

# Temperature-Dependence of Ultraviolet Absorption Cross-Sections of Alternative Chlorofluoroethanes:

## 2. The 2-chloro-1,1,1,2-tetrafluoro ethane – HCFC-124

DIDIER GILLOTAY and PAUL C. SIMON

*Institut d'Aéronomie Spatiale de Belgique, Avenue Circulaire 3, B-1180 Bruxelles, Belgium*

(Received: 27 May 1991)

**Abstract.** The temperature-dependent ultraviolet absorption cross-sections of  $\text{CF}_3\text{-CHFCl}$  (HCFC-124) have been measured between 170 and 230 nm for temperatures ranging from 295 to 210 K, with uncertainties between 2 and 4%. These results are compared with other available sets of determinations. Temperature effects are discussed and the photodissociation coefficients, presented with their temperature dependence, are calculated. Implication of the temperature dependences on the stratospheric chemistry is also discussed. Parametrical formulae are proposed to compute absorption cross-section values for wavelengths and temperatures useful in modelling calculations.

**Key words:** Alternative hydro-chloro-fluoro-ethanes, UV absorption cross-sections, photodissociation coefficients, temperature dependence.

### 1. Introduction

Since the 'Montreal Protocol on substances that deplete the ozone layer', alternative CFCs are actively pursued to replace the classical CFCs (CFC-11, CFC-12, CFC-113, CFC114, CFC-115, ...) in many of their applications.

Among these new molecules, partially hydrogenated halocarbons are relatively vulnerable to OH radical attack at tropospheric altitudes which will remove a great part of them before reaching the stratosphere where the remaining HCFC molecules will be photolysed or will react with stratospheric OH or  $\text{O}(^1\text{D})$  radicals.

Determinations of lifetime and ozone depletion potential of these molecules require an accurate knowledge of absorption cross-sections as a function of wavelength and temperature.

The purpose of this paper is to report measurements of the temperature-dependence of the absorption cross-sections of  $\text{CF}_3\text{-CHFCl}$  (HCFC-124), performed between 170 and 230 nm and for temperatures ranging from 295 to 210 K. These data are used to estimate the temperature-dependence of the photodissociation coefficients relative to those calculated at room temperature.

## 2. Experimental

Ultraviolet absorption cross-sections and their temperature-dependence were determined by means of the double beam experimental device previously described by Gillotay *et al.* (1989), which includes a deuterium lamp as the continuum light source, a 1 m McPherson 225 monochromator equipped with a 1200 lines/mm grating, 200 and 20 cm thermostated absorption cells (the 20 cm absorption cell being used as reference channel), EMR P-09-18 solar blind photomultiplier tubes as detector, and a data acquisition system.

Wavelength scanning is performed by means of a stepping motor; an increment of 1 nm usually being used for recording continuum absorption spectra. The slit widths are chosen to obtain a band width of about 0.1 nm with a wavelength repeatability of  $\pm 0.01$  nm.

Pressures inside the cell, ranging from  $2 \times 10^{-3}$  to  $1 \times 10^3$  Torr, are measured by means of capacitance manometers (type MKS Baratron 170-315) operating over three decades in the ranges 0 to 1, 0 to 10, and 0 to 1000 Torr. The calibration procedure of these manometers takes into account the precise measurements of the atmospheric local pressure at regular intervals and allows an accuracy of around 0.1%.

Low temperatures are measured with absolute uncertainties of around  $\pm 1$  K by means of five Pt 100 temperature sensors (a temperature stability of  $\pm 0.3$  K is usually observed at low values). The absolute value of the low temperatures is confirmed within  $\pm 1$  K by comparison with temperatures calculated from the perfect gas law.

The purities of HCFC-124 samples, provided by Solvay S.A. and DuPont de Nemours are, respectively, of 99.85 and 99.95%, as determined by gas-phase chromatography before and after the sampling procedure. Corrections have been made to take into account the absorption contribution of the main impurity, namely  $\text{CHF}_2\text{Cl}$  (0.14 and 0.045% respectively).

The determination of the absorption cross-sections is made after simultaneous recordings of incident (through the reference channel) and transmitted fluxes (through the measurement channel), measured under the same temperature conditions, using the Beer-Lambert law. Experimental conditions are summarised in Table I.

As previously explained, (Gillotay and Simon, 1991), in order to obtain data only in the range where the Beer-Lambert law is still applicable, only results corresponding to transmission values of between 10 and 85% are considered for the determination of the absorption cross-section, for a given pressure in the absorption cell.

Table I. Experimental conditions

$T$ (K)	Pressure range (Torr)	No. of exp <sup>a</sup>
296.4	902.8–0.5846	204
252.0	373.5–0.0860	131
229.9	76.67–0.2980	180
218.6	21.00–0.4965	148
206.7	9.50–0.1979	84

<sup>a</sup> Number of absorption spectra recorded under different experimental conditions.

### 3. Results

#### 3.1. Absorption Cross-Sections

Over the experimental temperature range, absorption spectra of HCFC-124 look like a continuum with absolute values ranging from about  $1.4 \times 10^{-19} \text{ cm}^2 \text{ molec}^{-1}$  at 170 nm to around  $6 \times 10^{-24} \text{ cm}^2 \text{ molec}^{-1}$  at 230 nm and 295 K, without any indications of structures in the spectra.

Numerical values of absorption cross-sections, interpolated from the experimental determinations are given for selected wavelengths (1 nm wavelength intervals and  $500 \text{ cm}^{-1}$  wavenumber intervals) in Tables II and III and are represented in Figure 1 for three temperatures (namely 295, 250, and 210 K). Wavelengths are defined in the vacuum.

According to the experimental conditions, and the previously published error budget (Simon *et al.*, 1988a), the values presented in Tables II and III are determined to be accurate within  $\pm 2\%$  at room temperature and around  $\pm 3$  to  $4\%$  at low temperatures.

3.1.1. *Ambient Temperature (295 K)*. At ambient temperature, available results obtained by four different groups (Orlando *et al.*, 1991; Allied-Signal Corporation, 1990; Molina and Molina, 1990, and this work) are in relatively good agreement (within  $\pm 10\%$ ) up to 215 nm, except for the values from Allied-Signal Corporation around 205 nm. A comparison of the relative absorption cross-section values is given in Figure 2 where the values of Orlando *et al.*, recommended by AFEAS in the WMO Report (1990), are taken as reference.

At longer wavelengths, discrepancies became much higher than the quoted accuracy of the different measurements (up to 30% at 220 nm).

3.1.2. *Low Temperature (210–270 K)*. Absorption cross-section has been measured at four low temperatures in a range as large as possible but limited by the vapour pressure. The absorption cross-section values decrease exponentially with temperature in the region of longer wavelengths and are practically constant

Table II. Absorption cross-sections of HCFC-124 (CF<sub>3</sub>-CHFCl) at 1 nm intervals for five selected temperatures (295, 270, 250, 230, 210 K)

$\lambda(\text{nm})$	$\sigma(\lambda) \times 10^{21} (\text{cm}^2 \text{molec}^{-1})$				
	295 K	270 K	250 K	230 K	210 K
170	136	133	131	128	126
171	123	120	118	116	113
172	111	108	106	104	102
173	99.2	96.5	94.4	92.4	90.3
174	88.5	85.9	83.9	81.9	80.0
175	78.5	76.0	74.1	72.3	70.4
176	69.3	67.0	65.2	63.4	61.7
177	60.9	58.7	57.1	55.4	53.8
178	53.3	51.3	49.7	48.2	46.7
179	46.4	44.6	43.1	41.7	40.4
180	40.3	38.6	37.3	36.0	34.7
181	34.8	33.3	32.0	30.9	29.7
182	30.0	28.6	27.5	26.4	25.4
183	25.8	24.4	23.4	22.5	21.6
184	22.0	20.8	19.9	19.1	18.2
185	18.8	17.7	16.9	16.1	15.4
186	16.0	15.0	14.3	13.6	12.9
187	13.5	12.7	12.0	11.4	10.8
188	11.4	10.7	10.1	9.54	9.03
189	9.62	8.94	8.44	7.96	7.51
190	8.08	7.49	7.04	6.62	6.23
191	6.78	6.25	5.86	5.49	5.15
192	5.67	5.21	4.87	4.55	4.25
193	4.74	4.33	4.03	3.75	3.49
194	3.95	3.59	3.33	3.09	2.87
195	3.28	2.97	2.75	2.54	2.35
196	2.73	2.46	2.26	2.08	1.92
197	2.26	2.03	1.86	1.71	1.56
198	1.87	1.67	1.53	1.39	1.27
199	1.55	1.38	1.25	1.14	1.03
200	1.28	1.13	1.02	0.927	0.839
201	1.06	0.930	0.837	0.754	0.679
202	0.875	0.763	0.684	0.613	0.549
203	0.722	0.626	0.558	0.498	0.444
204	0.596	0.513	0.455	0.404	0.358
205	0.492	0.421	0.371	0.327	0.289
206	0.406	0.345	0.302	0.265	0.233
207	0.335	0.282	0.246	0.215	0.187
208	0.276	0.231	0.201	0.174	0.151
209	0.228	0.190	0.163	0.141	0.121
210	0.189	0.155	0.133	0.114	0.0977
211	0.156	0.128	0.109	0.0923	0.0786
212	0.129	0.105	0.0885	0.0748	0.0632
213	0.107	0.0861	0.0722	0.0606	0.0509
214	0.0889	0.0708	0.0590	0.0492	0.0410
215	0.0739	0.0583	0.0482	0.0399	0.0330
216	0.0615	0.0481	0.0395	0.0324	0.0266
217	0.0513	0.0397	0.0323	0.0263	0.0215

218	0.0429	0.0328	0.0265	0.0214	0.0173
219	0.0359	0.0272	0.0218	0.0175	0.0140
220	0.0301	0.0226	0.0180	0.0143	0.0113
221	0.0253	0.0188	0.0148	0.0117	0.00919
222	0.0214	0.0157	0.0122	0.00956	0.00746
223	0.0181	0.0131	0.0101	0.00785	0.00607
224	0.0153	0.0110	0.00842	0.00645	0.00494
225	0.0130	0.00924	0.00701	0.00532	0.00404
226	0.0111	0.00779	0.00585	0.00439	0.00330
227	0.00953	0.00658	0.00489	0.00364	0.00271
228	0.00819	0.00558	0.00411	0.00302	0.00222
229	0.00707	0.00475	0.00346	0.00252	0.00183
230	0.00612	0.00406	0.00292	0.00210	0.00151

Table III. Absorption cross-sections of HCFC-124 (CF<sub>3</sub>-CHFCI) averaged over the spectral intervals of 500 cm<sup>-1</sup> used in atmospheric modelling calculations for five selected temperatures (295, 270, 250, 230, 210 K)

No.	$\lambda(\text{nm})$	$\sigma(\lambda) \times 10^{21} (\text{cm}^2 \text{molec}^{-1})$				
		295 K	270 K	250 K	230 K	210 K
42	166.7–169.5	162	159	156	154	152
43	169.5–172.4	124	121	118	116	114
44	172.4–173.9	97.6	94.9	92.8	90.7	88.7
45	173.9–175.4	81.9	79.4	77.4	75.5	73.7
46	175.4–177.0	67.6	65.3	63.5	61.8	60.1
47	177.0–178.6	54.8	52.7	51.1	49.6	48.1
48	178.6–180.2	43.9	42.1	40.7	39.3	38.0
49	180.2–181.8	34.8	33.3	32.0	30.9	29.7
50	181.8–183.5	27.2	25.8	24.8	23.8	22.8
51	183.5–185.2	20.8	19.7	18.8	18.0	17.2
52	185.2–186.9	15.8	14.9	14.1	13.5	12.8
53	186.9–188.7	11.8	11.0	10.4	9.89	9.36
54	188.7–190.5	8.82	8.19	7.71	7.26	6.84
55	190.5–192.3	6.31	5.81	5.44	5.10	4.77
56	192.3–194.2	4.53	4.13	3.84	3.58	3.33
57	194.2–196.1	3.19	2.89	2.67	2.47	2.28
58	196.1–198.0	2.24	2.01	1.84	1.69	1.55
59	198.0–200.0	1.55	1.38	1.25	1.14	1.03
60	200.0–202.0	1.06	0.930	0.837	0.754	0.679
61	202.0–204.1	0.715	0.620	0.553	0.493	0.439
62	204.1–206.2	0.478	0.408	0.360	0.317	0.280
63	206.2–208.3	0.319	0.269	0.234	0.204	0.178
64	208.3–210.5	0.212	0.175	0.151	0.129	0.111
65	210.5–212.8	0.138	0.112	0.0950	0.0805	0.0682
66	212.8–215.0	0.0906	0.0722	0.0602	0.0502	0.0419
67	215.0–217.4	0.0593	0.0463	0.0379	0.0311	0.0255
68	217.4–219.8	0.0385	0.0293	0.0236	0.0190	0.0153
69	219.8–222.2	0.0253	0.0188	0.0148	0.0117	0.00919
70	222.2–224.7	0.0168	0.0121	0.00933	0.00718	0.00553
71	224.7–227.3	0.0111	0.00779	0.00585	0.00439	0.00330
72	227.3–229.9	0.00749	0.00507	0.00370	0.00271	0.00198

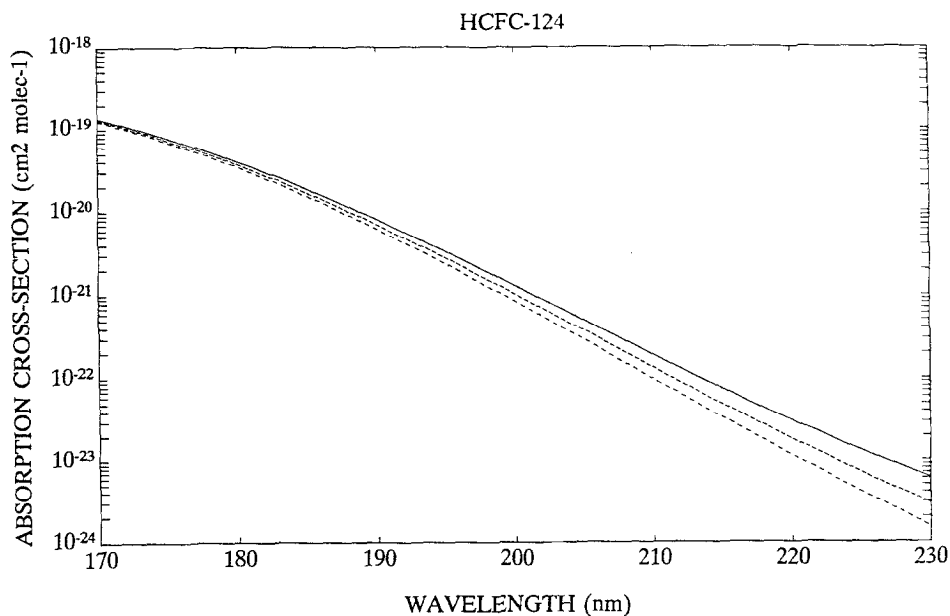


Fig. 1. Ultraviolet absorption cross-sections of  $\text{CF}_3\text{-CHFCl}$  (HCFC-124) between 170 and 230 nm at 295, 250 and 210 K.

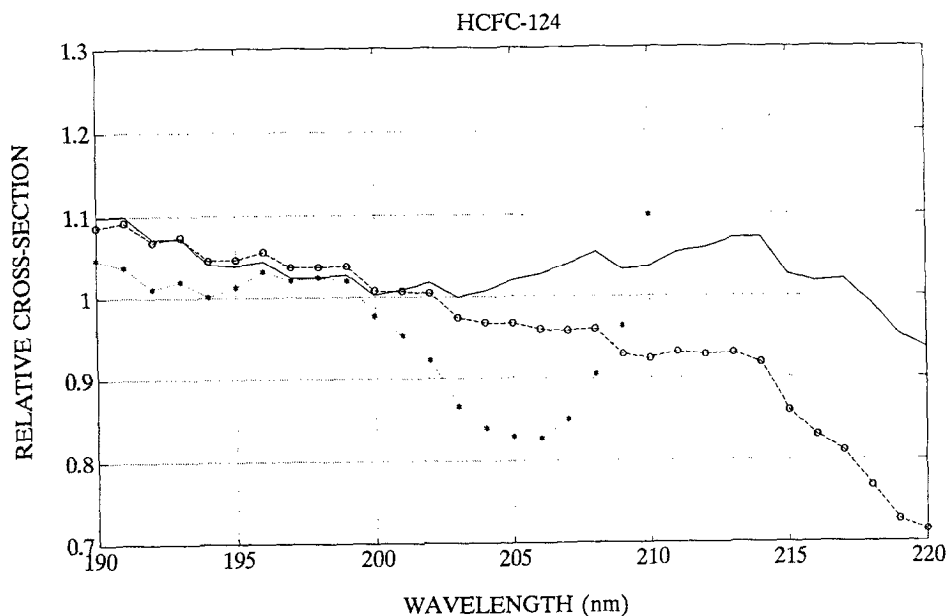


Fig. 2. Relative ultraviolet absorption cross-sections of  $\text{CF}_3\text{-CHFCl}$  (HCFC-124) between 170 and 230 nm at 295 K. Reference: WMO, (1990) = Orlando *et al.* (1991). — This work; --o-- Molina and Molina (1989); · · · · Allied-Signal Corporation (1989).

around 170 nm. The temperature effect is then the most significant at the lower temperature. This type of dependence has already been mentioned and illustrated for similar compounds (e.g. Simon *et al.*, 1988a and 1988b).

Figure 3 shows the relative values of the absorption cross-sections [ $\sigma(T)/\sigma(295\text{ K})$ ] versus the wavelengths relationships, for  $T = 270, 250, 230, 210\text{ K}$ , and illustrates the effect mentioned above. Also represented in this figure are the relative absorption cross-section values calculated from the data published by Orlando *et al.* (1991) at ambient and low temperature.

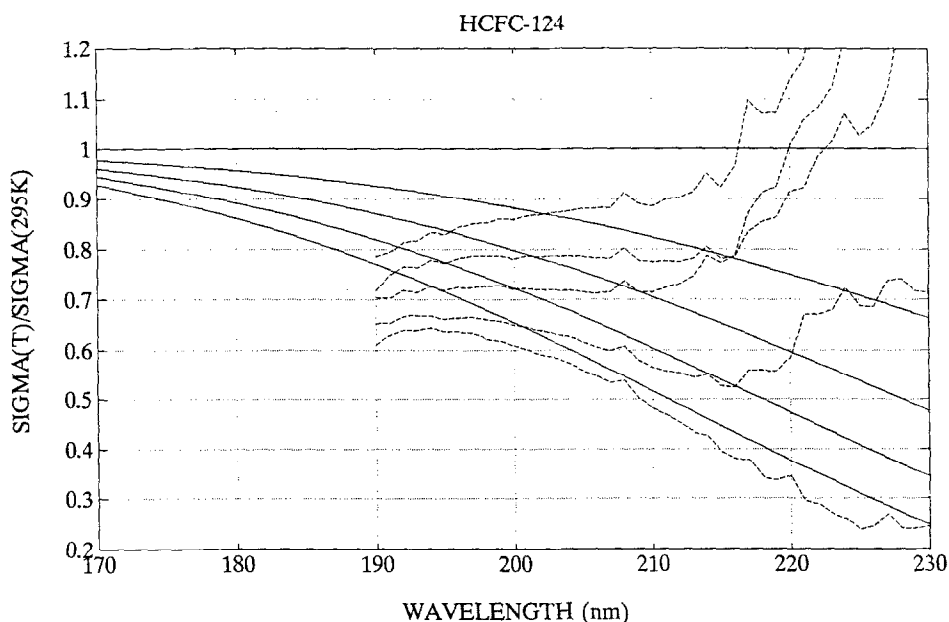


Fig. 3. Relative absorption cross-section  $\sigma(T)/\sigma(295\text{ K})$  of  $\text{CF}_3\text{-CHFCl}$  (HCFC-124) as a function of wavelength. — This work ( $T = 270, 250, 230, 210\text{ K}$ ); - - - Orlando *et al.* (1991); ( $T = 283, 263, 243, 223, 203\text{ K}$ ).

The temperature-dependences measured by Orlando *et al.* (1991) are greater for shorter wavelengths (below 200 nm) than those reported in this work and became smaller for longer wavelengths.

Moreover, as already reported for HCFC-123, HCFC-141b and HCFC-142b (Gillotay and Simon, 1991), inconsistencies are observed in the results of Orlando *et al.* for four of the five low temperatures, namely 283, 263, 243, and 223 K. In fact, the cross-section values at low temperatures are greater than those obtained at the ambient temperature (ratio greater than 1) which is not expected for similar measurements with other CFC (Simon *et al.*, 1988a, b; Hubrich and Stuhl, 1980; Chou *et al.*, 1977).

Experimental conditions (transmissions lower than 10% or higher than 85%; incident and transmitted UV fluxes not measured under the same conditions of

temperature) could explain these incoherences (Gillotay and Simon, 1991).

Numerical values interpolated through the absorption cross-section values obtained at four temperatures, are presented in Tables II–III for five selected temperatures (295, 270, 250, 230, and 210 K) which cover the usual atmospheric temperature conditions.

According to their exponential dependence on temperature, the absorption cross-sections can be represented by an empirical function:

$$\log_{10} \sigma(\lambda) = A(\lambda) + B(\lambda) \times T, \quad (1)$$

where the parameters  $A$  and  $B$  were determined by a polynomial least-square fit of the experimental data

$$\log_{10} \sigma(\lambda, T) = A_0 + A_1 \lambda + \dots + A_n \lambda^n + (T - 273) \times (B_0 + B_1 \lambda + \dots + B_n \lambda^n). \quad (2)$$

The computed values of  $A$  and  $B$  are given in Table IV. The values of absorption cross-sections calculated with expression (2) represent all the experimental results with differences smaller than 5%.

Table IV. Parameters  $A_i$  and  $B_i$  for polynomial function (see formula (3) in the text)

---

CF<sub>3</sub>-CHFCI (HCFC-124)

---

$A_0 = -101.230250$	$B_0 = -5.795712 \cdot 10^{-2}$
$A_1 = 1.333519$	$B_1 = 1.053901 \cdot 10^{-3}$
$A_2 = -6.888672 \cdot 10^{-3}$	$B_2 = -6.530379 \cdot 10^{-6}$
$A_3 = 1.114172 \cdot 10^{-5}$	$B_3 = 1.382056 \cdot 10^{-8}$

$T$  range: 210–300 K

$\lambda$  range: 170–230 nm

---

### 3.2. Photodissociation Coefficients

Photodissociation coefficients  $J$  for a given altitude  $z$ , zenith angle  $\chi$  and wavelength interval have been computed according to the relations

$$\begin{aligned} J^z &= \sigma_\lambda q_\lambda(z), \\ q_\lambda(z) &= q_\lambda(\infty) e^{-\tau_\lambda(z)}, \\ \tau_\lambda(z) &= \int_z^\infty [n(\text{O}_2)\sigma(\text{O}_2) + n(\text{O}_3)\sigma(\text{O}_3) + n(\text{air})\sigma_{\text{scatt.}}] \sec \chi \, dz, \end{aligned} \quad (3)$$

where  $\sigma$  are the absorption cross-sections;  $q_\lambda(z)$  and  $q_\lambda(\infty)$  are the solar irradiance at altitude  $z$  or extraterrestrial ( $z = \infty$ );  $n$  is the number of particles per volume unit; for solar zenith angles of 0 and 60° ( $\sec \chi = 1$  and 2); taking the values of



$\sigma(\text{O}_2)$ ,  $\sigma(\text{O}_3)$  from WMO (1986) and Kockarts (1976), of  $\sigma_{\text{scatt}}$  from Nicolet (1984) and the values of  $q(\infty)$  from WMO (1986), and taking into account the actual values of cross-sections which correspond to the temperature conditions prevailing at a definite altitude.

A comparison of either temperature dependent or independent photodissociation coefficients for different stratospheric altitudes (15 to 50 km) is presented in Table V where relative photodissociation coefficients  $J(T)/J(295)$  is given for the studied compound.

Obviously, the effect is maximum in the low stratosphere and gradually decreases, following the temperature profile in the stratosphere.

Table V. Photodissociation coefficients versus altitude

Z (km)	sec $\chi = 1$			sec $\chi = 2$		
	$J(\text{s}^{-1})$ $\sigma(295 \text{ K})^a$	$J(\text{s}^{-1})$ $\sigma = f(T)$	$J_{\text{rel}}$	$J(\text{s}^{-1})$ $\sigma(295 \text{ K})^a$	$J(\text{s}^{-1})$ $\sigma = f(T)$	$J_{\text{rel}}$
15	$3.987 \cdot 10^{-12}$	$2.401 \cdot 10^{-12}$	0.602	$3.218 \cdot 10^{-15}$	$1.969 \cdot 10^{-15}$	0.612
20	$8.503 \cdot 10^{-11}$	$5.255 \cdot 10^{-11}$	0.618	$1.074 \cdot 10^{-12}$	$6.633 \cdot 10^{-13}$	0.618
25	$6.658 \cdot 10^{-10}$	$4.373 \cdot 10^{-10}$	0.657	$4.018 \cdot 10^{-11}$	$2.602 \cdot 10^{-10}$	0.648
30	$2.923 \cdot 10^{-9}$	$2.026 \cdot 10^{-9}$	0.693	$5.075 \cdot 10^{-10}$	$3.454 \cdot 10^{-10}$	0.681
35	$8.318 \cdot 10^{-9}$	$6.193 \cdot 10^{-9}$	0.745	$2.958 \cdot 10^{-9}$	$2.166 \cdot 10^{-9}$	0.732
40	$1.669 \cdot 10^{-8}$	$1.345 \cdot 10^{-8}$	0.806	$9.350 \cdot 10^{-9}$	$7.432 \cdot 10^{-9}$	0.795
45	$2.499 \cdot 10^{-8}$	$2.169 \cdot 10^{-8}$	0.868	$1.753 \cdot 10^{-8}$	$1.506 \cdot 10^{-8}$	0.859
50	$3.224 \cdot 10^{-8}$	$2.892 \cdot 10^{-8}$	0.897	$2.496 \cdot 10^{-8}$	$2.219 \cdot 10^{-8}$	0.889
$\infty$	$1.471 \cdot 10^{-7}$					

<sup>a</sup> Temperature independent cross-section.

$J_{\text{rel}}$ : relative values  $J(T)/J(295 \text{ K})$

#### 4. Discussion

The value of the overall photodissociation coefficients between 15 and 35 km is mainly influenced by light of the 200–210 nm range due to a significant increase of the ozone optical depth in the stratosphere at wavelengths greater than 220 nm. Under these conditions, a significant reduction of overall photodissociation coefficients is only to be expected in the case of compounds whose absorption cross-section are strongly temperature-dependent in this wavelength interval.

Actually, important reductions of photodissociation coefficient are observed for HCFC-124 (up to 40%). The introduction of smaller photodissociation coefficients in atmospheric models theoretically increases altitudes of photolysis and, therefore, changes the altitude profile of the considered halocarbons in the stratosphere.

This effect could have minor atmospheric implications due to the fact that this compound is largely destroyed in the troposphere by reaction with OH radicals.

Consequently, its lifetime in the atmosphere is shorter than the fully halogenated halocarbons (global lifetime of 8 years for HCFC-124) (WMO, 1990).

A comparison of photodissociation rate and chemical loss rates is given in Figure 4, where the chemical loss rates are calculated with the rate constants from WMO (1990) and the concentration profiles of OH and O(<sup>1</sup>D) for a mid latitude, Spring/Fall atmosphere (U.S. Standard 1976). It can be seen that the loss process due to reaction with OH radicals is largely dominant.

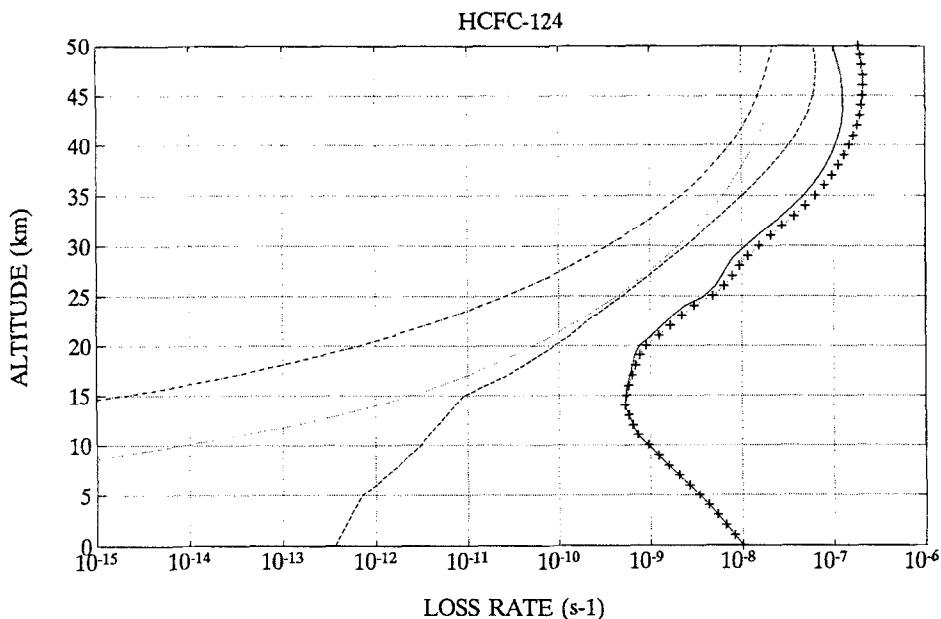


Fig. 4. Calculated loss rates per molecule of  $\text{CF}_3\text{-CHFCl}$  (HCFC-124) as a function of altitude. — Reaction with OH; ----- Reaction with O(<sup>1</sup>D); ···· Photolysis for  $\text{sec } \chi = 2$ ; - · - · Photolysis for  $\text{sec } \chi = 1$ ; +++ Total loss rate.

In conclusion, this work presents a complete and coherent set of experimental data showing a nonnegligible temperature-dependence of the absorption cross-sections and of the photodissociation coefficients of an alternative chlorofluoroethane. It gives fairly simple parametrical functions which can be used to approximate the absorption cross-section values with respect to temperature and wavelength within  $\pm 5\%$ .

Nevertheless, no major implication of the temperature dependence of the absorption cross-sections of this compound on the stratospheric photochemistry is expected because of the relatively short chemical lifetime ( $\approx 8$  yr) of this constituent in the atmosphere due to its reaction with OH radicals in the troposphere.

## Acknowledgements

The authors wish to thank Drs G. Maertens and J. Franklin from Solvay S.A. and Ir R. E. Breslau from duPont de Nemours for providing the studied compounds, and Mr L. Dierickx who performed some of the measurements.

## References

- Allied-Signal Corporation, 1989, in WMO Report 20: Scientific Assessment of Stratospheric Ozone: 1989, Volume II, Appendix: AFEAS Report.
- Chou, C. C., Smith, W. S., Vera Ruiz, H., Moe, K., Crecentini, G., Molina, M. J., and Rowland, F. S., 1977, The temperature dependences of the ultraviolet absorption cross-sections of  $\text{CCl}_2\text{F}_2$  and  $\text{CCl}_3\text{F}$ , and their stratospheric significance, *J. Phys. Chem.* **81**, 286–290.
- Gillotay, D., Jenouvrier, A., Coquart, B., Merienne, M. F., and Simon, P. C., 1989, Ultraviolet absorption cross-section of bromoform in the temperature range 295–240 K, *Planet. Space Sci.* **37**, 1127–1140.
- Gillotay, D., and Simon, P. C., 1991, Temperature-dependence of ultraviolet absorption cross-section of alternative chlorofluoroethanes, *J. Atmos. Chem.* **12**, 269–285.
- Hubrich, C., and Stuhl, F., 1980, The ultraviolet absorption of some halogenated methanes and ethanes of atmospheric interest, *J. Photochem.* **12**, 93–107.
- Kockarts, G., 1976, Absorption and Photodissociation in the Schumann-Runge bands of molecular oxygen in the terrestrial atmosphere, *Planet. Space Sci.* **24**, 589–604.
- Molina, M. J., and Molina, L. T., 1989, in WMO Report 20: Scientific Assessment of Stratospheric Ozone: 1989, Volume II, Appendix: AFEAS Report.
- Montreal Protocol on Substances that Deplete the Ozone Layer, Final Act, 1987, United Nations Environment Programme.
- NASA, 1976, U.S. Standard Atmosphere Supplements, 1976, U.S. Government Printing Office, Washington, D.C.
- Nicolet, M., 1984, On the molecular scattering in the terrestrial atmosphere: an empirical formula for calculation in the homosphere, *Planet. Space Sci.* **32**, 1467–1468.
- Orlando, J. J., Burkholder, J. B., McKeen, S. A., and Ravishankara, A. R., 1991, The atmospheric fate of several hydrochloro-fluoroethanes 2. Temperature dependence of UV absorption cross sections, *J. Geophys. Res.* **96**, 5013–5023.
- Simon, P. C., Gillotay, D., Vanlaethem-Meuree, N. and Wisemberg, J., 1988a, Ultraviolet absorption cross-sections of chloro- and chlorofluoro-methanes at stratospheric temperatures, *J. Atmos. Chem.* **7**, 107–135.
- Simon, P. C., Gillotay, D., Vanlaethem-Meuree, N., and Wisemberg, J., 1988b, Temperature dependence of Ultraviolet absorption cross-sections of chlorofluoroethanes, *Ann. Geophys.* **6**, 239–248.
- WMO, 1986, Atmospheric ozone 1985, WMO global ozone research and monitoring project, Report 16, vol. I, 355–367.
- WMO, 1990, Scientific Assessment of Stratospheric Ozone: 1989, Report 20, Volume II, Appendix: AFEAS Report.