup>-23</sup> cm<sup>2</sup>molecule<sup>-1</sup>) 1.37, <1, <15 for N(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>, N(C<sub>3</sub>F<sub>7</sub>)<sub>3</sub>, and  
37 N(C<sub>4</sub>F<sub>9</sub>)<sub>3</sub>, respectively. Including estimated Lyman-α photolysis leads to total global  
38 atmospheric lifetimes of >3,000 years. GWPs on the 100-year time-horizon are estimated to be  
39 9900, 8700, and 7800 for N(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>, N(C<sub>3</sub>F<sub>7</sub>)<sub>3</sub>, and N(C<sub>4</sub>F<sub>9</sub>)<sub>3</sub>, respectively.

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42 **Keywords:** Perfluoroamine, UV absorption spectrum, O(<sup>1</sup>D) kinetics, atmospheric model,  
43 atmospheric lifetime

44

## 45 **1. Introduction**

46  $N(C_xF_{2x+1})_3$ , perfluoroalkylamines (PFAs), are thermally and chemically stable semi-  
47 volatile compounds used in the electronics industry and heat transfer applications. Their  
48 industrial use may lead to their direct release into the atmosphere. There is currently very  
49 limited data for the atmospheric sources, distribution, and abundance of PFAs. Tropospheric  
50 measurements of  $N(C_4F_9)_3$  have been reported for urban Toronto, Canada with a mixing ratio of  
51  $\sim 0.18$  ppt [1]. The NILU-Norwegian Institute for Air Research reported a 0.55 ppq abundance  
52 of  $N(C_4F_9)_3$  in air samples at the Zeppelin station, Ny-Ålesund, Svalbard, Norway ( $79^\circ N$ ,  $12^\circ E$ )  
53 [2]. The detection of other PFAs in the atmosphere has not been reported to date. Previous  
54 laboratory studies, including work from this laboratory, have shown that PFAs are potent  
55 greenhouse gases due to their strong infrared absorption in the atmospheric window region  
56 [1,3,4]. PFAs are expected to be atmospherically persistent compounds and, therefore, have  
57 exceptionally large global warming potentials (GWPs) and, thus, their environmental and  
58 climate impacts need to be evaluated [5].

59 A comprehensive evaluation of the environmental impact of PFAs necessitates  
60 fundamental laboratory studies of their chemical and photochemical properties. To date, there  
61 are no laboratory measurements of the atmospheric removal processes for PFAs available in the  
62 literature. In general, quantifying the atmospheric loss processes for an atmospherically  
63 persistent compound is challenging due to their low reactivity with atmospheric oxidants, e.g.  
64 OH, Cl,  $NO_3$ , and  $O_3$ , and their weak absorption in the ultra-violet region of the spectrum. In  
65 their work, Hong et al.[1] assumed the global lifetime for  $N(C_4F_9)_3$  to be 500 years, based on  
66 similar kinetic and photochemical parameters to that of  $NF_3$  [6].

67 In this study, the UV photodissociation and  $O(^1D)$  reaction rate coefficient, the most  
68 likely stratospheric loss processes, for  $N(C_2F_5)_3$ ,  $N(C_3F_7)_3$ , and  $N(C_4F_9)_3$  were measured and the  
69 OH reaction rate coefficient estimated. The experimental results from this study were used to  
70 evaluate their partial and total global atmospheric lifetimes and global warming potential (GWP)  
71 using 2-D atmospheric model calculations and the radiative efficiencies determined in a previous  
72 study from this laboratory [3].

## 73 **2. Experimental Details and Methods**

74 In this study, experiments were performed to: (1) evaluate the UV absorption spectrum  
75 and 193 nm photodissociation of  $N(C_2F_5)_3$ ,  $N(C_3F_7)_3$ , and  $N(C_4F_9)_3$ , (2) measure the room

76 temperature reactive rate coefficients for the  $O(^1D) + N(C_2F_5)_3$ ,  $N(C_3F_7)_3$ , and  $N(C_4F_9)_3$   
77 reactions, and (3) estimate rate coefficients for the  $OH + N(C_2F_5)_3$ ,  $N(C_3F_7)_3$ , and  $N(C_4F_9)_3$   
78 reactions. The experimental setups and methods used for these measurements and estimates are  
79 described separately below.

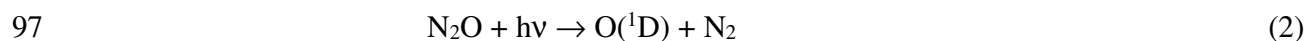
## 80 **2.1 UV Absorption Spectrum and Photodissociation**

81 The gas-phase UV absorption spectra of  $N(C_2F_5)_3$ ,  $N(C_3F_7)_3$ , and  $N(C_4F_9)_3$  were  
82 measured between 195 and 350 nm using a 0.5 m spectrograph equipped with a CCD detector.  
83 Absorption spectra were measured using a 95 cm Pyrex absorption cell with quartz windows and  
84 a 30 W  $D_2$  lamp light source. Perfluoroamine spectra were measured under static and gas flow  
85 conditions. The PFA samples were added to the absorption cell from either the head space of the  
86 liquid sample or from a dilute gas mixture that was prepared off-line. The PFA concentration in  
87 the absorption cell was determined from the measured absorption cell pressure and the ideal gas  
88 law. An absorption contribution to the measured spectra from minor PFA sample impurities,  
89 however, limited the quantitative determination of PFA absorption spectra.

90 The photodissociation yields of the PFAs,  $\sigma(\lambda) \times \Phi(\lambda)$ , where  $\sigma(\lambda)$  is the PFA  
91 absorption cross section at wavelength  $\lambda$  and  $\Phi$  is the photolysis quantum yield for loss of the  
92 PFA at that wavelength, were measured at 294 K using an actinometry method. The  
93 photodissociation yield of the PFAs was measured at 193 nm using pulsed laser photolysis (ArF  
94 excimer laser) of static PFA/ $N_2O$ / $N_2$  gas mixtures:



96 The PFA photolysis loss rate was measured relative to the photolytic loss of  $N_2O$ :



98 In the presence of a large excess of  $N_2$ , the  $O(^1D)$  produced in reaction 2 was rapidly quenched to  
99 its ground state:



101 This relative approach to determine the photodissociation of the PFAs has the advantage that UV  
102 absorption by sample impurities, which were a major interference in the UV absorption spectrum  
103 measurement, do not interfere with this measurement. Therefore, this approach provides an  
104 unequivocal measurement of PFA loss due to UV photolysis at 193 nm.

105 The photolysis beam passed through the quartz windows of the  $\sim 500 \text{ cm}^3$  reactor  
106 perpendicular to a set of multi-pass White optics, 125 cm path length, coupled to a Fourier  
107 transform infrared spectrometer. A retro reflector outside the exit window enabled a return of

108 the photolysis beam through the reactor. The overlap of the photolysis beam with the volume of  
 109 the reactor was relatively small, ~2.4% of the total volume. The reactor was filled with the PFA  
 110 and N<sub>2</sub>O and pressurized to ~600 Torr with N<sub>2</sub> bath gas. Infrared spectra were recorded in 200–  
 111 1500 co-adds at a spectral resolution of 1 cm<sup>-1</sup>. The PFA and N<sub>2</sub>O concentrations and their  
 112 change in concentration with photolysis were measured by infrared absorption during photolysis.  
 113 The initial PFA concentration was between  $1.2 \times 10^{15}$  and  $3.8 \times 10^{15}$  molecule cm<sup>-3</sup> and the  
 114 initial N<sub>2</sub>O concentration was  $\sim 9 \times 10^{16}$  molecule cm<sup>-3</sup>.

115 The concentration of PFA remaining after  $n$  laser pulses is given by:

$$116 \quad [\text{PFA}]_n = [\text{PFA}]_0 \times (1 - \sigma_{\text{PFA}}(193 \text{ nm}) \times \Phi_{\text{PFA}}(193 \text{ nm}) \times F)^n \quad (4)$$

117 where  $[\text{PFA}]_0$  is the initial PFA concentration,  $[\text{PFA}]_n$  is the PFA concentration after  $n$  pulses  
 118 and  $F$  is the photolysis laser fluence. The photolysis laser was operated at 20–30 Hz at a fluence  
 119 of  $\sim 20$  mJ cm<sup>-2</sup> pulse<sup>-1</sup> as measured with a power meter mounted after the reactor. A similar  
 120 equation can be written for the N<sub>2</sub>O loss. The photochemical conversion of PFA per laser pulse  
 121 was small and equation (4) is approximated by:

$$122 \quad \ln\left(\frac{[\text{PFA}]_0}{[\text{PFA}]_n}\right) = n_{\text{PFA}} \times \sigma_{\text{PFA}}(193 \text{ nm}) \times \Phi_{\text{PFA}}(193 \text{ nm}) \times F \quad (5)$$

123 The PFA photolysis yield was calculated using the relationship:

$$124 \quad \sigma_{\text{PFA}}(193 \text{ nm}) \times \Phi_{\text{PFA}}(193 \text{ nm}) = \sigma_{\text{N}_2\text{O}}(193 \text{ nm}) \times \Phi_{\text{N}_2\text{O}}(193 \text{ nm}) \times \frac{n_{\text{N}_2\text{O}} \ln([\text{PFA}]_0/[\text{PFA}]_n)}{n_{\text{PFA}} \ln([\text{N}_2\text{O}]_0/[\text{N}_2\text{O}]_n)} \quad (6)$$

125 where the N<sub>2</sub>O quantum yield at 193 nm is unity and its absorption cross section at 193 nm is  
 126  $8.95 \times 10^{-20}$  cm<sup>2</sup> molecule<sup>-1</sup> [7].

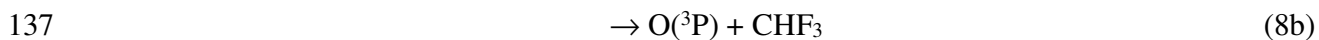
## 127 2.2 O(<sup>1</sup>D) Reactive Rate Coefficient

128 Rate coefficients for the O(<sup>1</sup>D) + PFA reaction were measured at room temperature (294  
 129 K) using a relative rate technique. The experimental setup and methods have been used  
 130 previously in this laboratory and only a brief description is given below [8,9].

131 The relative rate approach used in this work measures the rate coefficient for the reactive  
 132 channel for the O(<sup>1</sup>D) reaction, i.e., PFA loss, reaction 7a:



135 Rate coefficients were measured with O(<sup>1</sup>D) + CHF<sub>3</sub> as the reference reaction:



138 where the recommended total rate coefficient for reaction 8 is  $(9.60 \pm 0.48) \times 10^{-12} \text{ cm}^3$   
 139  $\text{molecule}^{-1} \text{ s}^{-1}$ , i.e., for the loss of O(<sup>1</sup>D) [7]. The reactive rate coefficient,  $k_{8a}$ , is  $2.4 \times 10^{-12} \text{ cm}^3$   
 140  $\text{molecule}^{-1} \text{ s}^{-1}$  [7]. Assuming that the PFA and CHF<sub>3</sub> are removed solely by reaction with O(<sup>1</sup>D),  
 141 the PFA and CHF<sub>3</sub> rate coefficients are related by the expression:

$$142 \quad \ln \left( \frac{[\text{PFA}]_0}{[\text{PFA}]_t} \right) = \frac{k_{\text{PFA}}}{k_{\text{CHF}_3}} \left[ \ln \left( \frac{[\text{CHF}_3]_0}{[\text{CHF}_3]_t} \right) \right] \quad (9)$$

143 where [PFA]<sub>0</sub>, [CHF<sub>3</sub>]<sub>0</sub>, [PFA]<sub>t</sub> and [CHF<sub>3</sub>]<sub>t</sub> are the concentrations of the PFA and CHF<sub>3</sub>  
 144 compound at times  $t_0$  and  $t$ , respectively.

145 The experimental apparatus consisted of a 100 cm long (5 cm i.d.) Pyrex photoreactor.  
 146 O(<sup>1</sup>D) radicals were produced by 248 nm pulsed laser photolysis (KrF excimer laser, 10 or 50  
 147 Hz) of O<sub>3</sub> along the length of the photoreactor:



150 where the O(<sup>1</sup>D) yield is 0.9 [7]. The initial PFA concentration was in the range  $(3.0\text{--}4.1) \times 10^{14}$   
 151  $\text{molecule cm}^{-3}$ , while the CHF<sub>3</sub> initial concentration was  $\sim 4.5 \times 10^{14} \text{ molecule cm}^{-3}$ . The  
 152 photolysis laser fluence was in the range 1.4–1.7 mJ cm<sup>-2</sup> pulse<sup>-1</sup>.

153 The PFA and CHF<sub>3</sub> loss was monitored by infrared absorption. The photoreactor was  
 154 coupled to a multi-pass absorption cell (KBr windows, 485 cm path length) of a Fourier  
 155 transform infrared (FTIR) spectrometer equipped with a liquid nitrogen cooled HgCdTe (MCT)  
 156 semiconductor detector. The gas mixture was circulated between the photoreactor and the multi-  
 157 pass absorption cell by a 12 L min<sup>-1</sup> Teflon diaphragm pump. Infrared spectra were recorded in  
 158 100 co-adds between 500 and 4000 cm<sup>-1</sup> at 1 cm<sup>-1</sup> resolution.

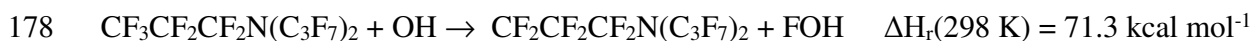
159 Kinetic measurements were performed by first adding the PFA and CHF<sub>3</sub> to the system  
 160 and then adding He bath gas to increase the total pressure to  $\sim 300$  Torr. After the gas mixture  
 161 was thoroughly mixed, as determined by infrared absorption, a  $t = 0$  infrared spectrum was  
 162 recorded. O<sub>3</sub>, in a He bath gas, was then added slowly to the photoreactor with the photolysis  
 163 laser and gas circulation on. Infrared spectra were recorded until the change in the PFA and  
 164 CHF<sub>3</sub> concentration ceased to decrease significantly, primarily due to the buildup of O<sub>2</sub> in the  
 165 system.

### 166 **2.3 Computational Methods**

167 The reaction of perfluoroamines with OH radicals is expected to make a negligible  
 168 contribution to their atmospheric loss. Here, we used theoretical methods to estimate upper-

169 limits for the reaction rate coefficients, at 298 K, for the reaction of OH radicals with N(C<sub>3</sub>F<sub>7</sub>)<sub>3</sub>.  
170 The other amines are expected to have a similar reactivity. Optimized structures, normal mode  
171 vibrational frequencies, and thermochemical parameters for N(C<sub>3</sub>F<sub>7</sub>)<sub>3</sub>, OH, and reaction products  
172 were calculated using the Gaussian 09 program suite [10]. The DFT functional B97-1 with the  
173 6-311 ++ G(2df,2p) basis set, with ultrafine grid numerical integration, was used for all  
174 calculations.

175 Reaction channels were explored where either OH abstracts an F atom to form FOH +  
176 radical, or where the OH radical adds to the amine to form a hydroxylamine and a C<sub>3</sub>F<sub>7</sub> radical  
177 (i.e., C-N bond cleavage):



182 Each of these reactions are endothermic and we have followed the approach adopted by the  
183 IUPAC and NASA kinetic data evaluation panels to estimate a rate coefficient assuming a pre-  
184 exponential factor,  $A$ ,  $1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  in this case, and a lower-limit activation  
185 energy equal to that of the reaction endothermicity. The F-atom abstraction channels have  
186 extremely low 298 K rate coefficients,  $<2.5 \times 10^{-51} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The hydroxylamine  
187 formation channel is calculated to have a rate coefficient of  $<2.2 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .  
188 Channel 11d is, however, expected to have a significant activation barrier to reaction, which was  
189 not evaluated in this work, due to steric hinderance towards product formation. The barrier  
190 would make the reaction rate coefficient considerably less.

## 191 2.4 Materials

192 N(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (perfluorotriethylamine, CAS# 359-70-6, 97%), N(C<sub>3</sub>F<sub>7</sub>)<sub>3</sub>  
193 (perfluorotripropylamine, CAS# 338-83-0, ~94.5%), and N(C<sub>4</sub>F<sub>9</sub>)<sub>3</sub> (perfluorotributylamine,  
194 CAS# 311-89-7, 99.5%) were obtained commercially with the stated purity given in parenthesis.  
195 The perfluoroamines are liquids at room temperature and were degassed in several freeze (77 K)-  
196 pump-thaw cycles and stored under vacuum in Pyrex reservoirs. He (UHP, 99.999%), N<sub>2</sub> (UHP,  
197 99.999%), and N<sub>2</sub>O (>99.99%) were used as supplied. Ozone was produced by flowing O<sub>2</sub>  
198 through a silent discharge and collected on silica gel in a trap at 195 K. Ozone was introduced  
199 into the O(<sup>1</sup>D) reaction cell by passing a small flow of He through the trap.



200 For the O(<sup>1</sup>D) reaction and photodissociation studies, PFA were introduced in the  
201 reactors using dilute PFA gas mixtures prepared manometrically in He and N<sub>2</sub> bath gas.  
202 Mixtures were prepared in 12 L Pyrex bulbs with the following mixing ratios: 0.01447% in He  
203 for (C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>N, 0.0167% in He and 0.01925% in N<sub>2</sub> for (C<sub>3</sub>F<sub>7</sub>)<sub>3</sub>N and 0.01233% in He and  
204 0.01403% in N<sub>2</sub> for (C<sub>4</sub>F<sub>9</sub>)<sub>3</sub>N). Pressures were measured using calibrated capacitance  
205 manometers. Uncertainties given throughout the paper are 2σ unless noted otherwise.

### 206 3. Results and Discussion

#### 207 3.1 UV absorption spectrum and photodissociation

208 UV absorption spectra of the PFA samples (taken from the liquid sample head space)  
209 were measured over the 200–350 nm wavelength range. Absorption was observed between 200  
210 and 300 nm for N(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> and between 200 and 250 nm for N(C<sub>3</sub>F<sub>7</sub>)<sub>3</sub> and N(C<sub>4</sub>F<sub>9</sub>)<sub>3</sub>. The  
211 measured absorption spectra were, however, irreproducible, due to changing impurity  
212 contributions, while the effective cross sections were small, with values of less than 10<sup>-20</sup> cm<sup>2</sup>  
213 molecule<sup>-1</sup> at 200 nm. The weak PFA UV absorption makes the measurements highly  
214 susceptible to interference by minor sample impurities that absorb strongly in the UV. Vacuum  
215 distillation of the liquid PFA samples did not yield consistent UV spectra. Examples of the  
216 measured spectra are given in the Supporting Information (**Figure S1**). However, in all cases, it  
217 was clear that absorption at wavelengths greater than 290 nm was not detectable, i.e., the  
218 corresponding effective PFA absorption cross section was <10<sup>-22</sup> cm<sup>2</sup> molecule<sup>-1</sup> in this  
219 wavelength region. Although we were unable to measure quantitative PFA UV absorption  
220 spectra, the measurements demonstrate weak absorption in the short (195–210 nm) and long  
221 (>290 nm) wavelength actinic regions.

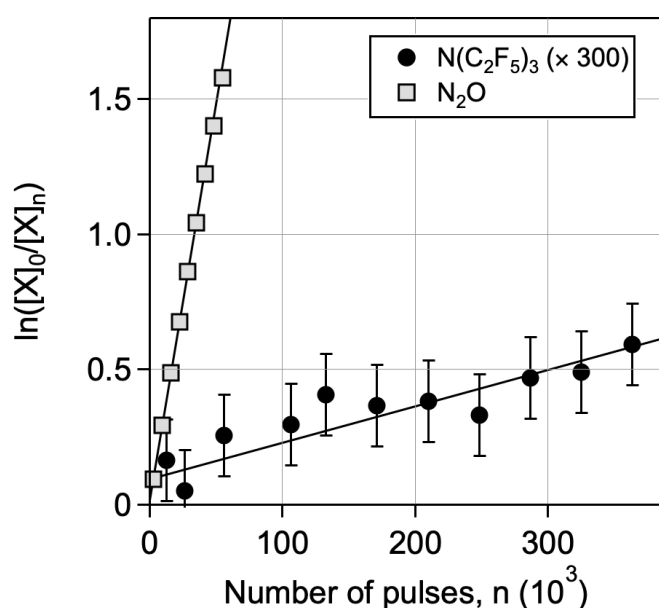
222 A summary of the experimental conditions and the PFA photolysis yield results are given  
223 in **Table 1**. PFA photodissociation at 193 nm was found to be inefficient and, thus, required  
224 fairly long exposure to the photolysis laser to achieve measurable PFA losses. A representative  
225 set of photolysis data is shown in **Figure 1**. Experiments were performed with a total number of  
226 photolysis pulses in the range (3.6–4.5) × 10<sup>5</sup>, corresponding to ~5 hours total photolysis time.  
227 The photochemical conversion rate of N<sub>2</sub>O exceeded that of the PFA by at least two orders of  
228 magnitude.

229

230 **Table 1.** Experimental conditions and results for the 193 nm photodissociation of  $\text{N}(\text{C}_2\text{F}_5)_3$ ,  
 231  $\text{N}(\text{C}_3\text{F}_7)_3$ , and  $\text{N}(\text{C}_4\text{F}_9)_3$  at 294 K

Perfluoroamine (PFA)	[PFA] ( $10^{15}$ molecule $\text{cm}^{-3}$ )	$[\text{N}_2\text{O}]$ ( $10^{15}$ molecule $\text{cm}^{-3}$ )	$\sigma(\lambda) \times \Phi(\lambda)$ ( $\text{cm}^2 \text{ molecule}^{-1}$ )
$\text{N}(\text{C}_2\text{F}_5)_3$	1.2	9.2	$1.37 \times 10^{-23}$
$\text{N}(\text{C}_3\text{F}_7)_3$	3.8	9.1	$<1 \times 10^{-23}$
$\text{N}(\text{C}_4\text{F}_9)_3$	2.5	8.9	$<1.5 \times 10^{-22}$

232  
 233



234  
 235 **Figure 1.** Loss of  $\text{N}(\text{C}_2\text{F}_5)_3$  (circles) and  $\text{N}_2\text{O}$  (squares) following 193 nm pulsed laser  
 236 photolysis. The  $\text{N}(\text{C}_2\text{F}_5)_3$  data has been multiplied by 300 for improved clarity. The lines are  
 237 linear least-squares fits to the data. The error bars on the  $\text{N}(\text{C}_2\text{F}_5)_3$  data points represent the  
 238 precision of the infrared spectral analysis. The precision error bars for  $\text{N}_2\text{O}$  are smaller than the  
 239 symbol size.

240  
 241 The background loss of PFA from the experimental apparatus measured in the absence of  
 242 photolysis was an additional issue in the interpretation of the photolysis results. Background loss  
 243 was measured before and after the photolysis experiments and the average value subtracted from  
 244 the observed PFA loss rate. For  $\text{N}(\text{C}_2\text{F}_5)_3$ , the background loss was negligible, but significant for  
 245  $\text{N}(\text{C}_3\text{F}_7)_3$  and  $\text{N}(\text{C}_4\text{F}_9)_3$  over the long duration of the experiment. The first-order rate coefficient  
 246 for the dark loss of  $\text{N}(\text{C}_3\text{F}_7)_3$  were  $2.02 \times 10^{-7}$  and  $1.82 \times 10^{-7} \text{ s}^{-1}$ , before and after respectively.  
 247 The total decay rate of  $\text{N}(\text{C}_3\text{F}_7)_3$  during 193 nm photolysis was  $2.92 \times 10^{-7} \text{ s}^{-1}$ . For  $\text{N}(\text{C}_4\text{F}_9)_3$ ,

248 dark loss rate coefficients were  $1.40 \times 10^{-6}$  and  $4.56 \times 10^{-7} \text{ s}^{-1}$ . The total decay rate of  $\text{N}(\text{C}_4\text{F}_9)_3$   
 249 during photolysis was  $1.41 \times 10^{-6} \text{ s}^{-1}$ .  $\sigma(193 \text{ nm}, 294 \text{ K}) \times \phi(193 \text{ nm}, 294 \text{ K})$  were determined to  
 250 be  $1.37 \times 10^{-23}$ ,  $<1 \times 10^{-23}$  and  $<1.5 \times 10^{-22} \text{ cm}^2 \text{ molecule}^{-1}$  for  $\text{N}(\text{C}_2\text{F}_5)_3$ ,  $\text{N}(\text{C}_3\text{F}_7)_3$ , and  $\text{N}(\text{C}_4\text{F}_9)_3$ ,  
 251 respectively.

252 Although photolysis yields were only measured at 193 nm, the UV absorption spectrum  
 253 measurements implies that photolysis yields at longer wavelengths would be lower for  
 254 wavelength greater than 193 nm.

### 255 3.2 O(<sup>1</sup>D) Reactive Rate Coefficient

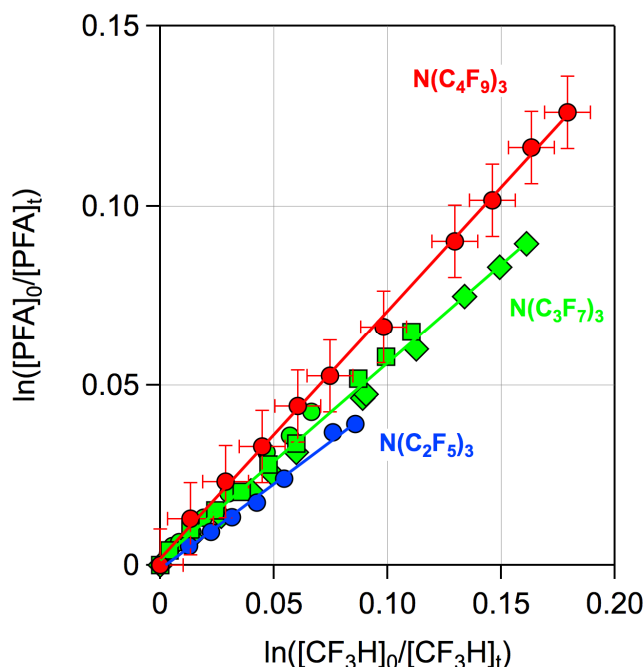
256 **Table 2** provides a summary of the 294 K O(<sup>1</sup>D) + PFA relative rate results obtained in  
 257 this work. **Figure 2** shows the raw relative rate data for the  $\text{N}(\text{C}_2\text{F}_5)_3$ ,  $\text{N}(\text{C}_3\text{F}_7)_3$ , and  $\text{N}(\text{C}_4\text{F}_9)_3$   
 258 reactions that includes multiple independent measurements for the  $\text{N}(\text{C}_3\text{F}_7)_3$  reaction. The  
 259 measured O(<sup>1</sup>D) rate coefficients show a slight systematic increase in reactivity with increased  
 260 carbon chain length in the PFA. Due to the low reactivity of the PFAs, the total loss of PFA  
 261 achieved with this experimental approach was <15%. It is worth noting that PFA loss in the  
 262 absence of O(<sup>1</sup>D) production was found to be negligible. The low conversion leads to greater  
 263 measurement precision uncertainty when compared with typical OH and Cl-atom relative rate  
 264 measurements that typically have precisions of a few percent. The fit precision uncertainties  
 265 given in **Table 2** are ~5%, or less. The independent experimental  $\text{N}(\text{C}_3\text{F}_7)_3$  reaction  
 266 measurement results agree to within ~15%. The final rate coefficient for the  $\text{N}(\text{C}_3\text{F}_7)_3$  reaction  
 267 was obtained from the least-square analysis of all the data.

269 **Table 2.** Summary of experimental conditions and rate coefficients,  $k(294 \text{ K})$ , obtained in this  
 270 work for the O(<sup>1</sup>D) +  $\text{N}(\text{C}_2\text{F}_5)_3$ ,  $\text{N}(\text{C}_3\text{F}_7)_3$ , and  $\text{N}(\text{C}_4\text{F}_9)_3$  reactions using a relative rate technique

Perfluoroamine (PFAM)	[PFA] ( $10^{14} \text{ molecule cm}^{-3}$ )	[CHF <sub>3</sub> ] ( $10^{14} \text{ molecule cm}^{-3}$ )	$k/k_{\text{Ref}}^a$	$k$ ( $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) <sup>a</sup>
$\text{N}(\text{C}_2\text{F}_5)_3$	3.6	4.6	$0.455 \pm 0.019$	$1.10 \pm 0.10$
$\text{N}(\text{C}_3\text{F}_7)_3$	4.0	4.4	$0.587 \pm 0.011$	$1.41 \pm 0.10$
	3.9	4.4	$0.649 \pm 0.018$	$1.56 \pm 0.12$
	4.1	4.4	$0.545 \pm 0.009$	$1.31 \pm 0.09$
			$0.563 \pm 0.012^b$	$1.36 \pm 0.10$
$\text{N}(\text{C}_4\text{F}_9)_3$	3.0	4.4	$0.703 \pm 0.011$	$1.69 \pm 0.11$

271 <sup>a</sup> 2 $\sigma$  fit precision uncertainty

272 <sup>b</sup> Rate coefficient ratio was obtained from a fit of all N(C<sub>3</sub>F<sub>7</sub>)<sub>3</sub> data combined  
273  
274



275  
276 **Figure 2.** Relative rate data for the O(<sup>1</sup>D) + N(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>, N(C<sub>3</sub>F<sub>7</sub>)<sub>3</sub>, and N(C<sub>4</sub>F<sub>9</sub>)<sub>3</sub> reactions with  
277 CHF<sub>3</sub> used as the reference compound. The different symbols for the N(C<sub>3</sub>F<sub>7</sub>)<sub>3</sub> reaction  
278 represent independent experiments. The lines are weighted linear least-squares fits to the data (a  
279 fit to the combined data for N(C<sub>3</sub>F<sub>7</sub>)<sub>3</sub>). For clarity, the estimated measurement uncertainty is  
280 only shown for the N(C<sub>4</sub>F<sub>9</sub>)<sub>3</sub> reaction. The obtained rate coefficient ratios and derived O(<sup>1</sup>D) rate  
281 coefficient results are given in **Table 2**.

282  
283 The measured rate coefficient ratios were placed on an absolute basis using the O(<sup>1</sup>D)  
284 rate coefficient of CHF<sub>3</sub> (channel 8a),  $(2.4 \pm 0.12) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [7]. Overall, the  
285 O(<sup>1</sup>D) reactive rate coefficients are slow, but consistent with values reported for other highly  
286 fluorinated compounds [7]. The estimated absolute uncertainty in the O(<sup>1</sup>D) reactive rate  
287 coefficients was determined from the precision and reproducibility of the experimental data and  
288 the uncertainty in the CHF<sub>3</sub> reference compound rate coefficient and estimated to be 9% for  
289 N(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> and 7% for N(C<sub>3</sub>F<sub>7</sub>)<sub>3</sub> and N(C<sub>4</sub>F<sub>9</sub>)<sub>3</sub>.

#### 290 4. Atmospheric Lifetimes and Global Warming Potentials

291 The NOCAR 2-D model was used to estimate the PFA globally averaged partial and total  
292 atmospheric lifetimes. The 2-D model details can be found elsewhere [11]. The total globally  
293 averaged atmospheric lifetime was computed as a combination of the partial global lifetimes:

$$294 \quad \frac{1}{\tau_{\text{Total}}} = \frac{1}{\tau_{\text{OH}}} + \frac{1}{\tau_{\text{O}^{\text{(1D)}}}} + \frac{1}{\tau_{\text{UV}}} + \frac{1}{\tau_{\text{Lyman-}\alpha}}$$

295 Loss of the perfluoroamines due to reaction with the OH radical was shown earlier to  
296 most likely be negligible and, therefore, is not considered further. The O<sup>(1D)</sup> + PFA reaction  
297 represents an atmospheric loss processes that occurs primarily in the stratosphere. The 2-D  
298 model calculated atmospheric lifetime with respect to O<sup>(1D)</sup> reaction, using the reactive rate  
299 coefficients measured in this work, was estimated to be >20,000 years for each of the PFAs  
300 included in this study.

301 PFA photolysis was determined in this study at 193 nm. The majority of stratospheric  
302 UV photolysis however is expected to occur in the wavelength region between 195 and 220 nm.  
303 For an accurate determination of photolysis lifetimes, the absorption cross sections in this  
304 wavelength region is needed. Our measured photolysis yield at 193 nm was used along with an  
305 assumed decrease of a factor of 10 every 10 nm toward longer wavelengths for the UV  
306 photolysis lifetime calculations. For comparison, the NF<sub>3</sub> UV absorption spectrum decreases at  
307 about this rate for wavelengths greater than 200 nm [6]. UV photolysis in the 200–220 nm  
308 wavelength region is, an inefficient atmospheric loss process leading to a calculated global  
309 atmospheric lifetime of greater than 50,000 years. Note that model calculations of atmospheric  
310 lifetimes this long have a high degree of uncertainty and should not be considered quantitative.

311 There are no PFA absorption cross section data at Lyman- $\alpha$  (121.567 nm) currently  
312 available in the literature. On the basis of a comparison with other fluorinated compounds, PFAs  
313 are expected to absorb strongly in the VUV with a Lyman- $\alpha$  cross section of  $\sim 10^{-17}$  cm<sup>2</sup>  
314 molecule<sup>-1</sup>. The partial global lifetime for Lyman- $\alpha$  photolysis was estimated to be >4,500  
315 years. A smaller Lyman- $\alpha$  absorption cross section would yield a longer lifetime. Although  
316 Lyman- $\alpha$  photolysis represents a long atmospheric lifetime, it may represent a significant  
317 atmospheric loss process for PFAs. A combination of the estimated lifetimes leads to PFA  
318 atmospheric lifetimes of at least  $\sim 3,000$  years as summarized in Table 3.

319  
320 **Table 3.** Partial and total global atmospheric lifetime, radiative efficiency (RE), and global  
321 warming potential (GWP) for N(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>, N(C<sub>3</sub>F<sub>7</sub>)<sub>3</sub>, and N(C<sub>4</sub>F<sub>9</sub>)<sub>3</sub> <sup>a</sup>

Perfluoroamine (PFAM)	$\tau_{UV}^b$ (Years)	$\tau_{O(1D)}$ (Years)	$\tau_{Lyman-\alpha}^c$ (Years)	$\tau_{Total}$ (Years)	RE <sup>d</sup> (W m <sup>-2</sup> ppb <sup>-1</sup> )	GWP <sub>100</sub> <sup>e</sup>
N(C <sub>2</sub> F <sub>5</sub> ) <sub>3</sub>	> 5 × 10 <sup>5</sup>	3 × 10 <sup>4</sup>	4500	3880	0.61	9900
N(C <sub>3</sub> F <sub>7</sub> ) <sub>3</sub>	> 8 × 10 <sup>5</sup>	2.5 × 10 <sup>4</sup>	4500	3795	0.75	8700
N(C <sub>4</sub> F <sub>9</sub> ) <sub>3</sub>	> 5 × 10 <sup>4</sup>	2.0 × 10 <sup>4</sup>	4500	3650	0.87	7800

322 <sup>a</sup> Lifetimes were estimated based on 2-D atmospheric model calculations (see text); <sup>b</sup> Assuming  $\sigma(\lambda)$  decreases of a  
323 factor of 10 every 10 nm for wavelengths greater than 193 nm; <sup>c</sup> Lifetime estimated assuming  $\sigma(\text{Lyman-}\alpha) = 1 \times$   
324  $10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ ; <sup>d</sup> RE values taken from Bernard et al. [3]; <sup>e</sup> Rounded-off estimated GWP relative to CO<sub>2</sub> for  
325 the 100-year time horizon  
326

327 In a recent study from this laboratory, the radiative efficiencies (REs) for  
328 perfluorotriethylamine (N(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>), perfluorotripropylamine (N(C<sub>3</sub>F<sub>7</sub>)<sub>3</sub>), and  
329 perfluorotributylamine (N(C<sub>4</sub>F<sub>9</sub>)<sub>3</sub>) were determined [3]. Combining these values with the  
330 atmospheric lifetimes obtained in the present work leads to large global warming potentials on  
331 the 100-yr time horizon for the PFAs as given in Table 3. The GWP values of the PFAs included  
332 in this study are of comparable magnitude to those of other highly fluorinated persistent  
333 atmospheric traces gases such as NF<sub>3</sub>, SF<sub>6</sub>, and CF<sub>4</sub>, which have GWP<sub>100</sub> values of 15750,  
334 23500, and 6630, respectively [5].

## 335 7. Conclusions

336 In this study, laboratory experiments were conducted that define the global annually  
337 averaged partial and total atmospheric lifetimes of N(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>, N(C<sub>3</sub>F<sub>7</sub>)<sub>3</sub>, and N(C<sub>4</sub>F<sub>9</sub>)<sub>3</sub>. The O(<sup>1</sup>D)  
338 reaction and UV photolysis loss processes evaluated in this work were used in 2-D atmospheric  
339 model simulations to evaluate the global total atmospheric lifetimes. PFAs are primarily  
340 removed in the stratosphere and lower mesosphere such that their removal and lifetimes depend  
341 on the modeled transport and turnover times for these regions of the atmosphere. Although the  
342 lifetimes are clearly long and GWPs large, a multi-model analysis would be useful to better  
343 define the possible range in lifetimes and GWPs for the atmospherically persistent PFAs  
344 included in this study.”

345 It was shown that PFAs are atmospherically persistent potent greenhouse gases (GHGs)  
346 with GWPs on the 100-year time horizon in the range 7800-9900 for N(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>, N(C<sub>3</sub>F<sub>7</sub>)<sub>3</sub>, and  
347 N(C<sub>4</sub>F<sub>9</sub>)<sub>3</sub>. GWPs were calculated using the radiative efficiencies reported by Bernard et al. [3]

348 and atmospheric lifetimes from this work, see Table 3. The present results provide a  
349 fundamental basis for guiding future policy decisions regarding the potential release of  
350 perfluoroamines into the environment.

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355 **Author Contributions:**

356 FB, DP, VP, and JB, experimental measurements and data analysis; DP and VP,  
357 theoretical calculations; RP, atmospheric modeling; FB and JB, manuscript writing  
358

359 **References**

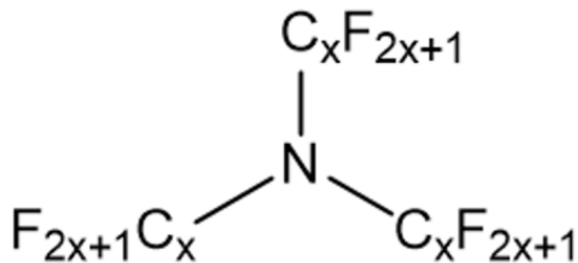
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395



## GAS-PHASE LOSS PROCESSES

Perfluoroamines (PFAs)



$x = 2 - 4$

**Mesosphere:**

- Lyman- $\alpha$  photolysis

**Stratosphere:**

- UV photolysis
- O(<sup>1</sup>D) reaction

**Troposphere:**

- OH reaction

**Atmospheric  
lifetime ( $\tau$ )**

**Radiative  
efficiencies  
( $RE$ )**

**Global Warming  
Potential (GWP)**

$$\text{GWP} = \frac{RE \times \tau \times \left[1 - e^{-T/\tau}\right]}{\text{Int RF}_{\text{CO}_2}(T)}$$

T: 100-year time horizon