Fourier Transform Infrared Spectroscopy and Global Warming Potentials of Cyclic Perfluorocarbons

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FOURIER TRANSFORM INFRARED SPECTROSCOPY AND GLOBAL 
WARMING POTENTIALS OF CYCLIC PERFLUOROCARBONS 

by 

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A.S., Grand Rapids Community College, 2009 
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This thesis entitled:
Fourier Transform Infrared Spectroscopy and Global Warming
Potential of Cyclic Perfluorocarbons
written by Kent Christian Kammermeier
has been approved for the Department of Chemistry and Biochemistry

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Veronica Vaida

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Veronica M. Bierbaum

Date __________

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.
Kammermeier, Kent Christian (M.S., Chemistry and Biochemistry)

Fourier Transform Infrared Spectroscopy and Global Warming Potentials of Cyclic Perfluorocarbons

Thesis directed by Professor Veronica Vaida

Perfluorocarbons are inert compounds with atmospheric lifetimes of thousands of years; they have very strong IR absorption bands in regions of the solar spectrum unoccupied by other significant absorbers. Vibrational FT-IR spectroscopy was performed on a series of six cyclic perfluorocarbons. These spectra were used to obtain radiative efficiencies and global warming potentials for these cyclic perfluorocarbons. These radiative efficiency and global warming potential values follow trends similar to those of the linear perfluorocarbon counterparts but are, in general, lower with respect to both values.
This thesis is dedicated to my family and friends. Without them, none of this would have been possible.
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CHAPTER I

INTRODUCTION

Perfluorinated compounds are synthetic molecules useful in many industrial applications. Perfluorocarbons (PFCs) have very few natural sources. As a result of the elevated dissociation energy of C–F versus C–H, these compounds are considered biologically safe and are used in the treatment of human respiratory complications. Because they are biologically safe, PFCs are widely used in industrial processes such as the manufacture of semiconductors and electronics. They are used in steelmaking, uranium isotope separation, and cosmetics. PFCs have also replaced chlorofluorocarbons (CFCs) as refrigerants and coolants as well as becoming useful solvents, fire suppressants, and more recently, atmospheric tracers. The atmospheric mole fraction of C₆F₁₄, only one of many PFCs, grew from 0.005 to 0.267 ppt between 1980 and 2011.

There are several features that make PFCs attractive in many applications. First, their inert nature resulting from increased bond dissociation energy makes these PFCs stable over very long periods of time (thousands of years). That is, PFCs will resist degradation and side reactions for much longer than other halogenated species such as halogenated ethers, ketones, or hydrofluorocarbons (HFCs) and hydrochlorocarbons. Second, besides CF₄ (observed to naturally occur in the atmosphere at approximately 40 ppt) PFCs have not been found in the natural environment. The atmospheric background levels of most PFCs are extremely low as a
result. Finally, the absorption spectra of PFCs show strong IR active C–F stretching transitions around 1200 cm$^{-1}$, a region of the solar spectrum where no major atmospheric component absorbs. These last two points combine to make the detection of PFC fluctuations in the atmosphere a simple and accurate process.

Use of PFCs in the tracer field illustrates the usefulness of these compounds.$^{10}$ The Department of Energy has determined that, over the 1000-year sequestration period,$^{22}$ a 1% loss of total sequestered CO$_2$ is acceptable. $^{23}$ PFC tracers may allow timely identification and neutralization of leak sites to keep CO$_2$ loss below this averaged 0.001% loss per year quota. This is achieved with minimal tracer concentrations and without biological consequences or environmental contamination. Unfortunately, like CFCs,$^{24}$ these compounds have undesirable effects on the atmosphere and climate.

PFCs are very potent greenhouse gases (GHGs). This is a result of strongly absorbing IR radiation outside the water absorption spectrum and very long atmospheric lifetimes. Because the unique 1200 cm$^{-1}$ C–F absorption range occurs where there are no other significant absorption sinks, there is a significantly larger impact on the greenhouse effect than other regions where water and other primary atmospheric constituents absorb. Radiation within that region likely escapes the atmosphere if not absorbed by these PFCs rather than being absorbed by some other chemical. The lifetime is also an important factor to the greenhouse gas potency of PFCs. PFCs used today will continue to persist within the atmosphere and influence the greenhouse effect for thousands of years into the future. Because of their potency and persistence within the atmosphere, responsible use of PFCs necessitates an evaluation and understanding of their greenhouse effects.
There has been limited work on the atmospheric influence of PFCs. A 1993 paper by A. R. Ravishankara et al. is the most authoritative source on the atmospheric lifetimes of PFCs. In their paper the atmospheric lifetime of CF$_4$, C$_2$F$_6$, C$_4$F$_{10}$, C$_5$F$_{12}$, C$_6$F$_{14}$, (CF$_3$)$_2$c-C$_4$F$_6$, and SF$_6$ are reported. The latest compilation of global warming potentials (GWPs) in the 2007 Intergovernmental Panel on Climate Change (IPCC) report. This report contains lifetimes, radiative efficiencies, and GWPs for CF$_4$, C$_2$F$_6$, C$_3$F$_8$, C$_4$F$_{10}$, C$_5$F$_{12}$, C$_6$F$_{14}$, C$_{10}$F$_{18}$, SF$_6$, NF$_3$, and SF$_3$CF$_3$. Most of the previous work has been on small, linear PFCs. General trends among these PFCs show that radiative efficiency increases and lifetime decreases as the PFC becomes larger. Large, cyclic PFCs may be a green alternative to their small, linear counterparts. They will likely be easier to detect at lower concentrations and decay earlier from the atmosphere. Evaluating a set of large, cyclic PFCs will help to determine these trends.

In this work, estimations of the atmospheric influence of six cyclic PFCs are reported. Infrared spectra of these PFCs were obtained and used to estimate their GWPs and halogenated global warming potentials (HGWPs). The calculated GWPs and HGWPs were compared to other PFCs and chemicals recognized as harmful atmospheric agents. This work was performed in collaboration with Dr. Jim B. Burkholder at the National Oceanic and Atmospheric Administration (NOAA) and Dr. Tom B. Watson at Brookhaven National Laboratory.

The experimental procedure will be described in Chapter II. This procedure will detail the sample preparation and the FT-IR spectroscopy used. The spectral results, calculations, and error analysis will be described in Chapter III. The spectral results will cover the quality of acquired spectra, the pressure dependence of the data, and the averaging of spectra to reduce spectral noise. The calculations cover the determination of radiative efficiency from the averaged spectra, the estimation of atmospheric lifetime, and finally the computation of GWPs and HGWPs. The
error analysis is a rough estimation of the sources of error in this study and their relative importance. The conclusion, discussed in Chapter IV, summarizes the results and compares them to other PFCs to draw out trends.
References for Chapter I


10. Watson, T. B.; Sullivan, T., Feasibility of a perfluorocarbon tracer based network to support monitoring, verification, and accounting of sequestered CO(2). *Environ Sci*


CHAPTER II

MATERIALS AND METHODS

This was a FT-IR study of a series of cyclic fluorinated hydrocarbons. Each fluorocarbon was carefully diluted with N₂, added to a glass cell, and spectroscopically analyzed at various pressures. All fluorinated hydrocarbon reagents were purchased from F2 Chemicals Ltd, stored under refrigeration, and used as received. Of all the samples, the 1,1,2,2,3,4-Hexafluoro-3,4-bis(tri-fluoromethyl) cyclobutane (PDCB) was the only isomeric mixture, containing 97% by weight PDCB and 3% 1,1,2,3,3,4-Hexafluoro-2,4-bis(tri-fluoromethyl)cyclobutane. The vacuum apparatus was modified to minimize the amount of Teflon, or polytetrafluoroethylene, exposed to the fluorinated compounds to avoid any intermolecular action between the PFC and Teflon.

2.1 Sample Preparation

This sample preparation was similar to the preparation of SO₂F₂ reported by Dr. Burkholder.¹ The strong absorption of these PFCs in the 1100–1400 cm⁻¹ region necessitated careful dilution of these compounds in an inert gas to avoid over-saturating the transition. It was also important to accurately monitor the number of PFC molecules per volume for each PFC spectra to later characterize their pressure-intensity dependencies. The vacuum apparatus is shown in Figure 1. Each PFC sample was first degassed in a 50 mL round bottom flask by three
freeze-pump-thaw cycles. After the final freeze-pump-thaw cycle, the rest of the vacuum system was purged with a small amount of the PFC sample gas and brought back down to pressures below 0.1 Torr, monitored with a 0–10 Torr Baratron. Then 2–5 Torr of the PFC sample was then introduced to the manifold and 12L glass mixing bulb. This sample is then carefully diluted using short bursts of N₂ to 740–780 Torr, re-evacuated to 100–150 Torr, and re-diluted with N₂ to 720–770 Torr. The dilution pressures were measured exactly using a 0–1000 Torr Baratron. The pressure changes from one PFC sample to the next were estimated based on spectra acquired previously by Stephen Hinton. After dilution, the mixing bulb was isolated. The 50 mL round bottom flask was removed and replaced with a 15.56 cm glass cell with KBr windows. This cell was then evacuated, purged with a small amount of sample gas, and re-evacuated. Then a portion of the diluted sample gas was added to the cell. The cell was sealed and removed from the vacuum system for FT-IR spectral analysis.

2.2 FT-IR Spectroscopy

A minimum of eight spectra were acquired for each PFC studied at varying pressures with a Bruker IFS66V/S FTIR. Background spectra, consisting of the evacuated glass cell purged with N₂, were acquired immediately prior to each set of spectra and about half way through each set of spectra. All spectra are acquired with 400 scans of the 500–8000 cm⁻¹ frequency region with a resolution of 0.25 cm⁻¹. After completion of a spectrum, the cell was again attached to the vacuum system, evacuated, and filled with a new portion of gas sample at lower pressure for the next spectrum.
Figure 1  Diagram of the vacuum system experimental setup containing a manifold connected to 0-10 and 0-1000 Torr Baratrons, 12 L mixing bulb, N\textsubscript{2} source, sample inlet, and the vacuum source. The 15.56 cm glass cell with KBr windows has been included.
References for Chapter II

CHAPTER III

RESULTS AND DISCUSSION

FT-IR spectra were acquired for six cyclic PFCs. These spectra were converted to concentration-independent cross-section format. Then GWPs and HGWPs were estimated. The cyclic PFCs studied are listed in Table 1 and their chemical structures are given in Figure 2.

Table 1  List of cyclic species with their molecular formulae and weights.

<table>
<thead>
<tr>
<th>Chemical Name [Abbreviation]</th>
<th>Structure</th>
<th>Mol. Weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfluoromethylcyclohexane [PMCH]*</td>
<td>C₆F₁₁CF₃</td>
<td>350.05</td>
</tr>
<tr>
<td>Perfluoro-1,2-dimethylcyclohexane [oPDCH]</td>
<td>C₆F₁₀(CF₃)₂</td>
<td>400.06</td>
</tr>
<tr>
<td>Perfluoro-1,3,5-trimethylcyclohexane [PTCH]</td>
<td>C₆F₉(CF₃)₃</td>
<td>450.07</td>
</tr>
<tr>
<td>1,1,2,2,3,4-Hexafluoro-3,4-bis(tri-fluoromethyl)cyclobutane [PDCB]**</td>
<td>C₄F₆(CF₃)₂</td>
<td>300.05</td>
</tr>
<tr>
<td>Perfluoromethylcyclopentane [PMCP]</td>
<td>C₅F₆CF₃</td>
<td>300.05</td>
</tr>
<tr>
<td>Perfluoro-iso-propylcyclohexane [iPPCH]</td>
<td>C₆F₁₁CF(CF₃)₂</td>
<td>450.07</td>
</tr>
</tbody>
</table>

* The 4-membered ring species, PMCH, is the only species previously studied.
** An isomeric mixture of 97% WT PDCB and 3% WT 1,2,3,3,4-Hexafluoro-2,4-bis(tri-fluoromethyl)cyclobutane was used.
Figure 2 Molecular structures of six PFCs investigated in this work. Species in the top row are similar; however, the number of CF₃ functional groups increases from left to right. Species in the bottom row increase in ring size from left to right.

3.1 Vibrational Spectra

Gas phase infrared spectra of PMCH, oPDCH, PTCH, PDCB, PMCP, and iPPCH with respective partial pressures of 0.483, 0.181, 0.463, 0.372, 0.938, and 0.314 Torr are given in Figure 3 acquired at 0.25 cm⁻¹ resolution and 295 K. These compounds show the most vibrational structure below 1300 cm⁻¹ and no detectable absorption above 1450 cm⁻¹. The most intense features are commonly found between 1100 - 1400 cm⁻¹ and represent the C–F stretching transitions. This C–F stretching assignment agrees with the assignment of similar fluorinated species.¹⁻⁸ By comparison with hydrocarbon species,⁹ the CCC ring breathing and trigonal bending transitions are assigned to bands in the 850–1050 cm⁻¹ region. Similarly, the CCC in-plane and out-of-plane bending are observed below 800 cm⁻¹.
Estimation of the GWP and HGWP values for these PFCs cannot be accomplished without accurate intensity information with respect to pressure or concentration. This accuracy was demonstrated using a linearity test by showing a linear dependence of the peak absorbance on the concentration of the PFC sample. For each PFC several peaks were chosen for comparison showing that linearity was maintained throughout the spectrum and not just at a single spectral point. Then absorbance was plotted against concentration of the sample gas and a linear fit was obtained for each peak. This test is illustrated for PTCH in Figure 4.

Figure 3 Vibrational FT-IR spectra of PMCH (a), oPDCH (b), PTCH (c), PDCB (d), PMCP (e), and iPPCH (f) acquired at 295 K with N₂ carrier gas and PFC partial pressures of 0.483, 0.181, 0.463, 0.372, 0.938, 0.314 Torr, respectively. Of the various spectra acquired for each PFC, those shown here were obtained at the greatest PFC concentration.
Figure 4  Pressure-absorbance linearity of PTCH spectra for transitions at 1282.5, 1001.1, 826.3, and 688.0 cm$^{-1}$. The peaks chosen for the linearity check are indicated with asterisks in the IR spectrum (from Figure 3c). Maximum absorbance values of each peak were plotted and linearly fitted for the spectra of PTCH at various pressures. Partial pressures have been converted to number concentrations for convenience.

The linearity test was performed 25 times among the six PFCs; approximately four times for each PFC. The $R^2$ value, a measure of the accuracy of the linear fit, for each of these 25 linear fits was greater than 0.990, indicating appropriate linear fits for all of the PFCs. The y-intercepts were statistically insignificant despite not always being within a single standard deviation of zero. This determination was justified because for 22 of the 25 plots, the y-intercept value was less than 1% the magnitude of the slope. For the other three plots, the intercept was less than 2% of the slope.
3.2 Vibrational Cross-Section

With linearity proven, the next step was to convert each spectrum from absorbance (AU) to cross section (cm$^2$ molecule$^{-1}$). This step removes the pressure dependence and allows for the averaging of spectra acquired at different pressures.

The conversion from absorbance, $A$, to cross section, $\sigma$, requires the ideal gas equation and the Beer-Lambert law. These equations are combined and written in terms of $\sigma$ in equation 1

$$\sigma = \frac{A}{P} \frac{R T}{N_a l}$$

where $A$ is the absorbance, $P$ is the pressure in Torr, $R$ is the ideal gas constant (62,364 mL Torr K$^{-1}$ mol$^{-1}$), $T$ is 295 K, $N_a$ is Avogadro's number and $l$ is the path length (15.56 cm$^{-1}$).

Using cross-section, the three highest pressure spectra became nearly identical above 650 cm$^{-1}$. To minimize error derived from the signal-to-noise ratio during the averaging of the cross section spectra, only the three spectra with the greatest pressure and best signal to noise were used for each PFC.

3.3 Radiative Efficiency

Calculating the radiative efficiency ($RE$) from an averaged cross-section spectrum is difficult. However, the $RE$ can be accurately determined using the method presented by Pinnock et al.$^8$ In this method, the 0–2500 cm$^{-1}$ spectral range is divided into 250 intervals, each spanning 10 cm$^{-1}$. The cross section values in each of these intervals are then averaged to give 250 values representing the 0-2500 cm$^{-1}$ range. Data gathered at very low wavenumbers are neglected.
because of losses in the spectral sensitivity in that region. Thus, the 650–2500 cm\(^{-1}\) region was examined, which corresponds to 185 averaged values instead of 250. The resulting radiative efficiency values are therefore the lower limits of the absolute values. Equation 2 was used with these 185 averaged values to calculate the radiative efficiency. It is given as

\[
RE = \sum_{i=65}^{250} 10(\text{cm}^{-1}) \sigma_{av}^i F_{\sigma}^i
\]

where \(F_{\sigma}^i\) is the radiative efficiency per unit cross section with units of W m\(^{-2}\) (cm\(^{-1}\))\(^{-1}\) (10\(^{-15}\) cm\(^2\) molecule\(^{-1}\))\(^{-1}\), which is derived from the solar spectrum and reported by Pinnock.\(^8\) Once the \(RE\) values were obtained, all that remains in obtaining GWPs was to compare observed \(RE\) values, radiative lifetimes, and PFC molecular weights to those of a standard.

<table>
<thead>
<tr>
<th>Name</th>
<th>Radiative Efficiency (W m(^{-2}) ppb(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>oPDCH</td>
<td>0.334</td>
</tr>
<tr>
<td>iPPCH</td>
<td>0.248</td>
</tr>
<tr>
<td>PDCB</td>
<td>0.212</td>
</tr>
<tr>
<td>PMCH</td>
<td>0.242</td>
</tr>
<tr>
<td>PMCP</td>
<td>0.215</td>
</tr>
<tr>
<td>PTCH</td>
<td>0.256</td>
</tr>
</tbody>
</table>

### 3.4 Atmospheric Lifetime

The atmospheric radiative lifetimes of most of the PFCs in this study have not been previously determined. However, the lifetimes and decay pathways of (CF\(_3\))\(_2\)-C\(_4\)F\(_6\) (PDCB) and
simpler PFCs such as $c$-$C_4F_8$, $C_5F_{12}$, $C_6F_{14}$, and $CF_4$ have been calculated.\textsuperscript{10} For PFCs, Lyman-$\alpha$ decay was found to be the primary decay pathway ($\geq 99\%$ where reported). Also, trends were observed that lifetime decreased with size of the PFC and appeared shorter for cyclic molecules than for their linear counterparts. Additionally, their PFC lifetimes for $CF_4$, $C_2F_6$, $c$-$C_4F_8$, $C_4F_{10}$, $C_5F_{12}$, and $(CF_3)_2c$-$C_4F_6$ are accepted community-wide and are used in the calculation and report of corresponding GWPs in the latest IPCC report.\textsuperscript{13}

The atmospheric lifetime of 2900 years was chosen for every cyclic PFC studied here. This is the best-estimate lifetime determined for PDCB. The previously referenced\textsuperscript{10} trends would suggest lifetimes shorter than that of PDCB for most cyclic PFCs but there is insufficient additional data to extrapolate how lifetime would change from 2900 years as the PFC becomes more complex than PDCB.

While a 2900-year atmospheric lifetime was assumed, the actual lifetimes could range anywhere from around 1000 years to over 5000 years. A lifetime discrepancy study was performed to examine the uncertainty introduced to GWP/HGWP values based on this range of possible lifetimes (Appendix A). This study shows that the maximum possible deviation of HGWP values from the 2900-year lifetime when considering the 20, 100, and 500 year time horizons are 0.65\%, 3.24\%, and 15.43\%, respectively.

3.5 \textit{Global Warming Potential}

The radiative efficiency values, atmospheric lifetimes, and molecular weights of these molecules may be compared to CO\textsubscript{2} to obtain the GWPs or can be compared to CFC-11 (trichlorofluoromethane) to obtain the HGWPs. The equations used for this calculation are
where $RE_i$ is the radiative efficiency, $\tau_i$ is the atmospheric radiative lifetime, and $M_i$ is the molar mass of species $i$. Also, $t$ is the time horizon of interest. Conventionally, the GWP and HGWP values are found for the 20-year, 100-year, and 500-year time horizons to illustrate the short-, mid-, and long-term effects of the sample gas.

Calculating the HGWP is simpler than the GWP because all the terms remain constant when changing the time horizon. There have been difficulties in the estimation of the atmospheric lifetime of CO$_2$ resulting, in large part, from the CO$_2$ transfers from the atmosphere to ocean and biosphere sinks. The CO$_2$ lifetimes used here were calculated from the parameters reported in table TS.2 of the 2007 IPCC Report. The GWPs, radiative efficiencies, molar masses, and known lifetimes were used with Equation 4 to calculate CO$_2$ lifetimes for each time horizon. This calculation was performed for a number of CFCs (CFC-11, 12, 13, and 113) and PFCs (PFC-218, 318, 3-1-10, 4-1-12, 5-1-14, and SF$_5$CF$_3$) listed in the report. The resulting CO$_2$ lifetimes generally agreed to within 2% for each time horizon, so the CO$_2$ lifetimes were then averaged for each time horizon. Averaged CO$_2$ lifetimes were 11.36 years, 44.19 years, and 152.7 years for the 20-, 100-, and 500-year time horizons, respectively. The GWPs and HGWPs of the studied cyclic PFCs with associated uncertainties and lifetimes are reported in Table 3.
Table 3 Calculated GWP and HGWP values for oPDCH, iPPCH, PDCB, PMCH, PMCP, and PTCH with lifetimes.

<table>
<thead>
<tr>
<th>Name</th>
<th>Lifetime (years)</th>
<th>HGWP (Relative to CFC-11)</th>
<th>GWP (Relative to CO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20-year horizon</td>
<td>100-year horizon</td>
</tr>
<tr>
<td>oPDCH</td>
<td>2900</td>
<td>0.566</td>
<td>1.12</td>
</tr>
<tr>
<td>iPPCH</td>
<td>2900</td>
<td>0.374</td>
<td>0.742</td>
</tr>
<tr>
<td>PDCB</td>
<td>2900</td>
<td>0.479</td>
<td>0.951</td>
</tr>
<tr>
<td>PMCH</td>
<td>2900</td>
<td>0.469</td>
<td>0.931</td>
</tr>
<tr>
<td>PMCP</td>
<td>2900</td>
<td>0.487</td>
<td>0.966</td>
</tr>
<tr>
<td>PTCH</td>
<td>2900</td>
<td>0.386</td>
<td>0.766</td>
</tr>
</tbody>
</table>

3.6 Error Analysis

The actual estimation method of converting the cross-section spectra to radiative efficiency was probably the largest source of error since it is an estimative approach and the entire 0–650 cm⁻¹ region was neglected. However, this error is not easy to quantify. An error analysis was attempted by first considering errors in the calculated cross-sections. The cross-section uncertainty was derived from the average baseline noise of 0.00021 AU (acquired from the 1500–2500 cm⁻¹ region of a single oPDCH spectrum), uncertainty in pressure measurements (six measurements of 0.0032–0.0213 Torr from two Baratrons during the dilution process), the uncertainty in temperature of approximately 1.0 K over the duration of the experiment, and the uncertainty in cell path length of 0.01 mm. This uncertainty was calculated for each spectral point between 650 cm⁻¹ and 2500 cm⁻¹ for each of the three spectra used for each PFC.
Second, the uncertainty in radiative efficiency was calculated for each PFC. This calculation required estimation of the uncertainty for literature-acquired $F_{\text{eq}}$ values. This uncertainty was estimated at 0.001 W m$^{-2}$ (cm$^{-1}$)$^{-1}$ (10$^{-15}$ cm$^2$ molecule$^{-1}$)$^{-1}$. Also required was the uncertainty from averaging each cross-section spectrum into the 185 10-cm$^{-1}$ sections followed by averaging the corresponding cross section values across the three spectra for each PFC.

Finally, the GWP and HGWP uncertainties were calculated based on the uncertainties for instantaneous radiative forcing values, molar masses, and lifetimes. These values for CFC-11, estimated from the 2007 IPCC report,$^{12}$ are 0.005 W m$^{-2}$ ppb$^{-1}$, 0.005 g/mol, and 0.5 year, respectively. For CO$_2$ they are 5×10$^{-7}$ W m$^{-2}$ ppb$^{-1}$, 0.005 g/mol, and 0.1 year. The uncertainty in molar masses of the fluorocarbons was assumed to be 0.005 g/mol and the uncertainty in lifetimes was assumed to be 200 years. Based on these values and everything considered, the most significant source of error was the uncertainty estimated for the instantaneous radiative forcing of the standards, CO$_2$ and CFC-11. As a reminder, this excludes the radiative efficiency estimation discussed at the beginning of this section.
References for Chapter III


CHAPTER IV

CONCLUSION

In this study we acquire accurate intensity FT-IR spectra of six long-lived fluorinated compounds at 8–10 partial pressures each, ranging from 17.0 mTorr to 0.938 Torr. These spectra are reported in cross-sectional format within the appendix. We use these spectra and estimated atmospheric lifetimes to obtain GWP and HGWP values at the 20-, 100-, and 500-year time horizons. These GWPs ranged from 3700 to 5600 for the 20-year horizon, 4400 to 6600 for the 100-year horizon, and 5500 to 8200 for the 500-year horizon. The calculated uncertainty and the lifetime dependence increase with the time horizon, but to differing extents. Uncertainties for these GWP/HGWP values were determined to be approximately 5–8% for the 20- and 100-year horizons and up to 15% for the 500-year horizon. The large possible deviation at the 500-year horizon results from the lifetime dependence as shown in the lifetime discrepancy study.

Comparison to the GWPs of other climate forcing agents reveals the potency of PFCs as greenhouse gases. As the standard for comparison, the GWP of carbon dioxide is unity across all time horizons. Most CFCs have comparable GWPs to these PCSs at the 20-year time horizon and decrease as the time horizon expands.\(^1\) HFCs tend to have GWPs slightly lower than CFCs and PFCs and tend to drop off at increased time horizons.\(^1\) PFCs are different than both CFCs and HFCs, since their GWPs increase as the time horizon expands. The average change in GWPs going from the 20-year to 500-year time horizon for CFCs shows almost a 12% decrease in GWPs. The same comparison of PFCs to HFCs reveals a decrease of 69%. Comparison of PFCs
to hydrochlorofluorocarbons shows that a decrease of 89% is observed. For PFCs, the GWPs increase by 101% going from the 20-year to 500-year time horizon. At larger time horizon, the GWPs of these PFCs far outweigh that of similar CFCs and HFCs.

Comparison of cyclic PFCs to linear PFCs reported in the 2007 IPCC report yields interesting results. Like the linear PFCs, the radiative efficiencies of these cyclic species generally increase as the molar mass increases. However, the cyclic species have radiative efficiencies that are significantly smaller than linear species of similar mass. Neglecting the 0-650 cm$^{-1}$ spectral range contributes to this difference but not in a significant way; for these PFCs, there are few observed bands in this region and they have low intensity compared to peaks found near 1200 cm$^{-1}$. The lower radiative efficiencies and lifetimes of cyclic PFCs compared with their linear counterparts of similar mass result in decreased GWPs.
References for Chapter IV

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A  *Atmospheric Lifetime Study*

The lifetimes chosen for these cyclic PFCs are based on best estimate lifetimes, not lower limit lifetimes. The shortest best estimate lifetime of a cyclic PFC found in the literature is 2900 years.\(^1,2\) Since the atmospheric lifetimes of the cyclic PFCs studied here may be shorter than 2900 years, as our lower limit we will consider the lifetime of the largest PFC listed in the fourth IPCC report, PFC-9-1-18.\(^1\) This molecule is a noncyclic molecule but is larger than any cyclic PFC examined here and is the lowest PFC lifetime included in the report. The upper limit is far less significant because the equations used for GWP and HGWP calculations set a horizontal asymptote based on the time horizon used. The upper limit is arbitrarily set to 5000 years. Results will be quite comparable between these six PFCs since identical lifetimes are chosen. Therefore iPPCH was chosen as the species to use in this lifetime study.

Possible deviations only appear significant at the 500-year time horizon where the lower limit lifetime is only twice the time horizon (Figure 5). The HGWP$s for the 20-year horizon were 0.372, 0.374, and 0.375 for atmospheric lifetimes of 1000, 2900, and 5000 years, respectively. That is a 0.65% difference between the lower limit and the 2900 year lifetime and a 0.14% difference between the 2900 year lifetime and 5000 years. The 100-year horizon revealed a 3.2% difference for the lower limit and a 0.72% difference for the upper limit. At the 500-year horizon we found a 15% between the lower lifetime limit and 2900 years while the upper limit showed a difference of 3.5%. Considering that radiative efficiencies and lifetimes have been
almost exclusively reported with only two significant figures, the differences in HGWPs for the 20- and 100-year horizons are negligible. Even with deviations up to approximately 15%, these HGWPs/GWPs at the 500-year horizon remain qualitatively comparable to that of other species.

Figure 5  Influence of oPDCH lifetime on calculated HGWP for 20-, 100-, and 500-year time horizons. Circles represent the 2900 year lifetime used for the cyclic PFCs. The boxes are results based on lowest best estimate lifetime of 2600 years. The vertical line at 1000 years is the lower limit HGWPs. It can be observed that the 20- and 100-year time horizons almost reach their asymptotic limit by the 1000 year lower limit.
References for Appendix A


Figure 6  Full Page Vibrational FT-IR Spectrum of PMCH at partial pressure of 0.483 torr in N₂ carrier gas.
Figure 7  Full Page Vibrational FT-IR Spectrum of oPDCH at partial pressure of 0.181 torr in N₂ carrier gas.
Figure 8. Full Page Vibrational FT-IR Spectrum of PTCH at partial pressure of 0.463 torr in N₂ carrier gas.
Figure 9  Full Page Vibrational FT-IR Spectrum of PDCB at partial pressure of 0.372 torr in N\textsubscript{2} carrier gas.
Figure 10  Full Page Vibrational FT-IR Spectrum of PMCP at partial pressure of 0.938 torr in N$_2$ carrier gas.
Figure 11  Full Page Vibrational FT-IR Spectrum of iPPCH at partial pressure of 0.314 torr in N\textsubscript{2} carrier gas.
Figure 12  Full Page Vibrational FT-IR Spectra of PMCH at partial pressures of 483 (greatest absorbance), 443, 389, 342, 291, 248, 217, 168, 128, 82.5, and 36.0 mTorr (least absorbance) in N$_2$ carrier gas.
Figure 13  Full Page Vibrational FT-IR Spectra of oPDCH at partial pressures of 181 (greatest absorbance), 155, 141, 116, 90.8, 71.1, 40.9, and 17.0 mTorr (least absorbance) in N$_2$ carrier gas.
Figure 14  Full Page Vibrational FT-IR Spectra of PTCH at partial pressures of 463 (greatest absorbance), 409, 357, 306, 258, 198, 150, 94.2, and 36.8 mTorr (least absorbance) in N$_2$ carrier gas.
Figure 15  Full Page Vibrational FT-IR Spectra of PDCB at partial pressures of 372 (greatest absorbance), 324, 264, 202, 172, 137, 101, 64.7, and 29.9 mTorr (least absorbance) in N₂ carrier gas.
Figure 16 Full Page Vibrational FT-IR Spectra of PMCP at partial pressures of 938 (greatest absorbance), 823, 679, 596, 506, 424, 316, 227, and 144 mTorr (least absorbance) in N$_2$ carrier gas.
Figure 17  Full Page Vibrational FT-IR Spectra of iPPCH at partial pressures of 314 (greatest absorbance), 280, 244, 204, 165, 139, 98.8, 67.7, and 24.3 mTorr (least absorbance) in N$_2$ carrier gas.