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temperature range 295-240 K

by

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FOREWORD

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ULTRAVIOLET ABSORPTION CROSS-SECTIONS OF BROMOFORM IN THE TEMPERATURE RANGE 295-240K

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Abstract

Ultraviolet absorption cross-sections of bromoform ($CHBr_3$) have been measured for temperatures ranging from 295 to 240 K with two different experimental equipments: a) with a fixed optical path of 200 cm for wavelengths ranging from 170 to 300 nm and b) with a multiple reflection cell in the wavelength region 252-310 nm. These two sets of data are in very close agreement (better than the uncertainties quoted for each measurement) in the overlap region. This fact allows to conclude to the full compatibility and complementarity of the two experimental devices in determining absorption cross-section of atmospheric constituents.

Résumé

Les sections efficaces d'absorption dans l'ultraviolet du Bromoforme ($CHBr_3$) ont été mesurées, pour des températures allant de 295 à 240 K, à l'aide de deux dispositifs expérimentaux différents : a) avec une cellule à trajet optique fixe de 200 cm pour les longueurs d'onde comprises entre 170 et 300 nm et b) avec une cellule à réflexions multiples pour l'intervalle de longueur d'onde 252-310 nm. Ces deux séries de données sont en excellent accord (meilleur que l'incertitude entachant chaque mesure) dans la région de recouvrement. Ce fait nous permet de conclure à la parfaite compatibilité et complémentarité des deux dispositifs expérimentaux pour la mesure des sections efficaces d'absorption de constituants minoritaires.

Samenvatting

De werkzame absorptiedoorsneden van bromoform ($CHBr_3$) in het ultraviolet werden gemeten voor temperaturen gaande van 295 tot 240 K met behulp van twee verschillende experimentele apparaten : a) met een cel met vast optisch traject van 200 cm voor golflengten vervat tussen 170 en 300 nm en b) met een cel met veelvuldige weerkaatsingen voor het golflengte-interval 252-310 nm. Deze twee reeksen gegevens stemmen goed overeen in het overlappingsgebied (beter dan de onzekerheden genoteerd voor elke meting). Hierdoor kunnen wij besluiten tot de perfecte compatibiliteit en het aanvullend karakter van de twee experimentele apparaten voor de meting van de werkzame absorptiedoorsneden van minderheidsbestanddelen.

Zusammenfassung

Die Absorptionquerschnitten im Ultraviolett von Bromoform ($CHBr_3$) wurden gemessen für Temperaturen zwischen 295 und 240 K mit Hilfe von zwei verschiedenen Experimentalgeräte : a) mit einer Zelle mit fester optischer Weglänge von 200 cm für Wellenlängen zwischen 170 und 300 nm und b) mit einer Zelle mit mannigfachen Reflektionen für den Wellenlänge-Intervall 252-310 nm. Diese zwei Serien Daten stimmen überein im Überlappungsgebiet (besser als die Unsicherheiten quotiert für jede Messung). So können wir beschliessen zu der Kompatibilität und dem komplementären Charakter dieser zwei Experimentalgeräte für die Messung der wirksamen Absorptionquerschnitten von Minoritätsbestandteilen.

1. INTRODUCTION

A non-negligible mechanism of destruction of the stratospheric ozone is the catalytic cycles involving halogen radicals. Particularly, recent studies (Yung et al., 1980; Prather et al.,1984; Rodriguez et al., 1986) show that bromine radicals can play a significant role in the ozone catalytic destruction in the stratosphere. Moreover, these radicals are attended to have an important contribution, by the channel of the reaction BrO + ClO, in the formation of the Antarctic springtime ozone hole.(Farman et al., 1985; Stolarski et al., 1986; Hills et al., 1987; Pyle and Farman, 1987; Solomon 1988; McElroy et al., 1989). R-Br species concentrations have been measured in the atmosphere by several authors (Fabian et al., 1981; Berg et al., 1984; Lal et al., 1985; Class et al., 1986; Cicerone et al., 1988) confirming their presence and potential impact on the earth's ozone layer. It is therefore important to have reliable measurements of the photodissociation properties of the source gases - tropospheric bromocarbons - (Molina et al., 1982; Gillotay and Simon, 1988; Gillotay et al. 1989; Gillotay and Simon, 1989) including the bromoform for which ultraviolet absorption cross-sections are presently unpublished. The purpose of this paper is to report an investigation of ultra-violet absorption cross-sections of bromoform ($CHBr_3$) measured, between 170 and 310 nm, for temperatures between 296 and 240 K, by means of two different experimental equipments, respectively located at the University of Reims (France), and the Institut d'Aéronomie Spatiale de Belgique (IASB) in Brussels (Belgium). The measurements performed in the two laboratories are compared and discussed. The photodissociation coefficients are calculated.

2. EXPERIMENTAL.

The absorption cross-sections have been measured by means of two different experimental equipments located respectively in Reims (France), hereafter labelled (R) and Brussels (Belgium), hereafter (B).

The first one (R), represented in figure 1, consists of an Argon arc light source providing continuous radiations between 115 and 330 nm, a 5 m long multiple reflection thermostated absorption cell, a 1.5 m Jobin-Yvon THR 1500 monochromator giving a dispersion of 0.26 nm/mm, a Hamamatsu R 955 photomultiplier and a data acquisition system. This experimental device has been described elsewhere by Lux et al. (1985, 1989).

The second, (B), previously described by Gillotay and Simon (1988), includes a Deuterium or a Tungsten filament light source, a 1 m Mc-Pherson type 225 monochromator, a beam splitter, a 2 m and a 20 cm thermostated absorption cell (one of the cell being the reference channel), EMR type 542 P-09-18 solar blind photomultipliers and a data acquisition system. It is presented in figure 2.

The major differences between both instruments and experimental procedures are the following :

1.a.: the absorption cell is illuminated with polychromatic light (interferometric filters limits the range of wavelengths) in (R) and with monochromatic light in (B).

  b.: the entire instrumentation is under vacuum in (B) (which permits to reach wavelengths down to 170 nm). In (R), only the absorption cell can be evacuated down to 10-4 torr and therefore, the absorption cross-section measurements are limited to wavelengths greater than 200 nm.

2. In (R), for each spectral region, pressure and optical path are adjusted to obtain an optical density close to 1 at the center of the wavelength range. (transmissions between 15 and 70 % over the wavelength range).
   In (B), for each pressure, only the wavelength region, for which transmissions range from 15 to 80 %, is taken into account for the calculation of the absorption cross-sections.

Figure 1. Experimental equipment for the measurement of absorption cross-section of the University of Reims (France).

S : Argon arc source   A,B,C : multiple reflection mirrors
L_1,L_2,L_3 : Lenses   M,M_1,M_2: Mirrors
G. : Grating   I.F. : interferometric filter
D. : Diaphragm   C.M. : Capacitance manometer
P : Mirror   C.P. : Coolant circulation pump
P.P.,V.P. : Vacuum pumps
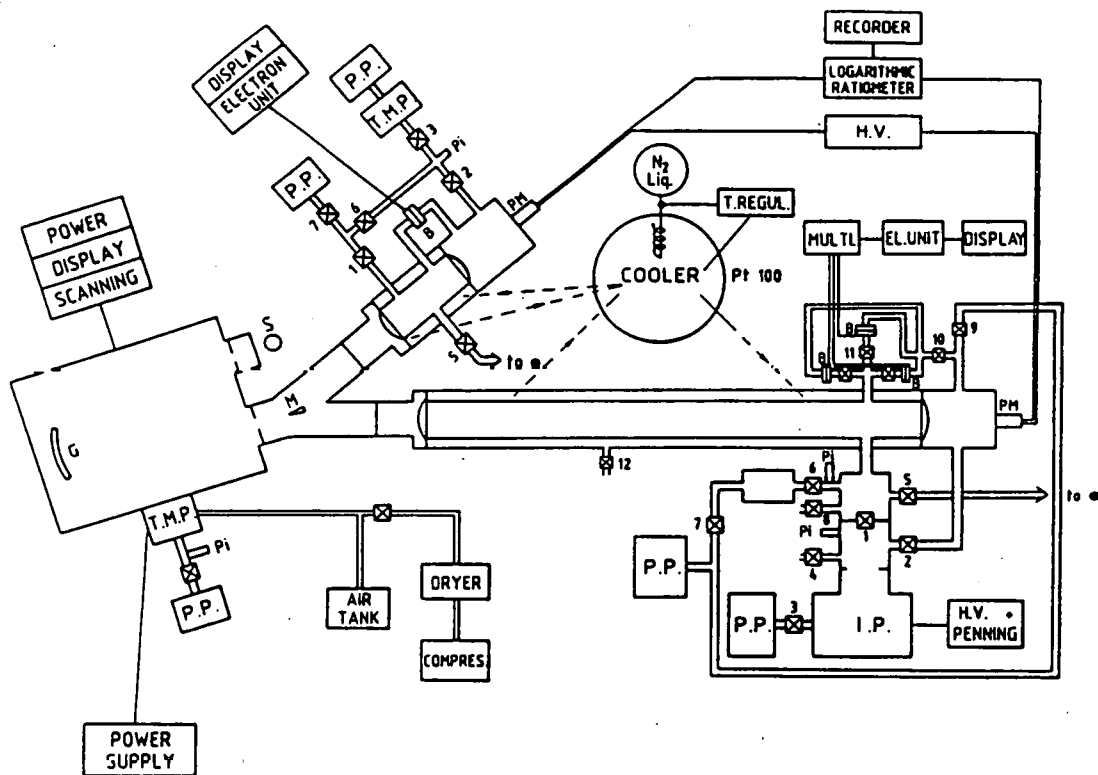* : Gas handling device

Figure 2. Experimental equipment for the measurement of absorption cross-section of the Institut d'Aéronomie Spatiale de Belgique - Brussels (Belgium).

S : Light source   G : Grating
M : Mirror   B : Capacitance manometer
PM : Photomultiplier   PP, IP, TMP : Vacuum pumps
* : Gas handling device

In both cases, pressure is measured by means of capacitance manometers MKS-Baratron with a precision better than 0.1 % and low temperatures are determined with absolute uncertainties of around ± 1 K. (low temperature stabilities of ± 0.2 K in (R) and) ± 0.3 K in (B) are usually observed.)

The measurements of absorption cross-sections of bromoform have been performed with the same sample in the two laboratories. This sample, kindly provided by Solvay S.A., has a purity of 99.99 % and contents less than 0.005 % ethanol, as determined by gas phase chromatography.

The experimental conditions are summarized in table 1.

TABLE 1. Experimental conditions.

UNIVERSITY OF REIMS

T (K)	Wavelengths (nm)	Optical Path (m)	Max. Pressure (torr)
292	252-264	10.83	0.0250
	262-268	10.83	0.0520
	266-278	10.83	0.1050
	276-289	20.81	0.1860
	287-300	80.69	0.2025
	298-310	160.53	0.5050
240	252-264	20.81	0.0145
	262-268	20.81	0.0250
	266-278	60.73	0.0258
	276-289	160.53	0.0256

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T (K)	Wavelengths (nm)	Optical Path (m)	Pressure range (torr)
295	170-300	2.00	4.585 -0.03225
273	170-290	2.00	0.8298-0.01580
250	170-290	2.00	0.0792-0.00712

3. RESULTS

Numerical values of absorption cross-sections, derived from the determinations made by the two laboratories, are given for selected wavelengths between 170 and 310 nm (2 nm intervals and 500 cm^{-1} wave-number intervals) in tables 2a-2b and illustrated in figures 3 and 4.

According to the error budgets previously published (Simon et al., 1988; MErienne et al., 1989), the values given in table 2 are determined with an accuracy of + 2% at room temperature. At low temperatures, the accuracy is of around + 3 % for the observed values and of + 4 % for the extrapolated values.

a. Ambient temperature

At ambient temperature, bromoform displays a continuous absorption in the 172-310 nm region with values ranging from 1.6 10-17 cm2 molecule-1 at 170 nm to 1.59 10-21 cm2 molecule-1 at 310 nm, and with maxima around 200 and 220 nm. Figure 5 gives a comparison of the determinations at room temperature over the overlap wavelength range (252-300nm). This figure also shows that the values determined in both laboratories agree within the + 2 % of quoted uncertainty for each measurement.

TABLE 2.a. Absorption cross-sections of CHBr3 at 2 nm intervals for five selected temperatures (295, 270, 250, 230, and 210 K).

$$[\sigma(\lambda) \times 10^{21} \ (cm^2 \ molec.^{-1})]$$

(nm)	295 K	270 K	250 K	230 K[*]	210 K[*]
170	16038	16063	16083	16103	16123
172	11732	11542	11392	11245	11099
174	9696	9261	8927	8606	8296
176	8720	8628	8555	8483	8412
178	8576	8566	8558	8550	8542
180	8313	8420	8506	8596	8682
182	7703	7839	7950	8062	8176
184	6833	6922	6994	7067	7140
186	5704	5784	5849	5915	5982
188	4708	4735	4756	4777	4780
190	3991	3972	3956	3941	3925
192	3602	3574	3551	3529	3507
194	3513	3519	3524	3529	3534
196	3661	3710	3749	3788	3828
198	3936	4017	4083	4150	4217
200	4164	4303	4418	4536	4657
202	4336	4454	4552	4651	4753
204	4406	4501	4579	4658	4738
206	4450	4514	4566	4618	4671
208	4514	4572	4619	4666	4714
210	4685	4748	4799	4850	4902
212	4934	5020	5089	5159	5230
214	5242	5337	5415	5494	5574
216	5535	5649	5742	5836	5932
218	5739	5873	5983	6095	6209
220	5826	5971	6090	6210	6334
222	5780	5910	6015	6123	6232
224	5578	5691	5784	5878	5973
226	5272	5371	5451	5533	5616
228	4868	4949	5017	5091	5161
230	4412	4481	4538	4595	4652
232	3974	4016	4042	4062	4088
234	3618	3619	3619	3619	3619
236	3239	3238	3237	3236	3235
238	2947	2947	2948	2948	2948
240	2728	2726	2723	2721	2718
242	2533	2523	2516	2508	2501
244	2337	2315	2291	2269	2244
246	2144	2107	2077	2046	2016
248	1939	1892	1854	1817	1777
250	1741	1686	1643	1599	1569
252	1577	1516	1468	1423	1378
254	1361	1298	1249	1202	1157
256	1164	1100	1052	1006	962
258	986	924	878	834	792

Table 2.a. (cont.)

(nm)	295 K	270 K	250 K	230 K*	210 K*
260	828	770	727	686	647
262	689	636	597	559	525
264	569	521	486	453	422
266	467	424	393	364	337
268	380	343	316	290	267
270	308	275	252	230	211
272	248	220	200	181	165
274	198	174	157	142	128
276	158	138	124	111	99.4
278	125	108	96.5	86.0	76.6
280	98.8	84.8	75.1	66.4	58.8
282	77.7	66.2	58.2	51.1	45.0
284	61.0	51.5	44.9	39.2	34.2
286	47.7	39.9	34.6	30.0	26.0
288	37.2	30.9	26.6	22.9	19.7
290	29.0	23.8	20.4	17.4	14.9
292	21.7				
294	16.7				
296	12.7				
298	9.60				
300	7.18				
302	5.37				
304	3.99				
306	2.96				
308	2.18				
310	1.59				

- -

* : Extrapolated values.

TABLE 2.b. Absorption cross-sections of CHBr3 averaged over the spectral intervals of 500 cm^{-1} used in atmospheric modelling calculations for five selected temperatures (295, 270, 250, 230, and 210 K)

$$[\sigma(\lambda) \times 10^{21} \; (cm^2 \; molec.^{-1})]$$

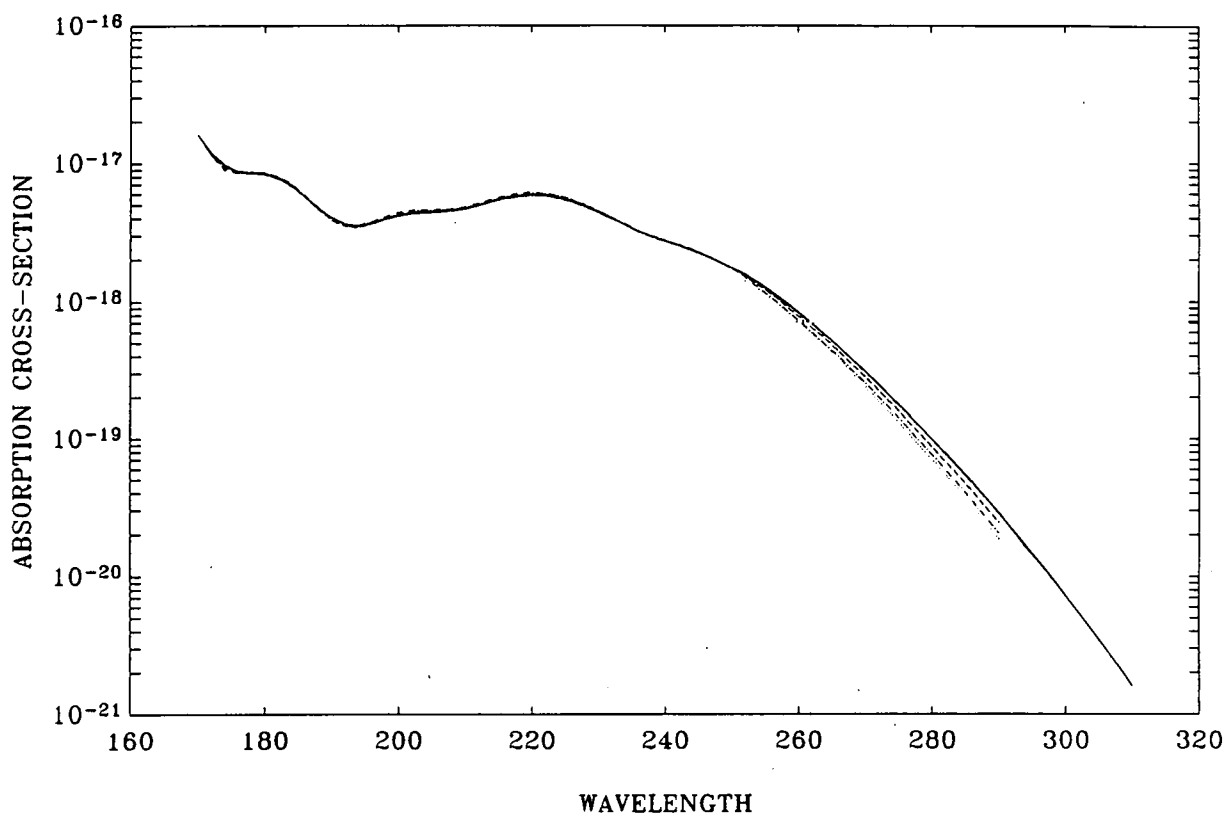| N°	λ(nm)	295 K	270 K	250 K	230 K[*]	210 K[*]
43	169.5-172.4	11764	11610	11487	11364	11243
44	172.4-173.9	10916	10574	10311	10056	9810
45	173.9-175.4	9213	8853	8576	8309	8050
46	175.4-177.0	8718	8640	8579	8517	8456
47	177.0-178.6	8588	8575	8565	8555	8544
48	178.6-180.2	8393	8469	8530	8592	8654
49	180.2-181.8	8029	8159	8264	8371	8479
50	181.8-183.5	7469	7592	7691	7792	7895
51	183.5-185.2	6694	6781	6851	6922	6994
52	185.2-186.9	5689	5769	5834	5900	5966
53	186.9-188.7	4766	4796	4821	4845	4870
54	188.7-190.5	4122	4110	4101	4092	4082
55	190.5-192.3	3686	3657	3635	3612	3590
56	192.3-194.2	3528	3520	3515	3509	3503
57	194.2-196.1	3589	3621	3647	3673	3700
58	196.1-198.0	3806	3870	3922	3974	4027
59	198.0-200.0	4054	4166	4258	4352	4448
60	200.0-202.0	4255	4387	4496	4608	4723
61	202.0-204.1	4377	4484	4570	4659	4749
62	204.1-206.2	4433	4508	4570	4633	4696
63	206.2-208.3	4487	4546	4594	4642	4691
64	208.3-210.5	4636	4696	4746	4795	4845
65	210.5-212.8	4900	4983	5050	5118	5187
66	212.8-215.0	5233	5328	5406	5484	5564
67	215.0-217.4	5550	5666	5760	5856	5953
68	217.4-219.8	5768	5906	6019	6134	6252
69	219.8-222.2	5813	5951	6064	6177	6296
70	222.2-224.7	5631	5748	5843	5940	6038
71	224.7-227.3	5272	5371	5451	5533	5616
72	227.3-229.9	4751	4830	4895	4966	5033
73	229.9-232.6	4122	4174	4211	4244	4281
74	232.6-235.3	3624	3624	3624	3624	3624
75	235.3-238.1	3141	3140	3140	3139	3139
76	238.1-241.0	2771	2769	2767	2765	2763
77	241.0-243.9	2498	2486	2476	2466	2456
78	243.9-246.9	2194	2161	2132	2103	2074
79	246.9-250.0	1898	1849	1810	1771	1733
80	250.0-253.2	1612	1552	1505	1460	1418
81	253.2-256.4	1285	1221	1173	1126	1081
82	256.4-259.7	986	924	878	834	792
83	259.7-263.2	716	662	622	584	549
84	263.2-266.7	517	472	438	407	378
85	266.7-270.3	365	329	302	278	255
86	270.3-274.0	246	218	198	180	164
87	274.0-277.8	159	139	125	112	100
88	277.8-281.7	100	86.2	76.3	67.6	59.9
89	281.7-285.7	62.6	52.9	46.2	40.3	35.2
90	285.7-289.9	37.2	30.9	26.6	22.6	19.7

[*] Extrapolated values

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Figure 3. Ultraviolet absorption cross-sections of CHBr₃ versus wavelength as a function of temperature (T= 296, 292, 275, 252 and 240 K).

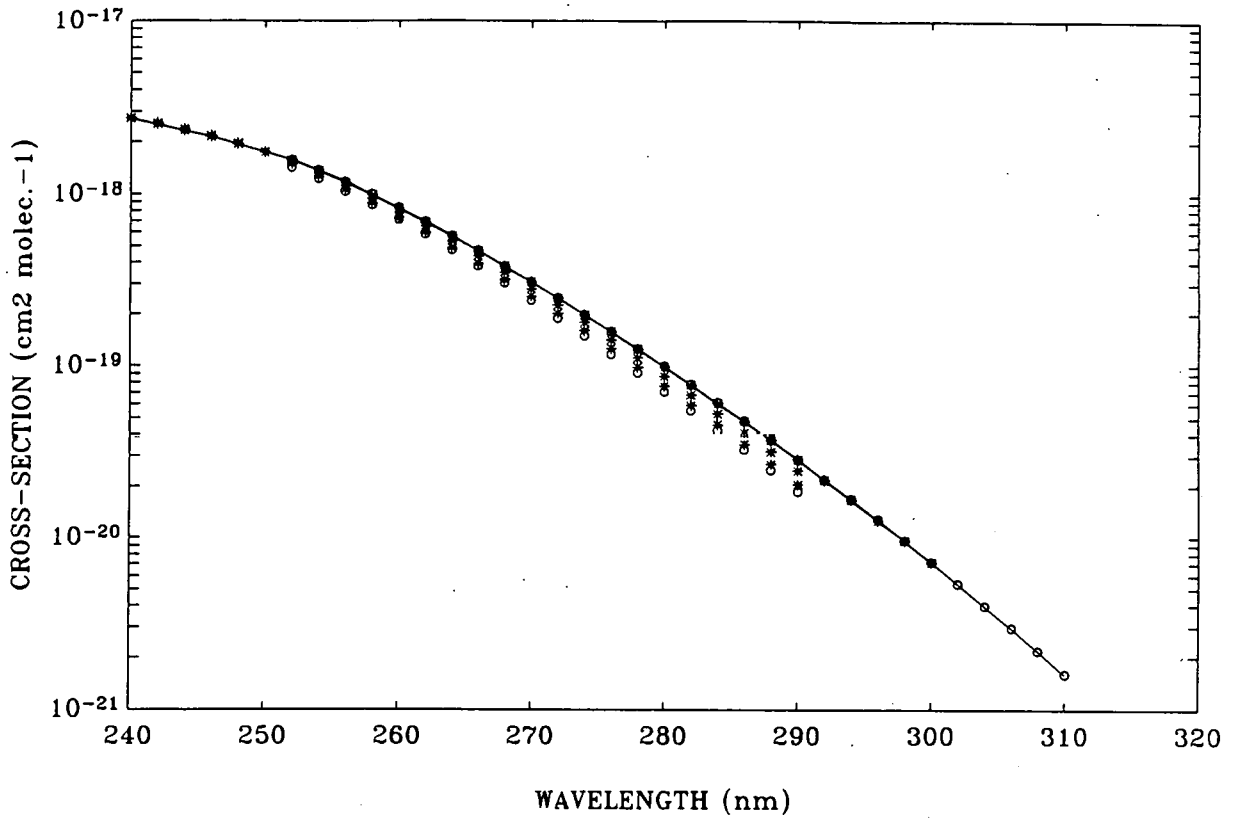Figure 4. Ultraviolet absorption cross-sections of CHBr₃ versus wavelength in the overlap region (252-300 nm) as a function of temperature (T= 296, 292, 275, 252 and 240 K).

    o : measurements performed in Reims
    * : measurements performed in Brussels

b. Low temperatures

Absorption cross-section changes with temperature depend on the chemical composition of the compound and the wavelength. In this case, measurements have been made at three low temperatures namely 273, 252 and 240 K (lower temperature being forbidden because of the very low vapor pressure of bromoform). As shown on figures 3, 4 and 6, for each wavelength, an exponential dependence of the absorption cross-section versus temperature is observed, with a decrease in the region of low absorption (for wavelengths greater than 250 nm) and with a small increase at the maxima of absorption (namely at 220 and 200 nm). Figure 6 also shows the very good agreement between both sets of measurements with respect to temperature dependence.

Because the temperature range 295-240 K is adequately covered by accurate measurements made at five temperatures, and because the exponential dependence of cross-section versus temperature is clearly established, extrapolation down to 210 K as well as interpolation at selected temperature can be made with an accuracy of + 4 %.

4. DISCUSSION AND CONCLUSIONS

Photodissociation coefficients of this molecule have been calculated, neglecting effects of multiple scattering, for given altitude (z), zenith angle (χ) and wavelength interval according to the relations :

$$J(z) = \sigma_\lambda \, q_\lambda(z) \qquad ; \ q_\lambda(z) = q_\lambda(\infty) \, e^{-\tau_\lambda(z)} \qquad (1)$$

$$\tau_\lambda(z) = [n(O_2)\sigma_\lambda(O_2) + n(O_3)\sigma_\lambda(O_3) + n(air)\sigma_{scatt}] \, \sec \chi \, dz \qquad (2)$$

where

z   is the altitude,

σ are the absorption cross-sections,

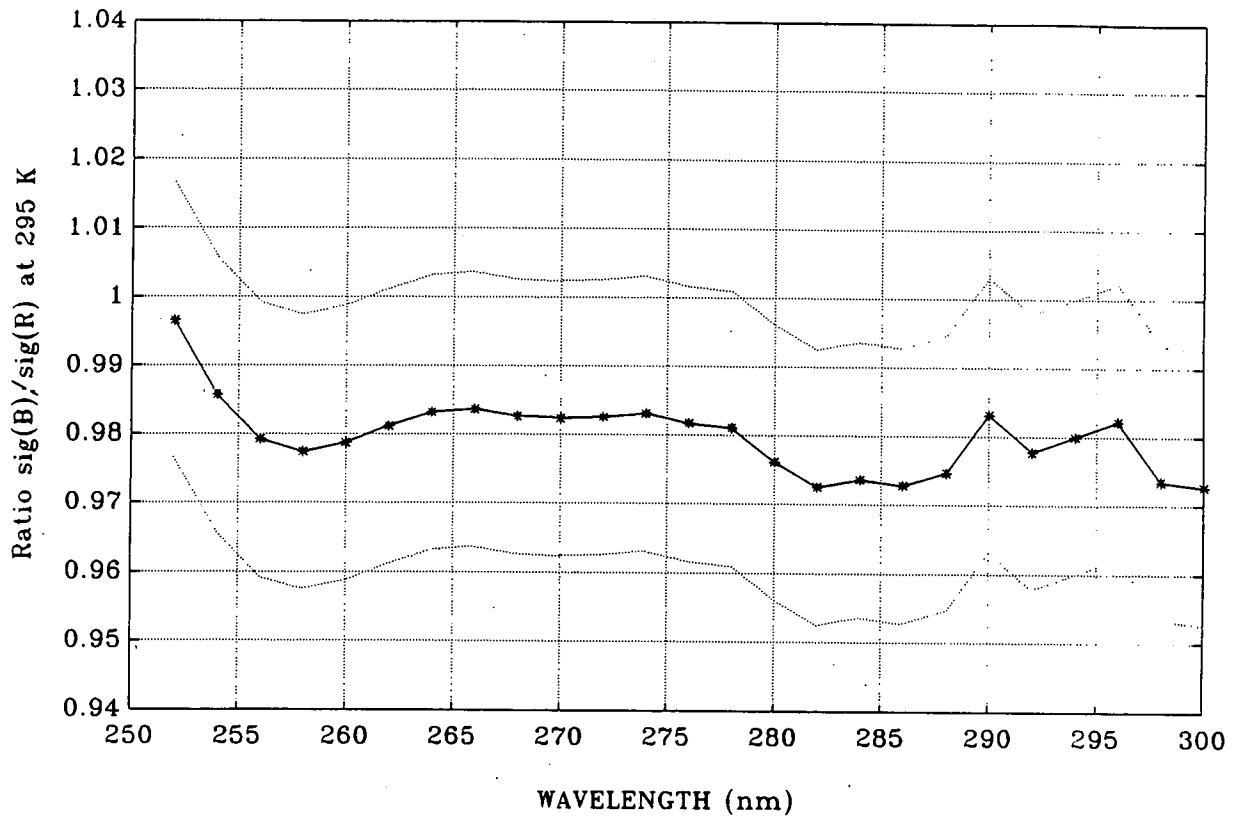q (z) and q (∞) are the solar irradiance at altitude z or extra-terrestrial (z = ∞),

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Figure 5. Relative values of absorption cross-sections sig(B)/sig(R) at 295 K as a function of wavelength.

sig(B) : values of absorption cross-section at 295 K
     calculated from the IASB's determination at 296 K.
sig(R) : values of absorption cross-section at 295 K
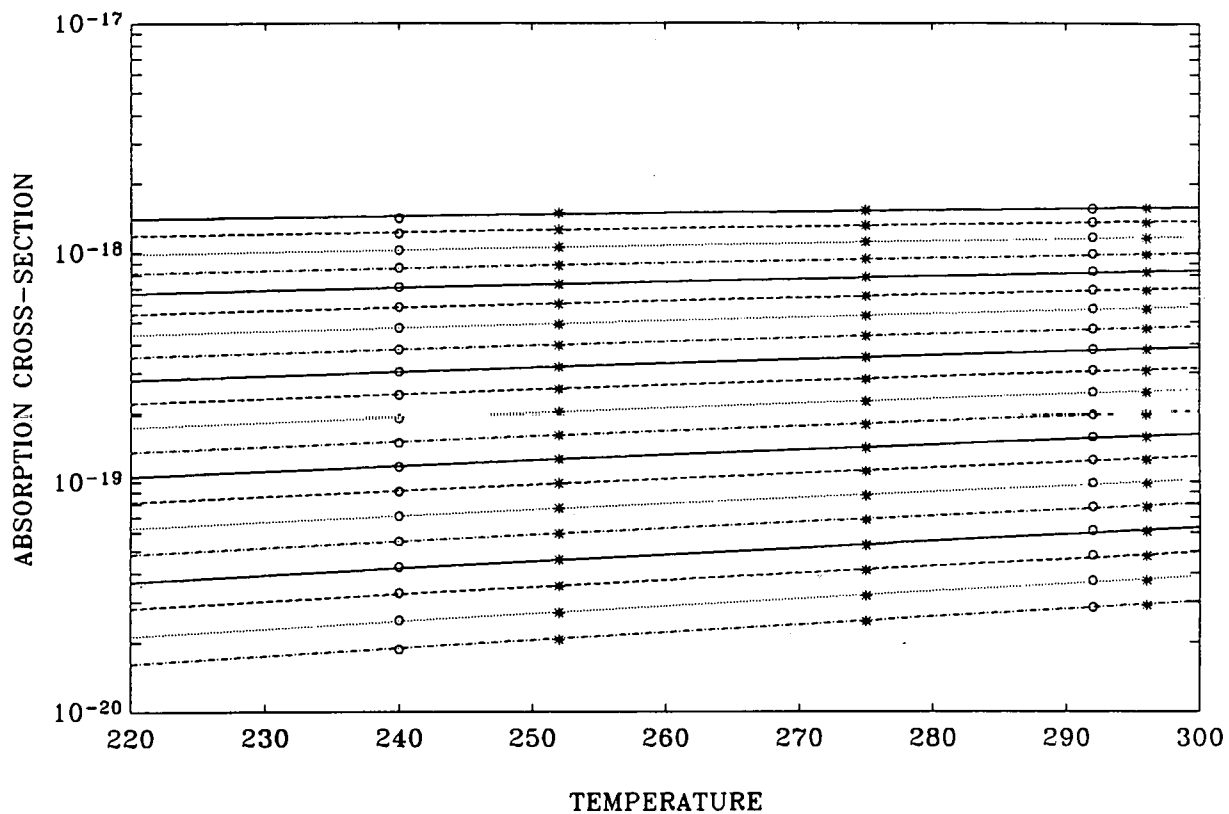   calculated from the Reims's determination at 292 K.

Figure 6. Absorption cross-sections of CHBr₃ between 252 and 290 nm, versus
temperature.
Wavelength increment between successive curves is 2 nm.

o : measurements performed in Reims
* : measurements performed in Brussels

n   is the number of particles per volume unit,

for solar zenith angles χ of 0° and 60° (secχ = 1 and 2), taking into account the values of $\sigma_\lambda(O_2)$ and $\sigma_\lambda(O_3)$ from WMO (1985) and Kockarts (1976), σ_{scatt} from Nicolet (1984) and the values of q (∞) from WMO (1985) and taking into account the actual values of cross-sections corresponding to the temperature conditions at each altitude. (Table 3).

TABLE 3. Temperature Model.

Altitude (km)	Temperature (K)
15	217
20	217
25	222
30	227
35	237
40	251
45	265
50	271

A comparison between the temperature-dependent and independent stratospheric photodissociation coefficients, given in table 4, shows a small increase of the photodissociation coefficients (up to 5 %) in the low stratosphere, due to the dependence of temperature of the cross-sections which, as described above, display an increase in the maxima of absorption (200-220 nm) and a decrease for the wavelengths greater than 250 nm. These coefficients are practically temperature-independent for altitude greater than 40 km.

Unfortunately, it is difficult to calculate with a good accuracy the temperature dependence of tropospheric photodissociation coefficients. Indeed, because of the very low vapor pressures of bromoform, the measurements of the weak absorption cross-sections at wavelengths greater than 290 nm, at the tropospheric temperatures (lower than 275 K), would require too high pressure or much longer optical paths.

TABLE 4. Photodissociation coefficients of $CHBr_3$ versus altitude in the stratosphere.

λ range : 170-290nm

sec χ = 1			
Z (km)	$J(s^{-1})$ $\sigma(295K)$[a]	$J(s^{-1})$ $\sigma = f(T)$	J_{rel}
15	$1.342 \cdot 10^{-7}$	$1.408 \cdot 10^{-7}$	1.049
20	$1.459 \cdot 10^{-6}$	$1.535 \cdot 10^{-6}$	1.053
25	$7.998 \cdot 10^{-6}$	$8.412 \cdot 10^{-6}$	1.052
30	$3.057 \cdot 10^{-5}$	$3.205 \cdot 10^{-5}$	1.048
35	$9.675 \cdot 10^{-5}$	$1.006 \cdot 10^{-4}$	1.039
40	$2.851 \cdot 10^{-4}$	$2.908 \cdot 10^{-4}$	1.020
45	$6.617 \cdot 10^{-4}$	$6.599 \cdot 10^{-4}$	.997
50	$1.010 \cdot 10^{-3}$	$9.998 \cdot 10^{-4}$	.990
	$1.298 \cdot 10^{-3}$		

sec χ = 2			
Z (km)	$J(s^{-1})$ $\sigma(295K)$[a]	$J(s^{-1})$ $\sigma = f(T)$	J_{rel}
15	$2.762 \cdot 10^{-10}$	$2.895 \cdot 10^{-10}$	1.048
20	$2.488 \cdot 10^{-8}$	$2.604 \cdot 10^{-8}$	1.047
25	$5.432 \cdot 10^{-8}$	$5.706 \cdot 10^{-8}$	1.051
30	$5.378 \cdot 10^{-6}$	$5.639 \cdot 10^{-6}$	1.049
35	$3.114 \cdot 10^{-5}$	$3.243 \cdot 10^{-5}$	1.041
40	$1.352 \cdot 10^{-4}$	$1.390 \cdot 10^{-4}$	1.028
45	$4.095 \cdot 10^{-4}$	$4.123 \cdot 10^{-4}$	1.007
50	$8.120 \cdot 10^{-4}$	$8.067 \cdot 10^{-4}$	.993
	$1.298 \cdot 10^{-3}$		

[a] Temperature independent cross-section.

J_{rel} relative value $J(T)/J(295K)$.

In conclusion, this work presents a complete and coherent set of data about temperature-dependent ultraviolet absorption cross-sections and stratospheric photodissociation coefficients of bromoform, performed with two different experimental equipments. The accuracy and the reproducibility of the measurements allow to conclude to the full compatibility and complementarity of the two different experimental techniques for the measurement of absorption cross-sections of atmospheric constituents.

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