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**Infrared Absorption Strengths
of Potential Gaseous Diffusion Plant Coolants
and Related Reaction Products**

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E.C.Angel

Technical Analysis and Operations Division

May 1993

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OF POTENTIAL GASEOUS DIFFUSION PLANT COOLANTS
AND RELATED REACTION PRODUCTS

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ABSTRACT

The DOE gaseous diffusion plant complex makes extensive use of CFC-114 as a primary coolant. As this material is scheduled for production curtailment within the next few years, a search for substitutes is underway, and apparently workable alternatives have been found and are under testing. The presently favored substitutes, FC-c318 and FC-3110, satisfy ozone depletion and operational chemical compatibility concerns, but will be long-lived greenhouse gases, and thus may be regulated on that basis in the future. A further search is therefore underway for compounds with shorter atmospheric lifetimes which could otherwise satisfy operational physical and chemical requirements. A number of such candidates are in the process of being screened for chemical compatibility in a fluorinating environment. This document presents infrared spectral data developed and used in that study for candidates recently examined, and also for many of their fluorination reaction products. The data include gas-phase infrared spectra, quantitative peak intensities as a function of partial pressure, and integrated absorbance strength in the IR-transparent atmospheric window of interest to global warming modeling. Combining this last property with literature or estimated atmospheric lifetimes, rough estimates of global warming potential for these compounds are also presented.

INTRODUCTION

Evidence supporting the theory that chlorofluorocarbons (CFCs) contribute to reduction of ozone concentration in the stratosphere has resulted in international action to phase-out production of these compounds. The planned production curtailment of CFCs in turn has significant implications for the operation of the United States Department of Energy's gaseous diffusion plant (GDP) uranium enrichment complex, since one of the regulated materials, CFC-114, is the primary coolant for the gaseous diffusion plants.

Most proposed commercial substitutes for CFCs are compounds termed HCFCs (hydrochlorofluorocarbons, themselves scheduled for later curtailment) and HFCs (hydrofluorocarbons). These compound classes are chemically similar to CFCs or PFCs (perfluorocarbons, i.e. fully fluorinated hydrocarbons), but differ in that they contain one or more hydrogen atoms in place of halogens. The addition of hydrogen makes these compounds susceptible to reaction with hydroxyl radicals in the lower atmosphere, thus leading to their earlier removal, shorter atmospheric lifetime, and diminished ozone depletion and global warming potential relative to CFCs.

Unfortunately, the gaseous diffusion complex imposes requirements on its coolant that are not generally found in commercial cooling applications. Most notable is that the coolant must possess a reasonable degree of chemical compatibility with UF_6 in the event of coolant inleakage into the UF_6 stream. UF_6 is a fairly potent fluorinating agent, so the possibility of rapid, exothermic, gas-phase or gas-surface reactions must be considered. In addition, gaseous diffusion equipment is routinely subject to off-line chemical cleanup treatments with more potent fluorinating agents, such as F_2 and ClF_3 , so the reactivity of residual coolant with these materials should also be minimal.

Because of this unique reactivity requirement, Martin Marietta Energy Systems, which operates the two diffusion plants under contract with DOE, has initiated contacts with potential producers of substitute coolants. The only candidate materials which could be produced in the quantities needed and which clearly satisfied the chemical compatibility requirement are $\text{c-C}_4\text{F}_8$ (also known as FC-c318 or FC-318), $\text{n-C}_4\text{F}_{10}$ (also known as FC-3110 or FC-31-10). These two candidates are both perfluorocarbons. They are strong infrared absorbers and are estimated to be long-lived in the atmosphere¹. As such, they will be potent greenhouse gases. These compounds are sometimes locally termed "second generation coolants" in contrast to the "first generation" CFC-114. It would obviously be desirable to find alternate

materials with shorter atmospheric lifetimes, but which are otherwise suitable as coolants.

Work to date on HFCs and HFEs (hydrofluoroethers) (locally referred to as "3rd generation coolants") strongly suggests that short atmospheric lifetime is closely related to reactivity in a fluorinating environment² -- that is to say, greater F₂ reactivity implies shorter atmospheric lifetime. An absolute criterion on the tolerable coolant-UF₆ reaction rate has not been established. Establishment of such a criterion would require arriving at a compromise acceptable to many groups representing numerous concerns (e.g. long-term environmental impact, short-term operational safety, nuclear criticality, operational efficiency, industrial hygiene, and others). While it is not clear what the outcome of such a compromise would be, it *is* clear that a necessary piece of information in its development would be the reactivity of coolants under consideration. Accordingly, a number of compounds likely to have good coolant properties have been procured and are undergoing reactivity testing.

The method used for reactivity testing^{3,4,5,6} utilizes infrared (IR) spectroscopy to quantitatively follow gas concentrations during the course of an experiment. It is therefore necessary to take spectra of compounds of interest for calibration purposes. This report displays selected calibration spectra and lists specific intensities for the major absorption peaks of the compounds under consideration. We have collected this information here partly to document IR information for the use of ourselves and others doing related work in the GDP coolant replacement effort.

One facet of the infrared spectra we have generated is also of use in the evaluation of environmental impacts of coolants. This property is the absorption strength in that part of the infrared spectrum which is more or less transparent in the atmosphere. The integrated absorption strength of a compound is roughly proportional to the global warming that would be induced by presence in the atmosphere of a given quantity of that compound. We list this value for each of the compounds examined. Where atmospheric lifetime estimates are available in the literature, we also use them to make an approximate estimate of the GWP (global warming potential) of these compounds. Where such information is not available, we offer tentative estimates based on chemical similarity arguments.

The IR data presented here were developed as a part of the previously mentioned study of gas-phase reactivity of potential coolants. Measurement of IR spectra is not the primary goal of the study, but a means to an end. As such

the experimental system is not optimized for precise IR spectral measurement. Some compromises in apparatus construction are necessary to permit it to accomplish its reaction kinetics tasks, and occur at the expense of introducing uncertainty in the IR calibration results. We have attempted to be careful to recognize and record systematic and random errors that may affect IR measurements. Detailed error analysis is presented in the Appendix.

Compounds examined include both prospective coolants and their fluorination reaction products. From the perspective of our kinetics studies, the reaction product spectra are useful for following the course of the reaction with UF_6 or other fluorinating agents. From an environmental perspective, their spectral properties are also important for the reason that a (small) fraction of the diffusion plants' fugitive coolant losses are to the UF_6 stream. By the time this fraction of the coolant is purged from the UF_6 stream, it will have had a good deal of time to react with UF_6 . By the time it escapes to the atmosphere, some or all of it may be converted to these reaction products. For reactive coolants, this small fraction must be considered in evaluation of global warming impact, since it is quite plausible for, say, 2% of the coolant, upon fluorination by UF_6 , to have a larger global warming impact than the 98% that is lost directly to the atmosphere.

For convenience, all the various varieties of fluorocarbons studied here (CFCs, HFCs, HFEs, PFCs, HCFCs, PFEs) will be referred to as fluorocarbons or FCs.

EXPERIMENTAL

The experimental apparatus in which these calibrations were performed is described in more detail in Reference 3. Briefly, it consists of a closed loop of stainless steel and monel tubing around which the gases under study are driven by a metal bellows pump. The majority of the volume of this loop is contained in a 5.1 cm diameter nickel reaction tube situated in a muffle furnace. The circulating gas also passes through an IR gas cell, which is situated in a Nicolet 5DXB Fourier Transform Infrared Spectrometer (FTIR). The cell has a nominal 2.16 cm optical path length, and is equipped with AgCl windows. Under vacuum or pressure, the AgCl windows are subject to a moderate degree of physical distortion, which can change the IR path length through the cell, of which more will be said later. IR Spectra were taken at 4 cm^{-1} resolution; 50 scans were co-added to yield each single spectrum.

The apparatus also contains several auxiliary manifolds for adding and remov-

ing reactant or cleanup gases, and for pumping the system to high vacuum. Evacuation of reactive gases after cleanup or an experiment is done through a chemical trap containing activated alumina and soda lime. High vacuum is achieved with a Balzers TPU050 turbomolecular pump typically capable of reducing the system pressure to 10^{-5} Torr. Gas pressures are measured with three MKS Model 310 Baratron (capacitance manometer) pressure transducers with ranges of 0-100 Torr and quoted accuracy of 0.08 Torr.

Materials were obtained from a variety of sources. For the most part, the materials examined will be referred to by their coolant codes. As this is can be somewhat cryptic, the chemical formulae of the compounds examined are listed in Table 1. HCFC-124 was provided by Allied Signal, Inc., and had a nominal purity of 99.5%, with the primary impurities being related HCFCs. The sample of FC-3110 was provided by 3M corporation, with a nominal purity of 96%, the primary impurities being related fluorocarbons. The sample of FC-c318 was provided by E. I. DuPont de Nemours, with a nominal purity of 99.94%. HFC-227ea, HFC-236ea, HFC-236fa, FC-218 were purchased from PCR, Inc. Purities were listed as being between 97-99%. F-tetrahydrofuran, f-methyl propyl ether, HFE-134, HFE-227ca, and 3-H-f oxetane were provided by Prof. J. L. Adcock et al. at the University of Tennessee, Knoxville, TN. CFC-114, CFC-115, and FC-14 were purchased from Matheson; the purities listed were 95%, 98%, and 99.7%, respectively. The FC-116 spectra derive from local spectral archives dating back 10 years taken of gas purchased from Matheson Gas Products, with a catalog-specified purity of 99.6%.

The general procedure for carrying out an IR calibration is to:

- (1) evacuate the system
- (2) Test for or remove non-condensable impurities (discussed below)
- (3) introduce the fluorocarbon gas at a partial pressure such that no peaks are saturated (i.e. completely opaque at any IR frequency of interest)
- (4) obtain and record a spectrum
- (5) reduce the partial pressure of the fluorocarbon
- (6) repeat steps 4 and 5 several times.
- (7) Use linear regression to fit data to Beer's Law (discussed below)

The physical conditions of each calibration are indicated in Table 2. The calibrations were done "neat", which is to say without intentional dilution of the fluorocarbon under study. Multiple data points were obtained by successively removing gas, in order to obtain spectra at a range of pressures.

Table 1: Chemical Formulae, Coolant Codes and Abbreviations

CFC-114	$\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}$	CFC-115	$\text{CF}_3-\text{CF}_2\text{Cl}$
FC-3110	$\text{CF}_3-\text{CF}_2-\text{CF}_2-\text{CF}_3$	FC-14	CF_4
FC-c318	$\begin{array}{c} \text{CF}_2-\text{CF}_2 \\ \quad \\ \text{CF}_2-\text{CF}_2 \end{array}$	FC-116	CF_3-CF_3
		FC-218	$\text{CF}_3-\text{CF}_2-\text{CF}_3$
f-THF	$\begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{CF}_2 \quad \text{CF}_2 \\ \quad \\ \text{CF}_2-\text{CF}_2 \end{array}$	HCFC-124	CF_3-CFHCl
		HFC-236ea	$\text{CF}_3-\text{CFH}-\text{CF}_2\text{H}$
f MPE	$\text{CF}_3-\text{O}-\text{CF}_2-\text{CF}_2-\text{CF}_3$	HFC-236fa	$\text{CF}_3-\text{CH}_2-\text{CF}_3$
		HFC-227ea	$\text{CF}_3-\text{CFH}-\text{CF}_3$
3H f-Oxetane	$\begin{array}{c} \text{CF}_2-\text{O} \\ \quad \\ \text{CFH}-\text{CF}_2 \end{array}$	HFE-134	$\text{CF}_2\text{H}-\text{O}-\text{CF}_2\text{H}$
		HFE-227ca	$\text{CF}_3-\text{O}-\text{CF}_2-\text{CF}_2\text{H}$
f-Oxetane	$\begin{array}{c} \text{CF}_2-\text{O} \\ \quad \\ \text{CF}_2-\text{CF}_2 \end{array}$		

The gas for calibration was taken from the gas phase of the sample container. Where liquid is present in the sample container, the gas phase will generally be significantly enriched in any non-condensable impurities. To avoid counting the partial pressure due to these impurities as due to the fluorocarbon under examination, in most cases an ancillary procedure was performed to determine the quantity of non-condensable material present in the gas. It was reasoned that plausible inadvertent diluents would either be infrared active (such as CO_2) and thus be evident on the infrared spectrum, or would still have a significant vapor pressure at liquid nitrogen temperature (e.g. N_2 , O_2 or Ar). The system loop was charged with approximately 10 to 20 Torr of the fluorocarbon gas, and a section of the small-diameter tubing was chilled with liquid nitrogen. The loop pressure was monitored during this process. In addition, infrared spectra were taken both in the "warm" and in the "cold" configuration. Ideally, the pressure should drop to essentially zero and all the

CFC would freeze in the cold section of the loop. If a significant concentration of non-condensable gas were present, however, it could form a diffusion block in the vicinity of the cold area. Infrared spectra were taken to provide a quantification of the amount of fluorocarbon left in the majority of the system volume after in the cold condition.

In most cases, the calculated inert gas content of the samples ranged from less than 0.1% to about 10%. Partial pressures used in IR calibrations incorporate this correction. In a few cases it was significantly higher, and for these, rather than estimating the content, we pumped the inert constituents off while the fluorocarbon was frozen.

Spectral results are plotted in absorbance units. Absorbance is defined as:

$$A \equiv \log_{10} I / I_0 \quad (\text{Eqn 1})$$

where I is the infrared intensity (at a given wavelength) with the gas sample present, and I_0 is the corresponding intensity with no sample present.

Absorbance units are convenient to use because they are proportional to the gas concentration (assuming Beer's Law holds). An "absorbance unit" (or AU) is dimensionless, and is the absorbance that diminishes the IR intensity by a factor of 10. In the literature, absorbance is sometimes calculated as a natural logarithm, rather than a base 10 logarithm, often without clarification of that point. To avoid confusion on this point, we will use the units AU_{10} and AU_e to indicate base 10 and base e absorbance units, respectively.

Calculation of absorbance (base 10) is done automatically by software inherent to the Nicolet spectrometer. This is done by ratioing absolute measured IR intensities in the sample spectrum and a background spectrum taken of the evacuated cell at some other time (usually just before the experiment). Since the sample and background spectra are not taken simultaneously, the possibility always exists that the spectrometer behavior will drift slightly. This might be due to the IR source changing intensity or focus, the IR windows physically or chemically changing, or the detector sensitivity changing. While not major problems, anything occurring along these lines can have the effect of causing the baseline to drift, which is to say that portions of the spectrum in which the sample is actually completely transparent may shift their absorbance away from $A=0$. Such baseline drift can be frequency dependent. To correct for this, we typically take an absorbance reading in an apparently transparent region near the peaks of interest, and correct the peak absorbances for this baseline value.

Table 2: Experimental Conditions of IR Calibrations

Coolant Compound	T(°C)	Path length cm	Inert Gas Content ¹	Flow?	Notes
<u>"1st Generation" Coolant</u>					
CFC-114	30	2	0.05%	yes	
<u>"2nd Generation" Candidates</u>					
FC-3110	30	1.98	0	no	[2]
FC-c318	28	2	0	yes	[2]
f THF	33	2	0.47%	yes	
f MPE	33	2	5.67%	yes	
<u>"3rd Generation" Candidates</u>					
HFC-227ea	36	2	17.08%	yes	
HFC-236ea	31	2	17.25%	yes	
HFC-236fa	30	2	16.00%	yes	
HFE-134	30	2	9.17%	yes	
HFE-227ca	30	2	0	yes	[2]
3H f Oxetane	32	2	2.20%	yes	
HCFC-124	30	2	0.33%	yes	
<u>Long-lived Fluorination Products</u>					
FC-14	30	2	4.69%	yes	
FC-116	--	7.62	---	no	[4]
FC-218	30	2	9.56%	yes	
f Oxetane	30	2	---	yes	[3]
CFC-115	30	2	2.58%	yes	

Notes:

- [1] Inert gas content derived from liquid N₂ freezeout of condensables.
 [2] inert gases removed before calibration
 [3] derived from mass balance in F₂ experiment
 [4] from archival spectra.

At a given frequency, partial pressures of infrared-active gases are related to absorbance by Beer's Law:

$$P = SA/l \quad (\text{Eqn 2})$$

where P = partial pressure, l is the IR path length through the gas sample, S is the specific absorbance for the peak in question, and A is the absorbance of that peak. We experimentally measure all these parameters except S . To obtain S , we use linear regression, fitting the experimental data for each peak to

$$Pl = SA + b \quad (\text{Eqn 3})$$

The regression gives values and standard deviation estimates for S and b . We do not force the fit to go through zero; the parameter b , which will ideally be near zero, contains any systematic error in either the IR baseline or in the pressure gauge zero offset.

The overall IR absorption strength of a compound is a parameter of interest in modeling global warming. In atmospheric chemistry literature, the region of interest is that lying between about 440 to 1535 cm^{-1} , which roughly corresponds to a region of the atmosphere's spectrum that is fairly transparent in the IR. The integrated absorbance of the compounds we have studied can be readily obtained from our spectra. The Nicolet 5DXB has a facility for computing integrated absorbance. We list the integrated absorbance values along with the other peak intensities in tables to follow. These values can be fit just like the peak absorbances to give an integrated IR intensity per unit pressure and pathlength. For direct comparison with literature values, we have converted these strengths from a base 10 logarithm basis to a natural logarithm basis.

It would probably be more accurate to compute IR band calibrations as a function of molar gas density rather than partial pressure. During calibration (and also during experiments), the IR cell temperature in our system is always between approximately 25°C and 32°C, (specific temperatures are reported in Table 2). The ideal gas law can be easily used to convert from a partial pressure basis to a molar density basis. In any case, literature values of integrated IR absorption strength include partial pressure, not density, units and that example will be followed here.

RESULTS

Sample IR spectra are presented in Figures 1 through 17 for each compound examined in this work. IR calibration results are listed in Tables 3 through 20. These tables list the peak frequency in cm^{-1} and the fitted specific absorbance, S , for the most prominent peaks. S is in units of $\text{Torr-cm}/\text{AU}_{10}$. Each fit utilized 4 data points unless otherwise indicated in the tables. The standard deviation estimate for S is also listed; it is based only on the goodness of fit (i.e. not incorporating any estimates of systematic or random error in the data that was fit). Also shown for each fit is the computed intercept, b , and its standard deviation estimate. To use the strengths in this table, one should use the Beer's Law formula given in Equation 2, above. The intercept should be ignored, as it is likely a reflection of various temporary instrument zero offsets. At the end of each table a similar result is given for the integrated absorbance, in units of $\text{AU}_e/\text{atm-cm}^2$.

A number of factors contribute to possible systematic errors in the results presented above. The most significant factor is uncertainty in the pathlength due to variable warping of the ductile IR windows. This can impose an uncertainty of approximately 5% on the resulting peak and overall strengths. Other errors are of lesser magnitude. These are discussed in some detail in the Appendix.

0 CFC114 APPROX. 10 TORR CIRCULATED AT 30C <CFC114.100> 05 Mar 93 11.27.1

Figure 1: Sample IR Spectrum of CFC-114

Figure 2: Sample IR Spectrum of FC-3110

FC-c318 APPROX. 10 TORR C4F8 CIRCULATED AT 28C <FC318.100> 12 Mar 9

Figure 3: Sample IR Spectrum of FC-c318

Figure 4: Sample IR Spectrum of f-Tetrahydrofuran

0 PERFLUORINATED METHYL PROPYL ETHER 10 TORR AT R.T. (33C) 10 JUN 82 1

Figure 5: Sample IR Spectrum of f-methyl propyl ether

2H-HEPTAFLUOROPROPANE APPROX. 10 TORR CIRCU. R. T. (36C) 12 AUG 82 1

Figure 6: Sample IR Spectrum of HFC-227ea

1. 1. 1. 2. 3. 3-HEXAFLUOROPROPANE APPROX. 10 TORR CIRCU. R.T. (31C)

Figure 7: Sample IR Spectrum of HFC-236ea

1.1.1.3.3.3 HEXAFLUOROPROPANE APPROX. 10 TORR CIRCULATED AT R.T. (29C)

Figure 8: Sample IR Spectrum of HFC-236fa

0.1 BIS-DIFLUOROMETHYL-ETHER APPROX. 10 TORR AT R. T. (30C) 24 Sep 92

Figure 9: Sample IR Spectrum of HFE-134

Figure 10: Sample IR Spectrum of HFE-227ca

Figure 11: Sample IR Spectrum of 3-H f-Oxetane

Figure 12: Sample IR Spectrum of HCFC-124

0 FC-14 (FC14.50) APPROX. 5 TORR FC-14 CIRCULATED AT 30C 29 Feb 93

Figure 13: Sample IR Spectrum of FC-14

Figure 14: Sample IR Spectrum of FC-116

FC218 APPROX. 5 TORR CIRCULATED AT 30C (FC218.50) 09 Mar 93 14.16

Figure 15: Sample IR Spectrum of FC-218

Figure 16: Sample IR Spectrum of f-Oxetane

CFC115 APPROX. 10 TORR CIRCULATED AT 30C (CFC115.100) 08 Mar 93

Figure 17: Sample IR Spectrum of CFC-115

IR Band Strength Tables

1st Generation Coolant

Table 3: CFC-114

Peak freq. cm^{-1}	S Torr-cm/AU ₁₀	σ_s	b	σ_b
847	59.6 ±	0.5	-0.032 ±	0.083
886	271.7 ±	5.3	0.166 ±	0.195
922	70.6 ±	0.4	0.033 ±	0.053
945	499.6 ±	11.0	0.488 ±	0.212
1052	51.3 ±	0.15	0.022 ±	0.029
1138	56.8 ±	0.16	0.007 ±	0.029
1185	36.1 ±	0.10	-0.029 ±	0.029
1194	39.7 ±	0.14	-0.036 ±	0.036
1231	294.5 ±	2.7	0.355 ±	0.088
1272	198.8 ±	1.2	0.359 ±	0.060
1292	772.7 ±	20.9	1.473 ±	0.240

Integral 440-1535 cm^{-1} 4197 ± 12 AU₀/atm cm^2

Notes applicable to all IR peak tables:

- * 1 point fit (forced through zero)
- ** 2 point fit
- *** 3-point fit
- **** 4 point fit

IR Band Strength Tables

2nd Generation Candidates

Table 4: FC-3110 (Measurement A)

Peak freq. cm ⁻¹	S Torr-cm/AU ₁₀	σ_s	b	σ_b
732	87.4 ±	0.5	-0.387 ±	0.082
902	59.6 ±	0.2	-0.085 ±	0.037
1152	54.9 ±	0.15	-0.035 ±	0.034
1194	180.2 ±	0.5	-0.247 ±	0.038
1239	22.8 ±	0.13	0.156 ±	0.070
1257	9.3 ±	0.05	0.535 ±	0.065 ***
1276	89.0 ±	0.2	-0.160 ±	0.028
1313	41.4 ±	0.07	-0.089 ±	0.022

Integral 440-1535 cm⁻¹ 6900 ± 18 AU_e/atm cm² ***

Table 5, cont'd FC-3110 (Measurement B)

Peak freq. cm ⁻¹	S Torr-cm/AU ₁₀	σ_s	b	σ_b
901	59.0 ±	0.1	-0.109 ±	0.024
1239	22.6 ±	0.09	0.193 ±	0.055
1257	9.6 ±	0.2	0.123 ±	0.277 **

Integral 440-1535 cm⁻¹ 7032 ± 37 AU_e/atm cm² **

IR Band Strength Tables

Table 6: FC-c318 All fits use 5 pressure measurements except as indicated.

Peak freq. cm ⁻¹	S Torr-cm/AU ₁₀	σ_s	b	σ_b
569	105.6 ±	1.6	-0.513 ±	0.156
963	15.1 ±	0.04	-0.032 ±	0.018 ****
1239	26.5 ±	0.05	-0.080 ±	0.019
1269	116.5 ±	0.6	0.099 ±	0.051
1290	46.6 ±	0.15	-0.010 ±	0.032
1339	45.3 ±	0.07	0.055 ±	0.015
Integral 440-1535 cm ⁻¹ 5271 ± 22 AU _e /atm cm ² ****				

Table 7: f-Tetrahydrofuran

Peak freq. cm ⁻¹	S Torr-cm/AU ₁₀	σ_s	b	σ_b
963	86.9 ±	0.3	0.024 ±	0.021
1035	69.2 ±	0.10	0.036 ±	0.009
1095	17.1 ±	0.15	0.093 ±	0.058
1205	28.1 ±	0.02	0.004 ±	0.005
1260	29.9 ±	0.09	0.021 ±	0.021
1332	92.4 ±	0.2	-0.015 ±	0.014
1348	99.9 ±	0.2	0.022 ±	0.016
Integral 440-1535 cm ⁻¹ 7912 ± 133 AU _e /atm cm ²				

IR Band Strength Tables

Table 8: f-methyl propyl ether

Peak freq. cm ⁻¹	S Torr-cm/AU ₁₀	σ_s	b	σ_b
754	202.8 ±	1.2	-0.024 ±	0.039
895	169.9 ±	1.3	-0.004 ±	0.049
1008	60.7 ±	0.4	-0.071 ±	0.042
1137	34.5 ±	0.3	-0.063 ±	0.061
1168	20.3 ±	0.2	-0.055 ±	0.063
1257	10.5 ±	0.06	0.119 ±	0.039
1350	61.3 ±	0.5	-0.042 ±	0.051
1285	21.7 ±	0.2	-0.082 ±	0.057

Integral 440-1535 cm⁻¹ 11516 ± 158 AU_e/atm cm²

3rd Generation Candidates

Table 9: HFC-227ea

Peak freq. cm ⁻¹	S Torr-cm/AU ₁₀	σ_s	b	σ_b
690	118.8 ±	4.4	0.070 ±	0.204
858	231.5 ±	12.7	-0.220 ±	0.314
909	150.6 ±	2.9	-0.215 ±	0.109
1128	31.5 ±	0.05	-0.095 ±	0.009
1222	24.6 ±	0.2	-0.011 ±	0.041
1244	26.1 ±	0.2	0.011 ±	0.041
1283	102.1 ±	2.7	0.049 ±	0.144
1306	27.1 ±	0.3	0.015 ±	0.060
1391	59.0 ±	1.3	0.071 ±	0.119

Integral 440-1535 cm⁻¹ 6175 ± 72 AU_e/atm cm²

IR Band Strength Tables

Table 10: HFC-236ea

Peak freq. cm ⁻¹	S Torr-cm/AU ₁₀	σ_s	b	σ_b
712	248.0 ±	1.0	-0.008 ±	0.022
878	254.7 ±	1.9	0.149 ±	0.040
1090	74.5 ±	0.6	0.002 ±	0.041
1121	63.5 ±	0.3	0.058 ±	0.029
1188	40.2 ±	0.04	0.042 ±	0.005
1220	33.4 ±	0.07	0.069 ±	0.012
1273	92.1 ±	0.3	0.025 ±	0.015
1298	125.9 ±	0.6	0.041 ±	0.025
1350	338.4 ±	12.4	0.417 ±	0.188
1386	210.9 ±	2.1	0.005 ±	0.054
1420	199.2 ±	1.4	-0.045 ±	0.038

Integral 440-1535 cm⁻¹ 5135 ± 55 AU_e/atm cm²

Table 11: HFC-236fa

Peak freq. cm ⁻¹	S Torr-cm/AU ₁₀	σ_s	b	σ_b
653	193.9 ±	1.3	-0.033 ±	0.039
658	199.2 ±	1.7	0.005 ±	0.055 ***
711	403.5 ±	2.3	-0.046 ±	0.036 ***
845	463.0 ±	NA	-0.362 ±	NA **
1408	41.3 ±	0.03	-0.013 ±	0.004
915	221.0 ±	2.0	-0.059 ±	0.051
1117	30.8 ±	0.2	-0.084 ±	0.031
1120	33.5 ±	0.2	-0.078 ±	0.027
1223	36.0 ±	0.12	-0.038 ±	0.019
1243	17.9 ±	0.07	-0.009 ±	0.021
1311	40.5 ±	0.08	-0.023 ±	0.012

Integral 440-1535 cm⁻¹ 7204 ± 33 AU_e/atm cm²

IR Band Strength Tables

Table 12: HFE-134

Peak freq. cm ⁻¹	S Torr-cm/AU ₁₀	σ_s	b	σ_b
785	349.9 ±	4.5	-0.027 ±	0.079
1008	123.6 ±	0.4	-0.104 ±	0.018
1015	134.5 ±	0.6	-0.260 ±	0.028
1089	72.2 ±	0.3	-0.095 ±	0.023
1140	18.7 ±	0.06	-0.022 ±	0.021
1198	74.7 ±	0.11	-0.026 ±	0.009
1362	245.0 ±	2.7	-0.178 ±	0.067
1379	199.1 ±	1.4	-0.136 ±	0.044

Integral 440-1535 cm⁻¹ 6874 ± 171 AU_e/atm cm²

Table 13: HFE-227ca All fits derive from 5 pressure measurements except as indicated

Peak freq. cm ⁻¹	S Torr-cm/AU ₁₀	σ_s	b	σ_b
568	590.8 ±	20.5	-0.096 ±	0.324
594	612.3 ±	19.0	-1.731 ±	0.334
696	751.0 ±	87.1	0.452 ±	1.143 ****
767	725.3 ±	87.0	0.514 ±	1.174 ****
796	265.6 ±	2.1	0.084 ±	0.072
853	584.2 ±	25.7	0.200 ±	0.399
914	325.7 ±	7.7	0.297 ±	0.213
1143	33.5 ±	0.6	-0.173 ±	0.159
1171	17.4 ±	.02	-0.004 ±	0.008
1240	14.0 ±	0.09	0.102 ±	0.060
1272	30.5 ±	0.07	-0.018 ±	0.021
1324	55.0 ±	0.2	0.023 ±	0.030
1430	1131.4 ±	77.2	1.502 ±	0.607 ****

Integral 440-1535 cm⁻¹ 9219 ± 10 AU_e/atm cm²

IR Band Strength Tables

Table 14: 3H-f-oxetane

Peak freq. cm ⁻¹	S Torr-cm/AU ₁₀	σ_s	b	σ_b
987	32.1 ±	0.09	0.025 ±	0.018
1107	93.0 ±	0.3	0.001 ±	0.021
1182	109.7 ±	0.5	0.018 ±	0.028
1221	53.9 ±	0.02	0.053 ±	0.003
1257	45.5 ±	0.11	0.012 ±	0.016
1296	52.4 ±	0.08	-0.030 ±	0.011
1334	168.1 ±	0.8	0.039 ±	0.031

Integral 440-1535 cm⁻¹ 5785 ± 181 AU_e/atm cm²

Table 15: HCFC-124 - All fits derive from 5 pressure measurements except as indicated

Peak freq. cm ⁻¹	S Torr-cm/AU ₁₀	σ_s	b	σ_b
696	217.0 ±	1.8	-0.588 ±	0.086
818	229.5 ±	1.0	-0.023 ±	0.044
885	115.5 ±	0.4	-0.164 ±	0.036
1101	97.9 ±	0.4	0.024 ±	0.046
1107	94.9 ±	0.5	0.036 ±	0.056
1167	42.8 ±	0.4	-0.463 ±	0.108
1173	47.8 ±	0.13	-0.087 ±	0.027
1215	41.1 ±	0.07	-0.039 ±	0.017
1286	73.7 ±	0.2	-0.099 ±	0.026
1298	74.9 ±	0.2	-0.120 ±	0.032
1377	241.3 ±	0.6	-0.012 ±	0.026

Integral 440-1535 cm⁻¹ 3861 ± 34 AU_e/atm cm²

IR Band Strength Tables

Fluorination Products

Table 16: FC-14

Peak freq. cm ⁻¹	S Torr-cm/AU ₁₀	σ_s	b	σ_b
1281	6.3 ±	0.11	-0.237 ±	0.063

Integral 440-1535 cm⁻¹ 3259 ± 109 AU_e/atm cm²

Table 17: FC-116

Peak freq. cm ⁻¹	S Torr-cm/AU ₁₀	σ_s	b	σ_b
714	98.6 ±	0.7	-0.112 ±	0.022 ***
1110	50.6 ±	NA	-0.010 ±	NA **
1116	18.1 ±	NA	-0.003 ±	NA **
1123	33.1 ±	NA	-0.017 ±	NA **
1250	6.3 ±	NA	-0.010 ±	NA **
1327	540.5 ±	NA	0.000 ±	NA *

Integral 440-1535 cm⁻¹ 5291 AU_e/atm cm² **

Table 18: FC-218

Peak freq. cm ⁻¹	S Torr-cm/AU ₁₀	σ_s	b	σ_b
731	117.7 ±	0.9	-0.414 ±	0.048
1007	29.6 ±	0.09	-0.068 ±	0.019
1153	34.8 ±	0.2	-0.103 ±	0.028
1209	50.4 ±	0.2	-0.073 ±	0.019
1262	6.5 ±	0.10	0.077 ±	0.089
1298	249.8 ±	4.1	-0.253 ±	0.102
1314	247.8 ±	2.2	-0.209 ±	0.055
1350	61.7 ±	0.12	-0.039 ±	0.012

Integral 440-1535 cm⁻¹ 7220 ± 17 AU_e/atm cm²

IR Band Strength Tables

Table 19: f-oxetane - These values derive from a single spectrum, with absorbance "fit" forced through zero. Further, the partial pressure was deduced from the material balance in the reaction of 3H-f Oxetane with F₂.

Peak freq. cm ⁻¹	S Torr-cm/AU ₁₀
1006	25.8
1115	153.2
1192	53.5
1230	58.8
1253	16.3
1296	52.9

Integral 440-1535 cm⁻¹ 6655 AU_e/atm cm²

Table 20: CFC-115

Peak freq. cm ⁻¹	S Torr-cm/AU ₁₀	σ_s	b	σ_b
648	436.0 ± 28.9		0.166 ± 0.415	
756	346.6 ± 14.1		-0.143 ± 0.267	
762	221.2 ± 1.6		-0.108 ± 0.048	
768	331.5 ± 1.7		-0.115 ± 0.033	
982	37.8 ± .02		-0.073 ± 0.003	
987	43.8 ± .05		-0.031 ± 0.007	
1130	39.5 ± 0.06		-0.066 ± 0.009	
1184	56.6 ± 0.11		-0.045 ± 0.013	
1241	14.9 ± .03		-0.026 ± 0.014	
1350	167.8 ± 1.6		-0.135 ± 0.063	

Integral 440-1535 cm⁻¹ 4995 ± 66 AU_e/atm cm²

DISCUSSION

The IR calibrations reported here, as previously stated, were intended primarily to allow us to quantitatively follow the course of reaction during our kinetics experiments.

A second use of the data is in the estimation of the global warming potential of these compounds. Published GWP values are often derived from elaborate atmospheric dynamics computations (known as general circulation models, i.e. GCMs) which are coupled to a chemical model of the reactions of atmospheric components with one another and with solar and infrared radiation. Such models attempt to simulate the flow of gases and energy through the atmosphere and can be used to compute many climatic effects, among them the average surface temperature of the earth. Such a model can be run with a hypothetical perturbation, such as the addition of a particular tonnage emission of a compound.

The various fluorocarbon gases we are concerned with all have absorption bands in the spectral region 900 to 1300 cm^{-1} , which is a region of the infrared spectrum that is somewhat transparent in the earth's atmosphere. These compounds can thus intercept incoming and outgoing IR radiation, changing the detailed heat balance of the atmosphere. One consequence of this is that additional FCs in the atmosphere are predicted to increase surface temperatures. The impact of a compound might be calculated in units of "degrees/kg" (the actual factor is on the order of 10^{-12} $^{\circ}\text{C}/\text{kg}$, though GCMs are constantly evolving and predictions change). The "instantaneous" GWP of a compound is simply the calculated warming caused by a fixed mass of that compound divided by the warming caused by the same mass of a reference compound. The reference compound is usually taken to be either CO_2 or CFC-11; we will use the latter in this document.

The warming caused by a particular compound will depend on the details of its infrared spectra (i.e. the strength and frequencies of absorption bands relative to the solar and thermal energy spectral envelopes and the absorption bands of other IR-active atmospheric constituents), and its dynamics in the atmosphere (mixing and destruction rate). To a reasonable approximation, however, one can neglect the details and merely compare the overall absorption strength of all the IR bands of the molecule, and arrive at a reasonably accurate estimate of the relative impact of two compounds⁷. The values we have measured and tabulated above for integrated IR absorbance strength, A , form the basis of comparison:

$$\text{GWP}_{\text{inst.,FC}} \cong \frac{A_{\text{FC}}/m_{\text{FC}}}{A_{\text{ref}}/m_{\text{ref}}} \quad (\text{Eqn 4})$$

where m is the molecular weight of the species in question.

We earlier estimated the internal uncertainty in our reported values of A as about 5% of the measured value (see Appendix for details). Only a few of the compounds we have examined have had their integrated absorbance measured and reported in the scientific literature. For comparison, Table 21 shows our values for three compounds with the preferred values used by Fisher taken from various sources cited in Reference 7. The average variation is on the order of 5% for these few examples.

Table 21: Comparison of Integrated
IR Absorbance Values.

<u>Compound</u>	<u>This Work</u>	<u>Ref 7</u>
CFC-114	4197	4141
HCFC-124	3861	4043
CFC-115	4995	4678

The GWP most often reported in the literature or news media is not the "instantaneous" one mentioned above, but is that effect integrated over a lengthy future time interval. The impact of a compound thus might be expressed in degree-years/ton. Again, the GWP is the ratio of the impact of the compound under consideration to that of a reference compound. The time intervals most often discussed for GWP purposes are 100, 200 and 500 years. Since GDP coolant replacement concerns relate to use of long-lived compounds, they appear in the least favorable light when considered over a long time period. The discussion that follows will therefore consider only the longest interval above, namely 500 years; in addition, we will also consider effects over an infinite time horizon.

Most compounds of concern in global warming or ozone depletion exhibit a characteristic exponential decay in the atmosphere; the quantity M remaining at time t after emission approximately follows the equation:

$$M(t) = M(0) e^{-t/\tau} \quad (\text{Eqn 5})$$

where τ is the characteristic lifetime of the compound. The major global warming gas, water vapor, of course does not follow such behavior. The second most important gas, CO_2 , also has several large non-gaseous reservoirs that operate on greatly varying time scales (from 1 day to hundreds of millions of years). Minor contributors such as CFCs, however, tend to have a single dominant destruction mechanism that removes a fixed fraction per unit time; this results in the stated exponential behavior. Literature values for lifetimes are calculated by combining experimental measurements of key atmospheric reaction rate constants with GCM results.

The two approximations, one for IR strength and the other for lifetime, can be combined to yield a reasonable approximation of long-term GWP. The GWP of a compound considered over the time horizon from $t = 0$ to $t = t_h$ is obtained by integrating over that time period:

$$\text{GWP} \cong \frac{A_{\text{FC}}/m_{\text{FC}}}{A_{\text{ref}}/m_{\text{ref}}} \tau (1 - e^{-t_h/\tau}) \quad (\text{Eqn 6})$$

The integrated absorbances, A , are obtained from the IR spectra discussed above, where, following Fisher⁷, we have integrated over the spectral interval 440 to 1535 cm^{-1} . We have combined our experimental IR absorbance strengths with literature-derived or estimated atmospheric lifetimes to make the GWP estimates reported in Table 22.

Where literature values are available for compounds of interest, we have adopted them. Of particular interest to the GDP coolant replacement program is an article recently published by Ravishankara, et al.¹ containing lifetime estimates for FC-3110, FC-c318. Values for these two compounds had not previously been published. In addition, the article also computes values for CFC-114 and CFC-115 which are somewhat (i.e. 1.5 to 4 times) longer than earlier estimates⁷.

Reference 1 lists two lifetimes for most compounds, a "minimum" and a "best estimate". The "minimum" was derived by assuming that all those mechanisms for which no destruction rate could be measured operated at their minimum detection limits. The "best estimate" neglected mechanisms for which no measurable rate was detected. Only a "minimum" lifetime was reported for FC-3110, and it did not derive from measurements, but rather was estimated by chemical similarity to compounds for which rates were measured. Nevertheless, it appears likely that this value will be adopted by the environmental regulatory community until a better one is forthcoming,

and it is the value we use here. This may lead to some confusion in comparing FC-c318 with FC-3110. The "minimum" FC-3110 lifetime of 2600 years should be compared with the "minimum" 1000 year estimate for FC-c318. We have however, used the 3200 year "best estimate" for FC-c318, as *that* value will likely be the one preferred for discussion of FC-c318. This may mislead one into thinking the lifetime of FC-c318 is longer than for FC-3110.

Lifetimes for several other compounds derive from Fisher et al.⁷ For a number of others, we have no available information. In some cases we have made fairly subjective guesses based on chemical similarity: FC-218 we guess as 5000 years, interpolating between the data and estimates for higher and lower PFCs found in Reference 1. For all the C₃ and C₄ perfluoroethers we use a value of 2000 years based on the perhaps tenuous assumption that this class of compound will have essentially the same C-C and C-F bond attack rates (chemical or photolytic) as PFCs, and that the ether linkage will open up modest additional photolytic "destruction opportunities"; thus their lifetimes should lie at or below the lower limit of the range for similar-sized PFC molecules.

A second fairly conjectural estimate for a few HFCs (as indicated in Table 22) derives from the observation that room temperature reaction rates of HFCs with atomic fluorine radicals are on the order of 24 times the equivalent rates for those HFCs with OH radicals². Where we have experimental reaction rate constants for atomic fluorine with hydrogen-containing species, but no other information, we have computed the presumptive OH radical rate constant, then translated this to an atmospheric lifetime by assuming an average atmospheric concentration of OH radicals of 490,000 molec/cc (which value is implicit in lifetime calculations in Reference 8). From the measured fluorine reaction rate for HFC-236fa, we have estimated an OH rate corresponding to an atmospheric lifetime of 95 years; for HFC-236ea, we have a lower limit on the fluorine reaction rate that translates into an upper limit on atmospheric lifetime of 16 years; for HFE-227ca we estimate 106 years.

Based on the effectiveness of this assumption when used to predict lifetimes for four compounds for which we have both fluorine reaction rates and published lifetimes, these values seem to be accurate only within a factor of 4.5, and are thus useful only for obtaining an order-of-magnitude estimate of GWP.

In Table 22, then, we summarize the integrated absorbances, lifetime, molecular weight, ozone depletion potential⁹ (ODP), and estimates of GWP for a 500 year and for an infinite time horizon.

A comment should be made about error propagation in these GWP estimates. The two key values that go into the GWP estimate are IR strength and atmospheric lifetime. The IR strengths are reasonably certain, but lifetimes are often very uncertain. If calculated over a period of time much longer than the atmospheric lifetime, the percent uncertainty in GWP will be the same as the percent uncertainty in lifetime. When calculated over a time period much less than the lifetime, however, uncertainty in lifetime has little effect on uncertainty in GWP. Thus 500 year GWPs for PFCs are probably "accurate" to around 20%, in spite of great uncertainty in lifetime. It is for this reason that the GWP listed here for FC-3110 and FC-c318 are very similar to the earlier estimate of one of the authors, (for FC-3110, 13 in this work vs. 18 in Ref. 10; for FC-c318, 12 here vs. 13 in Ref. 10), even though no estimates were available at that time for these compounds' atmospheric lifetimes. This point is discussed in more detail in the Appendix.

These GWP estimates could be refined considerably, but lead to a general picture with respect to the GDP coolant replacement program. First, all the fully fluorinated substitute coolant candidates will have a GWP somewhat larger (2 to 3 times) than that of CFC-114 when considered over a 500 year time horizon, and much larger (ca. 10 times) when considered over an infinite time horizon.

Third generation coolant candidates all have estimated GWPs of the same order or lower than that of CFC-114. Thus, if their use were permitted in the GDPs, the plants' contribution to global warming would probably modestly decrease (though not by a large proportion, since energy-related indirect CO₂ emissions would still dominate).

An example may be helpful in illustrating these points. This example is based on data and models elaborated in References 10 and 12. Assume that a GDP uses an average of 1500 MW of power throughout a year's operation. Power use is assumed to cause the indirect emission (at the electric generating plant) of .98 kg CO₂ per kwh, leading to the annual emission of CO₂ listed in Table 23 of 1.3×10^{10} kg per year.

The GDP's working inventory of coolant is taken as equal to 3.6 million kg, and annual fugitive emissions are assumed to be 3% of this inventory, or 108 thousand kg. Three alternative coolants are listed in the table, and in each case, it is assumed that the entire plant coolant inventory consists of the specified coolant (not a realistic near-term assumption for substitutes). The three coolants are the presently-used CFC-114, FC-3110 (a fully fluorinated cool-

Table 22: GWP Estimates, and information used in their derivation

<u>Compound</u>	<u>IR Strength</u>	<u>Atmos. Life.</u>	<u>Mol. Wt.</u>	<u>ODP Ref 9</u>	<u>GWP (500yr)</u>	<u>GWP (infinite)</u>	<u>Lifetime Ref. & notes</u>
<u>Reference Compound</u>							
CFC-11	2389	60	138	1.00	1.00	1.00	7
<u>"1st Generation"</u>							
CFC-114	4197	300	171	0.70	5.7	7.1	1 [C]
<u>"2nd Generation" candidates</u>							
FC-3110	6966	2600	238	-	12.8	73.	1 [D]
FC-c318	5271	3200	200	-	11.7	81.	1
f-THF	7912	2000	216	-	15.5	70.	
f-MPE	11516	2000	254	-	19.2	87.	
<u>"3rd Generation" candidates</u>							
HFC-227ea	6175	120	170	-	4.1	4.2	11
HFC-236ea	5135	<16	152	-	<0.50	<0.50	[E]
HFC-236fa	7204	95	152	-	4.3	4.3	[E]
HFE-134	6874	2.6	118	-	0.15	0.15	8
HFE-227ca	9219	106	186	-	5.0	5.0	[E]
3H-f-Oxetane	5785	26	148	-	0.98	0.97	8
HCFC-124	3861	6.6	137	0.02	0.18	0.18	7
<u>Long-lived Fluorination Products</u>							
FC-14	3292	50000	88	-	17.9	1790.	1
FC-116	5291	10000	138	-	17.9	368.	1
FC-218	7220	5000	188	-	17.5	184.	
f-Oxetane	6665	2000	166	-	17.0	77.	
CFC-115	4995	1700	155	0.35	13.4	53.	1 [C]

Notes:

- [A] Items in italics are estimates; if no reference is given, the estimate is the authors'.
- [B] Number of decimal digits reported should not be construed as indicative of authors opinion on number of valid significant digits. See text for estimate of uncertainty.
- [C] Reference 7 estimates were, for CFC-114, 200 yrs; for CFC-115, 400 yrs.
- [D] an estimated lower limit in Ref. 1; "best" might be 8000 yrs, comparing to FC-c318.
- [E] Lifetime estimated from assumption that $k[F] = 24 \times k[F]$; see Ref. 2.

ant) and 3H-f-Oxetane (a hydrogen-containing candidate). In the latter case, it is assumed that 2% of the losses of 3H-f-Oxetane are due to leaks into the UF₆ stream, and that before this portion of the coolant is ultimately purged from the system, it reacts with UF₆ to form f-Oxetane, a fully fluorinated ether. The contributions of these two species are added to obtain the overall impact of use of that coolant.

A time-integrated global warming forcing factor for CFC-11 of 1.34×10^{-10} °C-yr/kg is adapted from Ref 12. The impact for each coolant is obtained by multiplying this value by the quantity and GWP of the coolant in question:

$$\text{Global Warming Impact} = 1.34 \times 10^{-10} \text{ GWP}_{\text{FC}} M_{\text{FC}} \text{ (}^\circ\text{C-yr)}$$

The effective GWPs for CO₂ using approximations similar to those used in this document are $\text{GWP}_{500} = 0.0007$ and $\text{GWP}_{\text{inf}} = .0008$. The values for CO₂ are much smaller than those of fluorocarbons mainly because the IR spectrum in the atmosphere is already largely saturated (i.e. nearly opaque) in CO₂'s absorption bands.

Global warming impact figures (in units of °C-years) are shown in Table 23 for each compound. The 500-year impact gives the warming integrated over the first 500 years after emission. The average warming over this time would be 1/500th of the listed value. The infinite time horizon impact is the warming integrated over all future time.

Table 23: Example of Application of GWPs to estimate Global Warming Impacts of GDP operation

	Qty <u>kg/yr</u>	500 yr impact <u>°C-yrs</u>	Inf.horiz. impact <u>°C-yrs</u>
CFC-114	108000	8.3E-05	1.0E-04
FC-3110	108000	1.9E-04	1.1E-03
3H f-Oxetane	108000	1.9E-05	3.6E-05 (total)
98% as 3H f-Oxetane	105840	1.4E-05	1.4E-05
2% as f-Oxetane	2160	4.9E-06	2.2E-05
CO ₂	1.3E+10	1.2E-03	1.4E-03

The impact figures in Table 23, while quite approximate, put the relative contributions and effect of different alternatives in perspective. A fully fluorinated coolant would have over twice the impact of CFC-114 when considered over 500 years, and 10 times the impact on an infinite time basis. Over the longer time horizon, its impact approaches that of CO₂, though its impact is derived from a much smaller effect over a much longer period of time than is the case for CO₂.

Fully fluorinated reaction products of HFCs and HFEs have estimated GWPs equal to or larger than those of the fully fluorinated coolant candidates. Their contribution to the effective global warming contribution of the HFCs and HFEs in a GDP application is not large over a short time horizon, but can be significant when considered over an infinite time horizon. In the example above, the 2% leaking into the UF₆ stream has an effective contribution to 30% higher on a 500 year basis, and 150% higher on an infinite time horizon than the effect one would deduce from the listed GWP of the parent compound. Nevertheless, the HFE, as expected, has a smaller impact than CFC-114, and its impact is dwarfed by that of indirectly emitted CO₂, which in turn is dwarfed by the impact of the emissions of CO₂ *avoided* by use of enriched uranium, rather than coal, to produce electricity (a factor not covered in this report).

CONCLUSIONS

Spectral patterns and peak strengths have been obtained from IR measurements on several fluorocarbons.

We have also obtained the integrated IR absorbance strength for these compounds over the spectral range used in the atmospheric science literature for estimation of GWP. Using this information with measured or estimated values for atmospheric lifetime, we also estimate GWP for a number of compounds of interest.

The GWP estimates can be used to obtain a general picture of the relative global warming impact of GDP operation that would occur under various coolant choice scenarios. We expect that use of a fully fluorinated material will increase the global warming impact of the GDPs. In the most extreme case, when considered over an infinite time horizon, coolant-related contributions could increase to be a significant fraction of that of indirect (power-use related) CO₂ emissions. Use of third generation (HFC or HFE) coolants would keep the global warming impact of GDP operation similar to or slightly smaller than it is at present.

APPENDIX

Magnitude of Uncertainty in IR Strengths and GWP

A number of factors contribute to uncertainty in the peak strengths, integrated IR absorption strength, and GWP estimates. Our best evaluation of the values of these factors are detailed in this appendix.

Terms contributing to uncertainty in the IR peak and overall absorption strength are discussed below, and specific estimates for each factor are listed in Table A-1.

Regression Fit Uncertainty - The estimate of standard deviation of the slope of the fits, σ_S , was listed in the peak strength Tables 3 through 20. These values ranged from less than a percent to about 3%. This is the statistical uncertainty caused by scatter in the data, and includes no estimates of systematic error. Those peaks for which only one or two points were available can, of course, have no standard deviation estimate on their slope.

Pathlength -- IR Window Warpage: The experiments reported in this document were carried out using an IR gas cell with nominal path length of 2.16 cm. This cell used AgCl windows, which, in vacuum service, are subject to distortion. The distortion generally has the effect of bowing the windows inward, thereby reducing the path length by a millimeter or two. Micrometer measurements on the IR cell used in these experiments after various periods of service indicate that a typical path length in our experiments was actually about 2.0 ± 0.1 cm. As measurements were not taken of the path length in every experiment, we have assumed an IR path length of 2 cm throughout this report, except in those cases where a specific measurement was made immediately before or after a calibration series. The resulting absolute concentrations may thus be in error by about 5 percent due to this uncertainty. A single calibration (for FC-116) derives from archival spectral data done in a 3" (i.e. 7.62 cm) cell.

Pressure Measurements: The gas circulation during an experiment results in variation in the total gas pressure from place to place within the system, as determined by the flow rate and resistance of system components to gas flow. The actual pressure in the IR cell is, during experimental operation at approximately 2000 sccm flow rate, within 0.5% of that measured at the cell's manometer. Accuracy of the capacitance manometers was quoted as 0.08% of full-scale reading - considering the average pressure reading during a calibration, this contributes an uncertainty of approximately 1% to the pressure.

Table A-1 - Estimated uncertainties in factors influencing
Integrated IR Strength, S, expressed as a percent of S.

<u>Compound</u>	<u>Regress.</u> <u>Fit</u>	<u>Path</u> <u>Length</u>	<u>Flow</u>	<u>Pressure</u> <u>Gauge</u>	<u>Temp.</u>	<u>Max.</u> <u>Inert*</u>	<u>Overall</u> <u>uncert.</u>
<u>"1st Generation" Coolant</u>							
CFC-114	0.29%	5.0%	0.5%	1%	0.67%	4.8%	5.2%
<u>"2nd Generation" Candidates</u>							
FC-3110	0.44%	5.0%	---	1%	0.67%	---	5.2%
FC-c318	0.42%	5.0%	0.5%	1%	0.67%	---	5.2%
f-THF	1.68%	5.0%	0.5%	1%	0.67%	3.5%	5.4%
f-MPE	1.37%	5.0%	0.5%	1%	0.67%	6.8%	5.3%
<u>"3rd Generation" Candidates</u>							
HFC-227ea	1.17%	5.0%	0.5%	1%	0.67%	2.5%	5.3%
HFC-236ea	1.07%	5.0%	0.5%	1%	0.67%	---	5.3%
HFC-236fa	0.46%	5.0%	0.5%	1%	0.67%	0.8%	5.2%
HFE-134	2.49%	5.0%	0.5%	1%	0.67%	4.4%	5.7%
HFE-227ca	0.11%	5.0%	0.5%	1%	0.67%	---	5.2%
3HfOxetane	3.13%	5.0%	0.5%	1%	0.67%	3.8%	6.0%
HCFC-124	0.88%	5.0%	0.5%	1%	0.67%	---	5.2%
<u>Long-lived Fluorination Products</u>							
FC-14	3.31%	5.0%	0.5%	1%	0.67%	13.4%	6.1%
FC-116	---	1.3%	---	5%	1.50%	---	5.4%
FC-218	0.24%	5.0%	0.5%	1%	0.67%	---	5.2%
f-Oxetane	---	5.0%	0.5%	1%	0.67%	---	5.2%
CFC-115	1.32%	5.0%	0.5%	1%	0.67%	2.5%	5.3%

*"Max Inert" gas correction is the upper limit percentage by which S could exceed the reported value if inert content calculation assumptions are incorrect, as discussed in the text. This factor is not included in the overall uncertainty.

Temperature - Variation in temperature from one calibration to another will change the gas density in the IR cell, and consequently should change the apparent peak strength at a given pressure. Laboratory ambient temperatures, listed in Table 2, varied from 28 to 36°C, with most being between 30 and 33°C. As this measurement was not made directly in the spectrometer, we choose not to convolute the results by correcting for temperature, but note that relative strengths might vary by $2^{\circ}\text{K}/300^{\circ}\text{K}$, or 0.67%.

Condensable Impurities: This effect is hard to quantify. Condensable impurities in a sample would be retained or included through the removal or evaluation of non-condensable gases. As such they would contribute to the IR strength of the sample. Such gases, however, would likely have IR strengths comparable to the main compound, so that the only error would be due to difference in IR strengths between impurity and sample. As all the samples had at most a few percent impurity, this should not be a significant effect, and will be ignored.

Non-condensable Gas Impurities and IR Calibration: Most of the IR calibration values reported here incorporate the results of the freezeout procedure mentioned earlier. When this procedure was carried out and no residual fluorocarbon was detected, the only error likely would be a slight underestimate of the non-condensable gas content due to higher gas density in the vicinity of the cold region. The volume of this region, however, is a very small fraction (ca. 0.1%) of the total system volume, so such an error should be insignificant compared to others already discussed.

When residual fluorocarbon is still present in the IR cell after cooling a section of tubing to liquid nitrogen temperature, it is not absolutely certain what fraction of the system volume contains the observed partial pressure of fluorocarbon, and what fraction has been depleted by condensation of fluorocarbon. Fluorocarbon can remain in the gas only because the circulating pump has stalled (that is fails to move a significant volume of gas, a condition that we observe below about 1 to 1.3 Torr), and that diffusion of fluorocarbon into the cold region is too slow to further deplete the gas. Since the cold region is in a small-diameter, low volume section of tubing, we have assumed that the residual partial pressure of fluorocarbon observed in the IR cell is also present everywhere in the system except for an insignificant volume in the vicinity of the cold spot. If somehow (perversely!) the FC had been depleted everywhere *but* the IR cell, the inert fraction at room temperature would be higher than we have calculated. This would result in the reported sensitivity factors being too low by varying percentages ranging from no correction to about 5% for several species and 16% for FC-14, the most extreme case. We do not

regard this as a credible situation, and do not include this source of potential error in the reported results. We do, however, list this factor in Table A-1 under the heading of "Max Inert" [gas correction].

Overall IR Peak and Integrated Strength Uncertainties: Uncertainties in path length, pressure measurement, etc., if uncorrelated, suggest an overall error of about 5% for the reported IR peak sensitivity factors and integrated IR strength.

GWP Uncertainties: Uncertainty in the integrated IR strength will translate into a proportional uncertainty in GWP for all species. That is, if the IR strength is uncertain by 5%, the GWP will be uncertain by at least 5%. Often, however, the uncertainty in IR strength will be dwarfed by uncertainty in the atmospheric lifetime. This is somewhat complicated in the case of GWPs computed over a limited time horizon, since any warming effect beyond the time horizon will be ignored. In the most extreme case, for a material with a lifetime very much longer than the time horizon, uncertainty in lifetime will not significantly affect the limited-time-horizon GWP. If, for example, one were considering a 100 year time horizon for GWP calculation, it would not matter a great deal whether the lifetime were 5000 years or 50000 years; in either case, nearly all of the material would survive the entire 100 year period.

The following is an attempt to estimate uncertainties on atmospheric lifetime in order to derive an approximate uncertainty on GWP.

Several of the lifetimes we have used derive from Ref. 1. That work listed "minimum" and "best" values for lifetime. Their "minimum" was structured so as to give an estimate of the shortest credible lifetime based on various destruction mechanisms they considered; the "best" was structured to give an estimate of the longest credible lifetime considering the same mechanisms, but not considering uncertainty in the various destruction mechanisms' rates. We will take Ref. 1's "minimum" and "best" as minimum and maximum lifetimes, unless other literature values lie outside that range, in which case we will use the other literature values accordingly. For example, in the case of CFC-115, Ref. 1 gives values of 1100 and 1700 years as "minimum" and "best". Ref. 7, however, estimates a lifetime for CFC-115 of 400 years; we adopt 400 as a minimum and 1700 as maximum values for purposes of estimate a range for CFC-115's GWPs. For FC-3110, only a "minimum" lifetime of 2600 years was given in Ref. 1. A maximum of 8000 is estimated by scaling the minimum upward by the same factor reported for FC-c318.

Where lifetime is based on literature reports of measured OH radical rate

constants, and where specific values for uncertainties on those rates are given, those uncertainties will be taken as proportional to uncertainty in lifetime. Typical values in Ref 8 are 7 to 14% of the measured value. Where a literature value was available based on OH rate data but was reported without uncertainty information (generally in secondary sources) we assume an arbitrary 30% uncertainty.

A number of *ad hoc* estimates were made based on chemical similarity where no other information was available. For perfluoroethers, a nominal lifetime estimate of 2000 years was used. For purposes of estimating a range, a factor of two uncertainty will be used -- that is, a minimum lifetime of 1000 years and a maximum of 4000 years will be assumed. The lifetime for FC-218 was also guessed based on chemical similarity, and for it, too, a factor of two uncertainty is assumed.

Species for which the correlation between OH radical rates and atomic F radical rates was used to estimate lifetime, the correlation was so far found to be "accurate" to a factor of 4.6. In one case, the "maximum" lifetime of HFC-236fa (which derives from the OH:F correlation) was reduced to equal the maximum estimate for HFC-227ea (for which there *was* lifetime information), since HFC-236fa's lifetime is almost certainly smaller than that of HFC-227ea.

Table A-2 lists an estimate for minimum, nominal (i.e. the value used in the main report text), and maximum values for atmospheric lifetime. These were combined with the IR strength values (minimum, nominal, or maximum, chosen so as to reinforce deviation from the nominal GWP value) to give minimum, nominal, and maximum values for GWP on both a 500 year and an infinite time horizon. Computation of GWP estimates involves comparison with the IR strength and lifetime of CFC-11. The values for CFC-11 listed in Tables 22 and A-2 are assumed correct and not varied.

GWP results are presented in Table A-2. In some cases, the uncertainty in parameters values translates into an uncertain GWP, but in others, notably 500 year GWPs for fully fluorinated species, large uncertainties in lifetime do not greatly affect the GWP value. This is not, of course, to say that longer-term effects should be ignored in evaluating alternative compounds.

Table A-2: Global Warming Potential Estimates - Error Analysis.
Minimum, nominal, and maximum estimates for atmospheric lifetime and IR strength were combined to give minimum, nominal and maximum estimates for GWPs. See text for explanation.

	<u>Atmos. Lifetime (yr)</u>			<u>GWP (500 yr)</u>			<u>GWP(infinite)</u>		
	<u>min</u>	<u>nom</u>	<u>max</u>	<u>min</u>	<u>nom</u>	<u>max</u>	<u>min</u>	<u>nom</u>	<u>max</u>
<u>Reference Species</u>									
CFC-11	60	60	60	1	1	1	1	1	1
<u>"1st Generation" Coolant</u>									
CFC-114	90	300	300	2.0	5.7	6.0	2.0	7.1	7.4
<u>"2nd Generation" Candidates</u>									
FC-3110	2600	2600	8000	12.1	12.8	14.4	69	73	237
FC-c318	1000	3200	3200	9.4	11.7	12.3	24	81	85
f-THF	1000	2000	4000	13.1	15.5	17.5	33	70	149
f-MPE	1000	2000	4000	16.2	19.2	21.6	41	87	184
<u>"3rd Generation" Candidates</u>									
HFC-227ea	84	120	171	2.8	4.1	6.0	2.8	4.2	6.3
HFC-236ea	<3	<16	<71	<0.10	<0.50	<2.4	<0.10	<0.50	<2.4
HFC-236fa	21	95	171	0.89	4.3	7.8	0.89	4.3	8.2
HFE-134	2.4	2.6	2.9	0.12	0.15	0.17	0.12	0.15	0.17
HFE-227ca	23	106	486	1.0	5.0	16.	1.0	5.0	24.
3HfOxetane	22	26	30	0.79	0.98	1.21	0.79	0.97	1.21
HCFC-124	4.6	6.6	9.4	0.12	0.18	0.27	0.12	0.18	0.27
<u>Long-lived Fluorination Products</u>									
FC-14	25000	50000	50000	16.7	17.9	19.0	842.	1794	1911
FC-116	9100	10000	20000	16.9	17.9	19.2	317.	368	777
FC-218	2500	5000	10000	15.8	17.5	19.0	87.	184	388
f-Oxetane	1000	2000	4000	14.4	17.0	19.1	37.	77	162
CFC-115	400	1700	1700	8.4	13.4	14.2	12.	53	56

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