

INFRARED ABSORPTION CROSS SECTIONS OF ALTERNATIVE CFCs

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ABSTRACT

Absorption cross sections have been obtained in the infrared atmospheric window, between 600 and 1500 cm^{-1} , for 10 alternative hydrohalocarbons: HCFC-22, HCFC-123, HCFC-124, HCFC-141b, HCFC-142b, HCFC-225ca, HCFC-225cb, HFC-125, HFC-134a and HFC-152a. The measurements were made at three temperatures (287K, 270K and 253K) with a Fourier transform spectrometer operating at 0.03 cm^{-1} apodized resolution. Integrated cross sections are also derived for use in radiative models to calculate the global warming potentials.

1 INTRODUCTION

Because of their chemical inertness, chlorofluorocarbons (CFCs) remain in the troposphere for long time periods contributing to the warming of the atmosphere and, after photodissociation in the stratosphere, affect the ozone budget (IPCC, 1990; WMO, 1992). Since the international agreements (Montreal Protocol, 1987 and London Amendment, 1990) have established the phase-out for CFCs, alternative chemicals and technologies are being developed by industries to meet the future needs in refrigeration, foam-blowing, insulation and electronic cleaning and drying processes. 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. They contain at least one hydrogen atom which lead them to react with hydroxyl radicals in the troposphere, resulting in shorter lifetimes than those of CFCs and consequently lower Ozone Depletion Potential. But these compounds also absorb infrared radiation in the atmospheric window, so that their effectiveness as greenhouse gases must be assessed and compared with that of the CFCs.

Infrared absorption cross sections have been measured, as a function of the temperature, for the 10 alternative compounds given in Table 1.

Table 1. Hydrohalocarbons used as substitutes for CFCs

Hydrohalocarbon	Chemical formula
HCFC-22	CHClF_2
HCFC-123	CHCl_2CF_3
HCFC-124	CHClFCF_3
HCFC-141b	$\text{CH}_3\text{CCl}_2\text{F}$
HCFC-142b	CH_3CClF_2
HCFC-225ca	$\text{CHCl}_2\text{CF}_2\text{CF}_3$
HCFC-225cb	$\text{CClF}_2\text{CF}_2\text{CHClF}$
HFC-125	CHF_2CF_3
HFC-134a	CFH_2CF_3
HFC-152a	CH_3CHF_2

2 EXPERIMENTAL

The spectra have been recorded in the infrared atmospheric window, between 600 and 1500 cm^{-1} , using a Bruker IFS 120HR Fourier Transform Spectrometer. 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 HCFCs and HFCs were supplied by Solvay S.A (Belgium), E.I Du Pont de Nemours (USA) and Asahi Glass Company (Japan). The gas to be studied is introduced in a 5 cm long thermostatic cell closed by two pairs of KBr windows (Hurtmans *et al*, 1992). The cell, stabilized in temperature by a cooled liquid circulating in a double wall, is placed inside the sample chamber of the spectrometer which is then evacuated in order to eliminate infrared absorption interferences from ambient CO_2 and H_2O . Pressure and temperature of the gas are measured inside the cell using respectively an absolute MKS Baratron capacitance gauge and a transducer.

For each gas eighteen spectra have been recorded at six different pressures, ranging from 1 to 4 torrs, and three different temperatures (287K, 270K, 253K).

3 CROSS SECTIONS

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

$$I(\nu) = I_0(\nu) \exp(-\sigma(\nu)nl) \quad (1)$$

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

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

Cross sections were determined for each spectral data point, 0.0085 cm^{-1} apart, between 600 and 1500 cm^{-1} . In order to increase the accuracy, a linear least square fit was done for each point using all six pressures. For each of the three temperatures, the cross sections are obtained by this procedure. Examples of the cross sections results can be seen in figures 1 and 2. According to the experimental

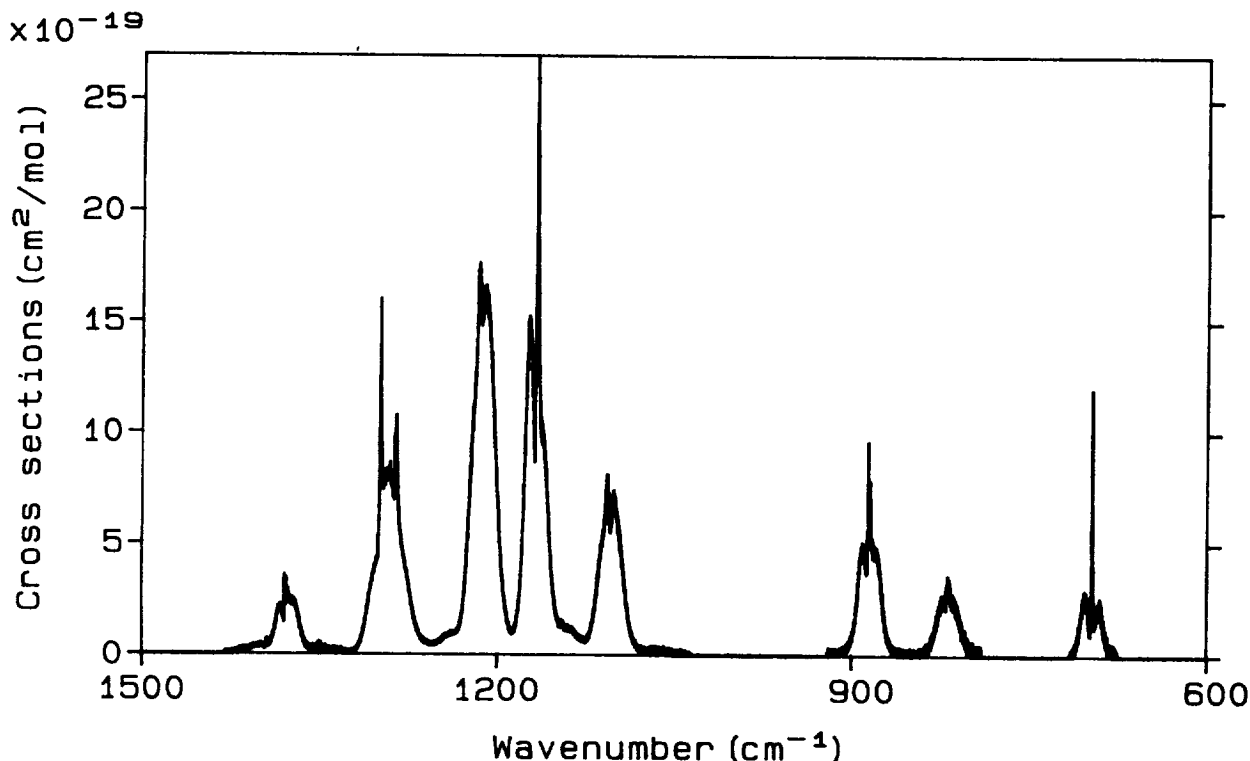


figure 1 : Cross sections ($\text{cm}^2/\text{molec.}$) in the atmospheric window (600 - 1500 cm^{-1}) for HCFC-124 (CHClFCF_3) at 287K

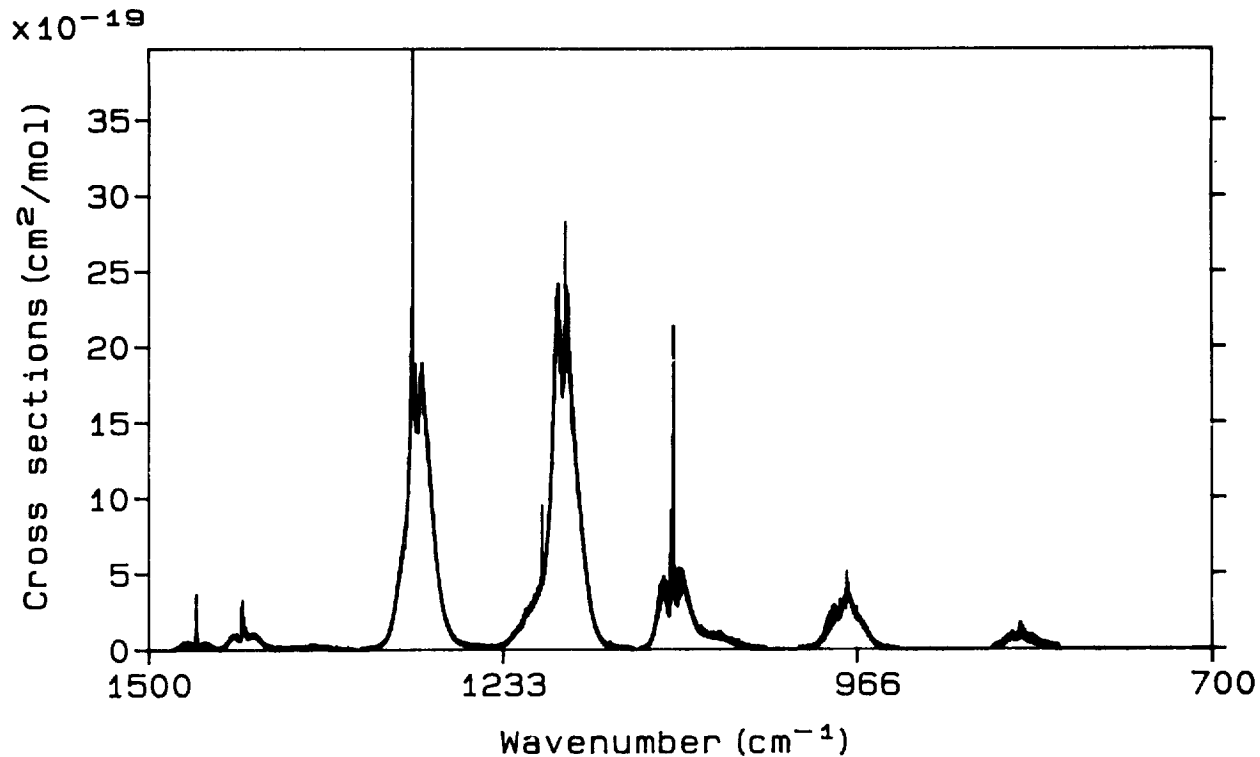


figure 2 : Cross sections ($\text{cm}^2/\text{molec.}$) in the atmospheric window ($600 - 1500 \text{ cm}^{-1}$) for HFC-134a (CFH_2CF_3) at 253K

conditions and the purity of the gas, cross sections are determined with an accuracy of 2% for the strong spectral features and 4% for the weak spectral features.

Table 2. Integrated cross sections ($\text{cm}/\text{molec.} \times 10^{17}$) between 600 and 1500 cm^{-1} for HCFCs and HFCs.

4 INTEGRATED BAND STRENGTHS

Integrated band strengths have been calculated using the formula :

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

The integration limits ν_1 and ν_2 were chosen in order to cover the main absorption features (each integration region may contain several vibrational bands). To obtain the results presented in Table 2, the integrated cross sections calculated for each region were added to obtain a global estimation for the entire atmospheric window. These results are given with an accuracy of 5%.

Molecule	Integrated cross sections		
	T = 287K	T = 270K	T = 253K
HCFC-22	10.26	10.16	9.98
HCFC-123	12.88	12.56	12.17
HCFC-124	14.43	-	-
HCFC-141b	7.75	7.29	6.83
HCFC-142b	11.13	10.95	10.83
HCFC-225ca	17.71	17.64	17.49
HCFC-225cb	15.58	16.45	16.51
HFC-125	16.11	-	-
HFC-134a	12.61	12.67	12.67
HFC-152a	6.88	7.02	7.07

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