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Infrared absorption spectra of $N(C_xF_{2x+1})_3$, $x=2$–5 perfluoroamines

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ABSTRACT

Infrared absorption spectra of the perfluoroamines ($N(C_2F_5)_3$, $N(C_3F_7)_3$, $N(C_4F_9)_3$, and $N(C_5F_{11})_3$) were measured over the 500–4000 cm^{-1} spectral region at 294 K using Fourier transform infrared (FTIR) spectroscopy at 1 cm^{-1} resolution. Spectral measurements were performed using static measurements of dilute perfluoroamines mixtures and by infusion of the pure compound into a calibrated gas flow. The perfluoroamines absorb strongly in the "atmospheric window" with integrated band strengths (10^{-17} cm^2 $molecule^{-1}$ cm^{-1}) between 570 and 1500 cm^{-1} of 59.9, 74.9, 88.9, and 98.7 for $N(C_2F_5)_3$, $N(C_3F_7)_3$, $N(C_4F_9)_3$, and $N(C_5F_{11})_3$, respectively. Radiative efficiencies (RE) for the perfluoroamines were estimated to be 0.61, 0.75, 0.87, and 0.95 W m^{-2} ppb^{-1} for atmospherically well-mixed conditions and including a +10% stratospheric temperature correction for $N(C_2F_5)_3$, $N(C_3F_7)_3$, $N(C_4F_9)_3$, and $N(C_5F_{11})_3$, respectively. Theoretical calculations of the perfluoroamines were performed at the B97-1/6-311++G(2df,2p) level of theory and optimized perfluoroamine geometries, vibrational band positions, and band strengths are reported. The theoretically calculated infrared spectra are in good agreement with the experimental spectra, while comparison of individual bands was not attempted due to the significant overlap of vibrational bands in the experimental spectra.

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1. Introduction

Symmetric perfluoroamines, $N(C_xF_{2x+1})_3$, are a subset of perfluoroalkylamines that are volatile and semi-volatile compounds used as electronic testing fluids and in low-temperature heat transfer applications. The commercial use of these compounds can lead to their direct release into the atmosphere. Hong et al. [1] observed perfluorotributylamine, $N(C_4F_9)_3$, in urban Toronto with mixing ratios of ~0.18 ppt. The kinetic and photochemical atmospheric loss processes for perfluoroamines are currently not well characterized, but these compounds are expected to be atmospherically persistent with lifetimes greater than 500 years [2]. Perfluoroamines are expected to be potent greenhouse gases, as well, due to the large number of C–F bonds in the molecule, which absorb strongly in the infrared atmospheric window region. Although the global atmospheric abundance of perfluoroamines is currently low, a more thorough understanding of their environmental impact requires further laboratory studies of their radiative properties [3].

In this study, the infrared absorption spectra of several perfluoroamines, $N(C_xF_{2x+1})_3$, $x=2$–5, were measured using Fourier transform infrared (FTIR) spectroscopy between 500–4000 cm^{-1}. Density functional theory (DFT) calculations were performed as part of this study and optimized perfluoroamine molecular geometries, vibrational spectra, and band strengths are reported and compared with the experimentally measured spectra. The radiative efficiencies (RE), which is a policy relevant metric for greenhouse gases, were calculated using the experimentally measured perfluoroamine infrared spectra. These perfluoroamines are shown to be potent greenhouse gases in comparison with other heat transfer and other perfluorinated compounds. To the best of our knowledge, the only perfluoroamine infrared absorption spectrum reported prior to this study is that of perfluorotributylamine, $N(C_4F_9)_3$, by Godin et al. [4] and Hong et al. [1]. The band strengths for $N(C_4F_9)_3$ obtained in the present study compare very well with those reported by Hong et al. [1]. The present study provides the fundamental spectroscopic data used to quantify these perfluoroamines in future laboratory kinetic and photochemical studies. In addition, a band strength trend analysis is presented to aid the prediction of

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spectra where experimental infrared absorption spectra are not available.

2. Experimental details

The infrared absorption spectra of perfluorotriethylamine ($N(C_2F_5)_3$), perfluorotripropylamine ($N(C_3F_7)_3$), perfluorotributylamine ($N(C_4F_9)_3$), and perfluorotripentylamine ($N(C_5F_{11})_3$) were measured at 294 K using Fourier transform infrared (FTIR) spectroscopy. Absorption spectra were recorded in 100–500 co-adds between 500 and 4000 cm^{-1} at 1 cm^{-1} resolution (Boxcar apodization). A single pass absorption cell, 15 cm path length with KBr windows, or a multi-pass absorption cell with 185 or 455 cm optical path lengths (KBr or Ge windows) were used in the course of these measurements. A liquid nitrogen cooled HgCdTe/B semiconductor detector was used for all the measurements.

Absorption spectra, $A(\nu)$ (base e), (or integrated band strengths) were determined using Beer's law:

$$A(\nu) = \sigma(\nu) \times L \times [\text{perfluoroamine}] \tag{1}$$

where $\sigma(\nu)$ is the infrared absorption cross section of the perfluoroamine at wavenumber ν , L is the absorption path length, and [perfluoroamine] is the perfluoroamine concentration. Two independent experimental approaches, static and infusion methods, were used to quantify the perfluoroamine infrared absorption spectra. The methods have been used previously in our laboratory [5] and are briefly described separately below.

Static Method: In this method, the perfluoroamine gas sample was added quantitatively to the FTIR absorption cell from dilute gas mixtures prepared off-line in a He bath gas. The perfluoroamines included in this study are stable compounds and this approach enables an accurate determination of the perfluoroamine concentration. The perfluoroamine concentration in the absorption cell was calculated using the measured absolute pressure, the mixing ratio of the dilute sample, and the ideal gas law. Measurements were performed with over a factor of ~10 range in perfluoroamine concentration. The range of perfluoroamine concentrations were (molecule cm^{-3}): $(0.550–4.02) \times 10^{14}$ for $N(C_2F_5)_3$, $(0.0063–1.32) \times 10^{16}$ for $N(C_3F_7)_3$, $(0.478–3.53) \times 10^{14}$ for $N(C_4F_9)_3$, and $(0.314–2.81) \times 10^{14}$ for $N(C_5F_{11})_3$. Over the course of the study, replicate measurements were performed using independently prepared and aged gas mixtures. The use of the aged gas mixtures confirmed the stability of the prepared samples. The absorption spectra (band strengths) were obtained from a linear least-squares fit of A versus [perfluoroamine] that included 10, or more, individual spectrum measurements.

Infusion Method: In this method, the pure perfluoroamine liquid sample was added from a gas-tight calibrated syringe pump to a calibrated flow of He carrier gas. The diluted perfluoroamine sample flowed through the FTIR single-pass absorption cell (15 cm), i.e., spectra were recorded under gas flow conditions. The septum and injection port of the syringe were maintained at a slightly elevated temperature, 50–60 °C, to ensure vaporization of the perfluoroamine liquid sample. The perfluoroamine injection rate was varied between 0.025 and 3 $\mu L\ min^{-1}$ over the course of the measurements. The perfluoroamine concentration was calculated using the calibrated gas and liquid flow rates and the density of the perfluoroamine compound. A summary of the experimental conditions used in the infusion measurements is given in Table 1. Spectra recorded over a range of perfluoroamine concentrations were included in the linear least-squares fit to Eq. (1).

The perfluoroamine samples used in this study were obtained commercially with the stated purities given in parenthesis: $N(C_2F_5)_3$ (97%; CAS 359–70–6), $N(C_3F_7)_3$ (94.5%; CAS 338–83–0), $N(C_4F_9)_3$ (99.5%; CAS 311–89–7), $N(C_5F_{11})_3$ (85%; CAS 338–84–1). All samples were degassed in several freeze (77 K)–pump–thaw cycles prior to use. The samples were also vacuum distilled to remove possible volatile impurities. Note that the $N(C_5F_{11})_3$ sample contained a $N(C_3F_7)_3$ impurity, observed by infrared absorption, that was removed by distillation. The samples were stored under vacuum in Pyrex reservoirs. For reference, the approximate vapor pressure, in Torr, of the samples at 294 K are ~80 for $N(C_2F_5)_3$, ~7 for $N(C_3F_7)_3$, ~0.4 for $N(C_4F_9)_3$, and ~0.03 for $N(C_5F_{11})_3$.

Table 1
Summary of conditions and concentrations used in the infusion method measurements.

	Liquid flow rate ($\mu L\ min^{-1}$)	Gas flow rate ($cm^3\ min^{-1}$)	Liquid density [a] ($g\ cm^{-3}$)	Concentration Range (10^{15} molecule cm^{-3})
$N(C_2F_5)_3$	0.1–2	484	1.736	0.582–11.6
$N(C_3F_7)_3$	0.25–3	485.7	1.822	1.08–13.0
$N(C_4F_9)_3$	0.1–2	487.1	1.88	0.346–6.93
$N(C_5F_{11})_3$	0.025–0.2	487	1.94	0.0729–0.586

[a] Liquid densities as provided by the commercial supplier.

For the static method measurements, dilute mixtures of the samples were prepared manometrically in a He (UHP, 99.999%) bath gas in 12 L Pyrex bulbs. The following perfluoroamine mixing ratios were used over the course of the study: 0.0047, 0.00674 and 0.0163% for $N(C_2F_5)_3$, 0.00554, 0.594, and 1.034% for $N(C_3F_7)_3$, 0.00369 and 0.0237% for $N(C_4F_9)_3$, and 0.00264 and 0.00322% for $N(C_5F_{11})_3$. The uncertainty in the bulb mixing ratio was estimated to be ~5% for $N(C_2F_5)_3$, ~4% for $N(C_3F_7)_3$, ~7% for $N(C_4F_9)_3$ and ~12% for $N(C_5F_{11})_3$. Pressure was measured using calibrated 10 and 1000 Torr capacitance manometers. Uncertainties given throughout the paper are 2σ unless noted otherwise.

3. Results and discussion

The infrared absorption spectra of the perfluoroamines included in this work are characterized by broad diffuse vibrational bands as shown in Fig. 1, (digitized absorption spectra are provided in the Supplementary Material). The spectra are characterized by strong absorption features in the C–F, 1200–1400 cm^{-1}, and C–N, 1020–1220 cm^{-1}, stretch regions. The absorption spectra show significant overlap of vibrational bands in this region, with the vibrational band congestion increasing with the increase in the length of the carbon chain and number of C-F bonds. In general, the larger perfluoroamines have greater peak cross sections in this region due, in part, to the greater overlap of vibrational bands.

The spectra measured using the static and infusion methods for $N(C_2F_5)_3$, $N(C_3F_7)_3$, and $N(C_4F_9)_3$ obeyed Beer's law with high precision, to better than 2%, for the range of perfluoroamine concentrations included in this study. For $N(C_2F_5)_3$, $N(C_3F_7)_3$, $N(C_4F_9)_3$, and $N(C_5F_{11})_3$ there was an overall good agreement between the infusion and static methods where integrated band strengths over the 570–1500 cm^{-1} spectral region agreed to within 2, 2, 4, and 6%, respectively. Beer's law plots for each of the perfluoroamines are provided in the Supporting Material. Replicate measurements performed with different dilute mixtures were also found to be in good agreement. $N(C_5F_{11})_3$ is the lowest volatility compound included in this study, which may have contributed to the slightly higher scatter in the experimental data for this molecule. The measured spectra were independent of total bath gas pressure over the range 2–325 Torr (He). Due to the greater potential systematic error in the dilute sample preparations for $N(C_5F_{11})_3$ used in the static method measurements, the results from the infusion method are preferred. For $N(C_2F_5)_3$, $N(C_3F_7)_3$, and $N(C_4F_9)_3$ an average of the static and infusion methods is recommended. The integrated band strengths obtained using the static and infusion methods, as well as, the recommended values are given in Table 2.