Infrared Cross Sections and Global Warming Potentials of 10 Alternative Hydrohalocarbons

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Absorption cross sections have been obtained in the infrared atmospheric window, between 600 and 1500 cm^{-1}, for 10 alternative hydrohalocarbons: HCFC22, HCFC123, HCFC124, HCFC141b, HCFC142b, HCFC225ca, HCFC225cb, HFC125, HFC134a and HFC152a. The measurements were made at three temperatures (287 K, 270 K and 253 K) with a Fourier transform spectrometer operating at 0.03 cm^{-1} apodized resolution. Integrated cross sections have been introduced into a two-dimensional radiative-chemical-dynamical model in order to calculate the global warming potential (GWP) of each gas.

1. INTRODUCTION

Substitutes for the currently used chlorofluorocarbons (CFCs) have been introduced worldwide since the latter were recognized to be responsible for the depletion of stratospheric ozone [*Molina and Rowland*, 1974; *Stolarski and Cicerone*, 1974]. The international agreements [*Montreal Protocol* and *London Amendment*, 1990] have established the phaseout of CFCs by the year 2000 for industrialized nations and 10 years later for developing countries. Alternative chemicals and technologies are being developed by industries to meet the future needs in refrigeration, foam blowing, insulation, electronic cleaning and drying processes [*Fisher et al.*, 1991]. The partially halogenated hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) were found to have the same physical properties as CFCs and to be environmentally more acceptable compounds. Unlike the long-lived CFCs, which are essentially removed through UV photolysis processes in the stratosphere, hydrohalocarbons contain at least one hydrogen atom and hence react with hydroxyl radicals in the troposphere. According to their reactivity with OH their lifetimes range from 1.5 to 35 years, resulting in a lower ozone depletion potential(ODP) [*Wuebbles*, 1983; *Fisher et al.*, 1990a; *World Meteorological Organization(WMO)*, 1992].

The potential contribution of HCFCs and HFCs as greenhouse gases has to be considered owing to their strong absorption bands located in the IR atmospheric window. The ability of one gas to participate to the radiative forcing of the atmosphere is characterizable by a parameter, the global warming potential(GWP), which is calculated from the infrared absorption spectra and the amount of gas present in the atmosphere over a specified period of time [*Fisher et al.*, 1990b; *WMO*, 1992].

Although hydrohalocarbons are present in very small amounts in the present day atmosphere, some have reached the minimum concentration levels of a few parts per billion by volume (ppbv) required to be measured in the ambient air [*Pollock et al.*, 1992]. As these concentrations are going to increase in the forthcoming years, spectroscopic infrared data are necessary in order to determine atmospheric abundances of these trace gases using infrared spectroscopy.

This paper reports the accurate measurements of infrared absorption cross sections, as a function of the temperature, for HCFC22 (CHClF$_2$), HCFC123 (CHCl$_2$CF$_3$), HCFC124 (CHClFCF$_3$), HCFC141b (CH$_3$CCl$_2$F), HCFC142b(CH$_3$CClF$_2$), HCFC225ca (CHCl$_2$CF$_2$CF$_3$), HCFC225cb(CClF$_2$CF$_2$CHClF), HFC125 (CHF$_2$CF$_3$), HFC134a (CFH$_2$CF$_3$) and HFC152a (CH$_3$CHF$_2$). This data set has been introduced into the National Center for Atmospheric Research(NCAR) coupled radiative-chemical model in order to obtain global warming potentials for the substitutes.

2. Experiment

The spectra have been recorded in the infrared atmospheric window, between 600 and 1500 cm^{-1}, using a Bruker IFS 120HR Fourier transform spectrometer. A globar source and a mercury-cadmium-telluride (MCT) detector, maintained at liquid N$_2$ temperature, were employed. With an apodized resolution of 0.03 cm^{-1} a hundred scans were necessary to obtain a good signal to noise ratio; the baseline noise does not exceed 0.01 in absorbance units.

The samples were provided by Solvay (HCFC22, HCFC123, HCFC141b, HCFC142b, HFC134a), E.I. du Pont de Nemours (HCFC124, HFC125, HFC152a) and Asahi Glass Company (HCFC225ca, HCFC225cb). Each of these compounds was provided with a purity analysis: eight of them were guaranteed to have a volumic purity higher than 99.98% and two were analyzed to be purer than 99.0% (HCFC124, HFC125). The gas to be studied was introduced into a laboratory-built thermostatic cell [*Hurtmans et al.*, 1992]. The 5-cm-long cell was constructed of anodized aluminium and closed by two pairs of KBr windows. Its exact length was measured by interferometry with an accuracy of 0.2%. The cell was placed inside the sample chamber of the spectrometer which was then evacuated in order to avoid interferences with ambient CO$_2$ and H$_2$O. The pressure of the gas to be analyzed was measured using a 100-torr full scale absolute MKS Baratron capacitance gauge (model 390 HA), stabilized at 45°C. According to the gauge manufacturer the error associated with the measured pressure is lower than 0.15% in the range of pressure used (1-4 torr). The temperature of the cell can be stabilized anywhere between -30° and +60°C by liquid circulating in a double wall within the body of the cell. The temperature stabilization was provided by a cryostat (Neslab ULT80) and methanol was used as a circulating fluid. The temperature of the gas is measured inside the cell by a transducer accurate to ±0.2°C. The nominal temperatures (287 K, 270 K, 253 K) were reproduced in each individual measurement to within 0.5°C.

For each species, 18 spectra have been recorded, at six different pressures and three different temperatures. In addition, similar measurements were made for CFC12, in order to allow a comparison with the numerous data available in the literature for this compound.

3. Results

3.1. Temperature Dependent Cross Sections

According to the Beer-Lambert law the transmission of radiation through a homogeneous gas sample is described by the relation

$$I(\nu) = I_0(\nu)\exp\left(-\sigma(\nu)nl\right) \qquad (1)$$

where I_0 and I are the intensities of the incident and transmitted radiation at wavenumber ν, n is the concentration of the gas (molecule/cm^3) and l is the optical path (centimeters); σ is the absorption cross section (cm^2/molecule) and can be written

$$\sigma(\nu) = \frac{1}{nl} \ln \frac{I_0}{I}(\nu) \qquad (2)$$

For the relatively heavy molecules studied here, the individual rotational lines are merged into a continuum (Q branches) or grouped in peaks (P and R branches), as can be observed in Figure 1. The 0.03 cm^{-1} resolution is however insufficient to perform a complete rotational analysis of the bands. All the absorption features are convolved with a shape function which includes both the line profile (Doppler, Lorentz or Voigt according to the experimental conditions) and the instrumental line shape due to the finite resolving power of the instrument. To avoid the problem of the finite spectral resolution, different techniques have been used. Pressure-broadening techniques by a foreign nonabsorbing gas are described by *Wilson and Wells* [1946], *Penner and Weber* [1951] and *Kagann et al.* [1983]. The curve of growth method, which requires the measurement of an equivalent width, is discussed by *Benedict et al.* [1956]. *McDaniel et al.* [1991] have used a method of data reduction which eliminates the need for addition of inert gas into the cell. In our experiment, which uses a Fourier spectrometer, the finite resolution is associated with the limited displacement δ of the scanning mirror. This truncation corresponds formally to a multiplication of the interferogram with a boxcar function. After Fourier transformation the spectrum is thus the convolution of the "true" spectrum with a sinx/x function (x=1/δ), which is the Fourier transform of a boxcar. By multiplying the interferogram by a well-chosen smoothing function, the strong sidelobes in the spectrum are damped. We have thus simply apodized our data with a Norton-Beer strong function [*Griffiths and de Haseth*, 1986] in order to minimize the instrumental distortion and to preserve the true line surface.

The cross sections were determined using equation(2) for each spectral data point, 0.0085 cm^{-1} apart, between 600 and 1500 cm^{-1}. Some care must be taken in obtaining the base e absorbance ln I_0/I: a small baseline shift, due to the very slow heating of the source and of the detector, often occurs. To avoid this, two empty cell background spectra were taken, one before and one after each recorded spectrum, and the mean value of these has been used as I_0. The quality of the baseline was checked each time by observing zero absorbance in areas where no absorption occurs. Secondly, all the pressures were chosen to prevent saturation of the spectra: a maximum of 75% absorption was allowed. Neglecting these two precautions would lead to large errors in the determined cross sections.

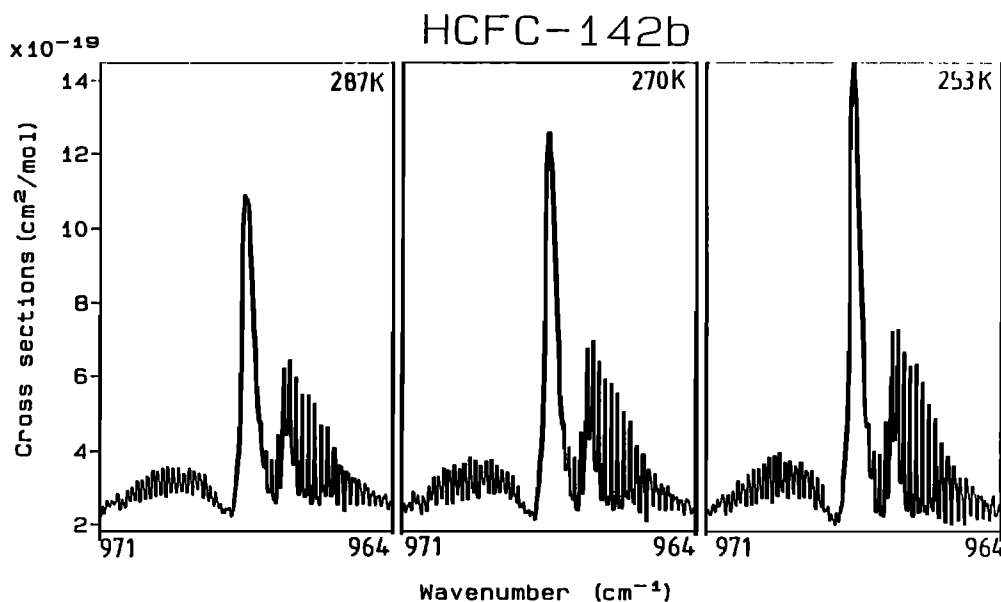In order to increase the accuracy a linear least squares

Fig. 1. Temperature dependence of the absorption cross sections, between 964 and 971 cm^{-1}, for HCFC142b.

fit was applied for each point using all six pressures. For each of the three temperatures the cross sections were obtained by this procedure and zero values have been set in the regions where no absorption occurs and only noise was recorded. It should be noted that no dependence of these cross sections on pressure was found, in contrast to the results reported by McDaniel et al [1991] for eight CFCs measured at six different temperatures. The uncertainties associated with these cross sections, at 0.03 cm^{-1} resolution, range from 1-2% for strong absorptions to 3-4% for weak absorptions. They were obtained by adding the uncertainties due to the following sources of error, described in chapter 2: pressure and temperature measurements, purity determination, pathlength, and standard deviation in the least squares fit. An example of the obtained cross sections is plotted in Figure 2 for HCFC141b, at 287 K, between 700 and 1500 cm^{-1}. The complete set of data is available on PC diskettes upon request.

Atmospheric abundances of CFCs have been determined by IR Fourier transform spectroscopy using laboratory spectroscopic data [Zander et al., 1987]. As the emissions of hydrohalocarbons are expected to increase in the future, the temperature dependent cross section data obtained in this work can be used as reference spectra for atmospheric detection of these species by satellite, aircraft, or balloon-borne infrared spectrometers. As reported by Varanasi [1992], it is important to know the temperature and the pressure dependence of the spectral features in order to derive correct concentrations. As can be seen in Figure 1, the intensity of a strong Q branch may increase by as much as 33% with a 35 K decrease in temperature. No systematic studies of the pressure-broadening effects have been undertaken.

3.2. Integrated Band Strengths

Integrated band strengths have been calculated using the formula

$$\sigma_{int} = \int_{\nu_1}^{\nu_2} \sigma(\nu)d\nu = \sum_{\nu_1}^{\nu_2} \sigma(\nu)\Delta\nu \qquad (3)$$

Two different sets of data have been calculated. To obtain the results presented in Table 1 and 2, the integration limits ν_1 and ν_2 were chosen in order to cover the main absorption features. Some integration regions may contain several vibrational bands. In Table 1 the integrated cross sections σ_{int} obtained for CFC12 and HCFC22 are compared with the numerous results published in the literature. The uncertainties on the last given digit are indicated in parentheses. Some results, originally reported in cm^{-2}atm^{-1}, have been transformed into cm molecule^{-1} units. Our results for these two molecules agree well with the results reported by most of these authors. In Table 2 the integrated band strengths determinated for all 10 HCFCs and HFCs are given for the three temperatures investigated. A small temperature dependence appears to exist for some of these bands.

A second set of data has been derived in order to be used in atmospheric radiative models (see section 3.3), constant intervals of 100 cm^{-1} have been chosen to divide up the spectrum. These tables are also available upon request.

A set of experiments was carried out in order to test the effect of the instrument resolution on the measured values of the integrated cross sections, at a resolution
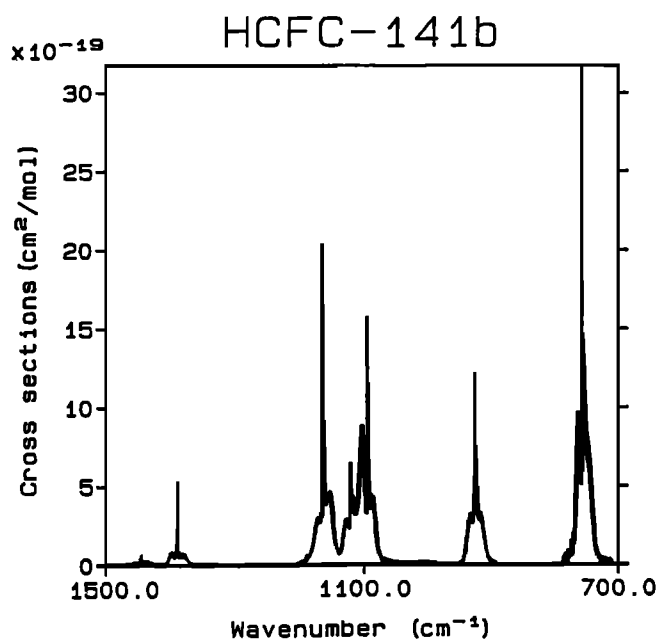
Fig. 2. Absorption cross sections, at 287 K, between 700 and 1500 cm^{-1}, for HCFC141b.

5 times higher (0.006 cm^{-1}) and 5 times lower (0.15 cm^{-1}) than measured previously. Peak cross sections were strongly affected by resolution changes, but no significant differences were found for the integrated values.

3.3. Global Warming Potentials

In order to compare the effect on the climate caused by the emission of radiatively active gases, a relative index has been introduced: the global warming potential [Intergovernmental Panel on climate Change(IPCC), 1990]. The GWP of a well-mixed gas is defined as the time-integrated commitment to radiative forcing from the instantaneous release of 1 kg of a trace gas expressed relative to that from the release of 1 kg of a reference gas

$$GWP = \frac{\int_0^n a_i c_i \, dt}{\int_0^n a_{ref} c_{ref} \, dt} \tag{4}$$

where a_i and a_{ref} are the instantaneous radiative forcings due to a mass unit increase in the concentration of the gas, c_i and c_{ref} are the concentrations of the trace gas i and of the reference gas remaining at time t after its release, and n is the number of years over which the calculation is performed. The gas chosen as reference is generally CO_2 for climate studies [IPCC, 1990] or CFC11 for halocarbons or ozone-related studies [Fisher et al., 1990b]. The radiative forcing due to a perturbation in the concentration of a greenhouse gas is given by the net radiative flux change (in W m^{-2}) induced by this perturbation at the tropopause. Due to an incomplete understanding of all the interaction feedback mechanisms on clouds, oceans, and polar ice, a characterization in terms of direct heat trapping or radiative forcing is generally preferred to a characterization by a change in the Earth's surface temperature. Because CFCs and alternatives are present in very small quantities and their absorption bands do not overlap with those of the main greenhouse gases, the radiative forcing associated with such compounds increases linearly with the amount of absorber. For the more abundant gases where saturation effects occur, the dependence is better approximated by a square root or a logarithmic function.

The cross section data we have measured for 10 hydrohalocarbons have been introduced in the NCAR radiative-chemical-dynamical two-dimensional interactive model [Brasseur et al., 1990] and GWP values have been obtained, relative to CFC11, for time horizons corresponding to 5, 10, 20, 50, 100, 200, and 500 years.

Radiative forcings of HCFCs and HFCs have been determined with a new version of the radiative code used in the NCAR community climate model version 1 (CCM1) [Kiehl et al., 1987]: the new longwave scheme takes into account the thermal radiative effects of H_2O, CO_2, CH_4, O_3, N_2O, CFC11, and CFC12 [Briegleb, 1992]. In this wideband model, the averaged integrated cross sections over intervals of 100 cm^{-1} have been introduced for each of the HCFCs and HFCs. The small temperature dependences of these data have been neglected due to the larger uncertainties present in other parameters. The forcings calculated by the model, rel-

TABLE 1: Integrated Cross Sections (cm molecule^{-1} × 10^{17}) for CFC12 and HCFC22

Molecule	Integration Limits[a], cm^{-1}	Varanasi and Ko [1977][b] 296 K	Kagann et al. [1983][b] 296 K	Massie et al [1985][b] 296 K	Varanasi et al. [1988][b] 300 K	Fisher et al. [1990b] 296 K	McDaniel et al [1991] 293 K	This Work 287 K
CFC12	850–950	5.322(161)	5.832(186)	6.131(615)	5.809(49)	5.742(?)	5.455(545)	5.880(124)
(CF$_2$Cl$_2$)	1070–1130	4.644(89)	4.602(157)	7.139(715)[c]	4.615(45)	7.142(?)[c]	4.206(421)	4.497(76)
	1130–1190	2.935(56)	3.134(105)		2.931(57)		2.925(292)	3.083(71)
HCFC22	765–855	-	-	-	2.233(8)	2.284(?)	2.132(213)	2.357(90)
(CHClF$_2$)	1060–1210	-	-	-	7.179(93)	6.751(?)	6.007(601)	6.825(171)
	1275–1380	-	-	-	-	1.269(?)	0.882(88)	1.081(89)

[a] The limits of integration are those used in the present work.
[b] Reported by Mc Daniel et al. [1991].
[c] Integration limits ~ 1070-1190 cm^{-1}.

TABLE 2: Integrated Cross Sections $\left(\text{cm molecule}^{-1} \times 10^{17}\right)$ for HCFCs and HFCs

Molecule	Integration Limits, cm^{-1}	Integrated Cross Sections			Uncertainties
		287 K	270 K	253 K	
HCFC22	765–855	2.36	2.32	2.25	(0.09)
(CHClF$_2$)	1060–1210	6.83	6.73	6.64	(0.17)
	1275–1380	1.08	1.11	1.09	(0.09)
HCFC123	740–900	2.39	2.30	2.08	(0.14)
(CHCl$_2$CF$_3$)	1080–1450	10.49	10.26	10.09	(0.37)
HCFC124	675–715	0.53	-	-	(0.04)
(CHClFCF$_3$)	790–920	1.81	-	-	(0.14)
	1035–1430	12.09	-	-	(0.52)
HCFC141b	710–790	2.37	2.22	2.16	(0.08)
(CH$_3$CCl$_2$F)	895–955	1.09	1.02	1.00	(0.06)
	990–1210	3.95	3.72	3.33	(0.20)
	1325–1470	0.34	0.33	0.34	(0.12)
HCFC142b	650–705	0.75	0.69	0.68	(0.05)
(CH$_3$CClF$_2$)	875–1030	2.58	2.51	2.40	(0.14)
	1075–1265	7.19	7.11	6.96	(0.20)
	1360–1475	0.61	0.64	0.78	(0.09)
HCFC225ca	695–865	3.02	3.02	3.00	(0.08)
(CHCl$_2$CF$_2$CF$_3$)	1010–1420	14.69	14.62	14.49	(0.42)
HCFC225cb	715–880	3.19	3.45	3.48	(0.16)
(CClF$_2$CF$_2$CHClF)	890–990	1.65	1.73	1.68	(0.09)
	1025–1375	10.74	11.27	11.36	(0.36)
HFC125	700–745	0.53	-	-	(0.04)
(CHF$_2$CF$_3$)	840–890	0.67	-	-	(0.05)
	1060–1465	14.91	-	-	(0.51)
HFC134a	815–865	0.25	0.21	0.24	(0.04)
(CFH$_2$CF$_3$)	935–1010	0.79	0.81	0.84	(0.07)
	1035–1130	1.41	1.43	1.47	(0.09)
	1135–1340	9.71	9.76	9.68	(0.23)
	1345–1485	0.45	0.46	0.44	(0.11)
HFC152a	840–995	1.15	1.17	1.15	(0.14)
(CH$_3$CHF$_2$)	1050–1205	4.40	4.44	4.51	(0.16)
	1320–1490	1.34	1.40	1.41	(0.15)

TABLE 3: Lifetimes (years), Radiative Forcings, and GWPs relative to CFC11

Halocarbon	Lifetime	Radiative Forcing		Global Warming Potential (years)						
		per molecule	per kilogram	5	10	20	50	100	200	500
CFC11[a]	57.0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
HCFC22	14.3	0.85	1.35	1.19	1.06	0.86	0.56	0.41	0.35	0.34
HCFC123	1.5	0.90	0.81	0.25	0.13	0.07	0.04	0.03	0.02	0.02
HCFC124	6.0	0.94	0.95	0.67	0.50	0.32	0.17	0.12	0.10	0.10
HCFC141b	9.7	0.66	0.77	0.63	0.53	0.39	0.22	0.16	0.14	0.13
HCFC142b	21.1	0.82	1.12	1.04	0.97	0.86	0.64	0.50	0.43	0.41
HCFC225ca	2.4	1.08	0.73	0.32	0.19	0.10	0.05	0.04	0.03	0.03
HCFC225cb	6.8	1.31	0.88	0.65	0.50	0.34	0.18	0.13	0.11	0.11
HFC125	33.9	0.91	1.04	1.01	0.98	0.93	0.82	0.71	0.64	0.62
HFC134a	13.1	0.78	1.06	0.92	0.81	0.64	0.41	0.29	0.25	0.24
HFC152a	1.5	0.50	1.03	0.31	0.17	0.09	0.05	0.03	0.03	0.03

GWP, global warming potential.
[a]Used as reference gas.

ative to CFC11, are reported in Table 3 on a molecule per molecule basis and on a kilogram per kilogram basis. As the location and the intensity of the absorbing bands differ for each species, the relative forcings can be smaller or greater than unity. Our values are generally in agreement (better than 10%) with the radiative forcings reported by IPCC [1990] [from Fisher et al., 1990b], except for HCFC123 and HFC125 for which our values are higher by 12% and lower by 15%, respectively. The results of Fisher et al. [1990b] are based on unpublished cross section values; it is therefore difficult to comment further on the observed discrepancies. Radiative forcings for HCFC225ca and HCFC225cb are reported, to our knowledge, for the first time.

For all the greenhouse gases included in the model, the vertical concentration profiles from 0 to 85 km and the atmospheric lifetimes have been determined with an updated version of the two-dimensional model described by Brasseur et al. [1990]. Current ground level concentrations have been used as a boundary condition for all the major gases (including HCFC22) and set at 2.5 ppt for all the other hydrohalocarbons. Due to the very small quantities of hydrohalocarbons introduced in the model, no indirect effects, such as changes in the distribution of stratospheric or tropospheric O_3, were included. Atmospheric lifetimes were obtained using the rate coefficients for reaction with OH from WMO [1992] for tropospheric removal and the photodissociation rates were computed by using the UV absorption cross sections from Gillotay and Simon [1991a,b]. These lifetimes are reported in Table 3 and are in general agreement with the other published results [IPCC, 1990; WMO, 1992]. All the GWPs relative to CFC11 obtained for the different time scales are summarized in Table 3. The differences between our results and the GWP values reported, relative to CO_2, in WMO [1992] are lower than 10% and are mostly due to the different lifetimes used, except for HFC125. For this substitute, GWP values lower by 25% were found and are mainly due to the discrepancy in the radiative forcings.

CO_2 is often prefered as a reference gas to compare the impact on global warming of all the radiatively active gas (CH_4, N_2O, ...). In this work, model calculations have also been performed relative to CO_2 but were found to be less representative and are not presented here. The uncertainties associated with the lifetime of CO_2 and the strong nonlinear dependence of the radiative forcing on the concentration changes make CFC11 a better choice.

4. DISCUSSION AND CONCLUSION

In this paper, experimental infrared cross section data at relatively high resolution and at three atmospheric temperatures have been obtained for hydrohalocarbons. Global warming potentials have been determined for different time horizons, using integrated cross

sections into a two-dimensional radiative-chemical model.

Fisher et al. [1990b] were the first to calculate the GWPs of CFCs and substitutes using CFC11 as a reference gas. They conclude that all substitutes are environmentally preferable to CFC11, but in their work it was assumed that the integration time was set to infinity. We agree with their general conclusion. The integration over different time horizons obtained in this work shows that as expected, the warming effect decreases exponentially with a time constant equal to the atmospheric lifetime of the species. But these calculations also show that for three compounds (HCFC22, HCFC142b, HFC125) the GWPs (relative to CFC11) are higher than unity for a 5- to 10-year period. Moreover, these compounds maintain a relatively strong GWP for a very long time. Therefore taking into account the fact that for some industrial applications, larger quantities of CFC alternatives are sometimes needed to replace the present CFCs in order to obtain an equivalent efficiency, their contribution to the global warming may remain important. We hope that the present results will help in the definition of future regulations.

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