Infrared Spectra and Radiative Efficiencies of Atmospherically Persistent Perfluoroamines: $N(C_xF_{2x+1})_3$, x = 2-5

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1 Introduction

Perfluorinated amines ($N(C_xF_{2x+1})_3$, PFAm) are persistent greenhouse gases

- $(C_4F_9)_3N$ has a reported radiative efficiency of 0.86 W m^{-2} ppb^{-1} (Hong et al. 2013)
- $(C_4F_9)_3N$ mixing ratio of 0.18 ppt observed in urban Toronto, Canada (Hong et al., 2013) (($(C_4F_9)_3N$ used in heat transfer and electronics testing)
- Other PFAms have not been observed to date

Atmospheric loss processes and lifetimes for PFAms are NOT well characterized

- Atmospheric lifetimes are expected to be >250 years

Objectives of This Study

Laboratory measurements used to evaluate key atmospheric metrics for this class of compounds

Global Warming Potential (GWP)

$$GWP = \frac{RE \times \tau_{PFAm} \times \left[1 - e^{-T/\tau}\right]}{\mathrm{Int}\,RF_{CO_2}(T)}$$

T: Time Horizon

Radiative efficiencies (RE)
Infrared spectroscopy

Atmospheric lifetimes (τ)
Atmospheric loss processes: UV photolysis, O(^{1}D) reaction

2 Experimental Details

- Infrared Spectroscopy-

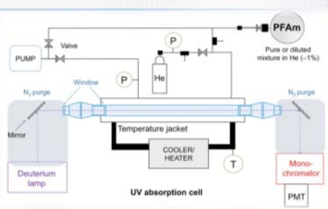
Measure infrared absorption spectra

- **Spectral range:** 600-4000 cm^{-1}
- **Detector:** HgCdTe (MCT)
- **Resolution:** 1 cm^{-1}
- **Pathlength:** 15, 185 and 455 cm
- **Temperature:** 294 K
- **Total pressure:** 10-600 Torr (He bath gas)

- UV Photolysis -

Measure UV absorption spectra

- **Light source:** Deuterium lamp
- **T** = 294 K
- **λ range of interest:** 195–235 nm

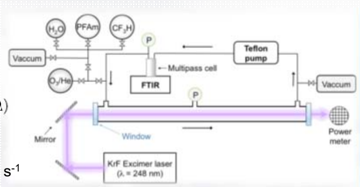


- O(^{1}D) Reaction -

Measure O(^{1}D) Rate Coefficient

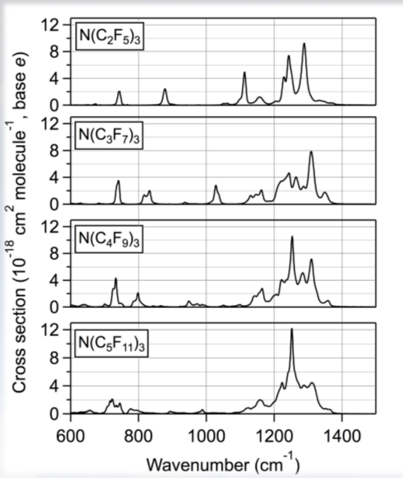
- **Relative rate method**
- **O(^{1}D) source:**
  $O_3 + h\nu$ (248 nm) → O(^{1}D) + O_2 ($^1\Delta$)
- **T** = 294 K, **P** = 300 Torr
- **Reference:** CF_3H

$k(CF_3H+O(^1D)) = 2.4\times10^{-12}$ cm^3 molecule^{-1} s^{-1}
(Burkholder et al., 2015)



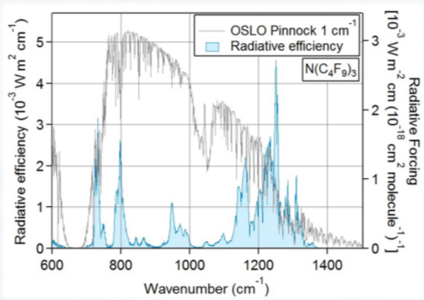
3 Results

3.1 Infrared absorption spectra



- PFAms absorb strongly in the mid-IR region
- IR absorption falls within the atmospheric window
- IR band strength increases with increasing chain length (increase of C-F bonds)
- $(C_4F_9)_3N$ spectrum is in good agreement with that reported by Hong et al. (2013), but not with Godin et al. (2016)
- No data available for other compounds

3.2 Radiative efficiencies (RE)



- RE calculated using the methodology reported in Hodnebrog et al. (2013)
- RE from PFAm are higher than those of HFCs and CFCs which have REs typically ≤ 0.3 W m^{-2} ppb^{-1} (WMO, 2014)

Compound	Chemical formula	RE* (W m^{-2} ppb^{-1})	Reference
Perfluorotriethylamine	$N(C_2F_5)_3$	0.63	This work
Perfluorotripropylamine	$N(C_3F_7)_3$	0.74	This work
Perfluorotributylamine	$N(C_4F_9)_3$	0.87	This work
		0.77	Godin et al. (2016)
		0.86	Hong et al. (2013)
Perfluorotripentylamine	$N(C_5F_{11})_3$	0.80	This work
HFC-134a	CH_2FCF_3	0.16	WMO (2014)

* Absorption below 500 cm^{-1} does not contribute significantly (preliminary theoretical Gaussian calculations)

PFAms have very high RE values and are potent greenhouse gases (GHGs)

4 Discussion and Atmospheric Implications

4.1 Atmospheric Lifetime (τ) Evaluation

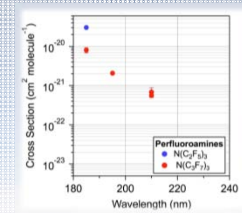
$$\frac{1}{\tau_{Total}} = \frac{1}{\tau_{O(1D)}} + \frac{1}{\tau_{UV}} + \frac{1}{\tau_{Lyman\text{-}\alpha}} + \ldots$$

PFAm loss expected to be in the upper atmosphere (Stratosphere / Mesosphere)

4.2 Atmospheric Loss Processes

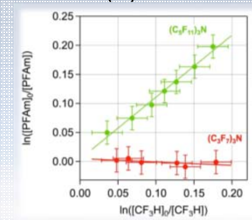
Preliminary Laboratory Results

- **UV photolysis**



- **Weak absorption in the critical actinic region (200-220 nm)**
- **Sample purity a possible issue**

- **O(^{1}D) reaction**



- $k((C_5F_{11})_3N) = 2.55\times10^{-12}$ cm^3 molecule^{-1} s^{-1}
- $k(C_3F_7)_3N < 0.3\times10^{-12}$ cm^3 molecule^{-1} s^{-1}

Studies for other compounds ongoing

- **Additional Studies:** Lyman-α and Photodissociation measurements

Preliminary results indicate that UV photolysis may be the predominant atmospheric loss process for PFAms

5 Future Research Directions

- **Theory (Gaussian)**
  - Identify infrared bands
  - Evaluate trends in infrared spectra
- **Atmospheric 2-D Modeling**
  - Quantify atmospheric loss processes
  - Identify regions of atmospheric loss
  - Determine global and local lifetimes
- **Field observations**
  - Detection/sensitivity analysis
  - Identification of PFAms in background and urban environments
- **Laboratory Studies**
  - Cyclic compounds (e.g. morpholines)
  - Non-symmetric PFAms ($N(C_xF_{2x+1})(C_yF_{2y+1})(C_zF_{2z+1})$)

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