

Ultraviolet absorption cross-sections of methyl bromide at stratospheric temperatures

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ABSTRACT. The absorption cross-sections of methyl bromide (CH_3Br) are measured between 180 nm and 260 nm at temperatures of 295 K, 255 K, 227 K and 209 K. A parametrical formula is proposed to compute the absorption cross-sections for wavelengths between 200 nm and 260 nm and for temperatures between 210 K and 300 K.

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INTRODUCTION

A well-known mechanism of destruction of the stratospheric ozone is the catalytic cycles involving halogen radicals. According to Yung *et al.* (1980), one of the most important source of atomic bromine in the atmosphere would be the photodissociation of methyl bromide which is mostly of natural origin. Presently, a good estimation of the mean concentration of methyl bromide is of the order of 10 pptv in the troposphere (Singh, 1977 ; Singh *et al.*, 1977, 1979 ; Rasmussen and Khalil, 1980, 1984 ; Penkett *et al.*, 1981 ; Berg *et al.*, 1984) with a rapid decrease above the tropopause (Fabian *et al.*, 1981). Since stratospheric data are preliminary, we do not presently have a realistic concentration profile *versus* the altitude. Nevertheless CH_3Br does not seem to be negligible in the ozone budget in lower stratosphere (Wofsy *et al.*, 1975).

The knowledge of accurate absorption cross-sections with their temperature dependences is needed for photodissociation calculations of methyl bromide in the stratosphere. The only recent data on the ultraviolet absorption cross-sections of methyl bromide are those published by Robbins (1976) and by Molina *et al.* (1982) measured at room temperature. Considering the temperature profile in the stratosphere, it is needed to extend these measurements in the range 210-270 K. The present work presents a new investigation of absorption cross-sections of methyl bromide in the 200 nm region and clearly establishes a significant decrease of absorption cross-sections in the range of stratospheric temperature, for wavelengths greater than 210 nm.

EXPERIMENTAL

The ultraviolet spectrum of methyl bromide in the 180-260 nm wavelength range has been studied as a function of temperature with a classical single beam equipment. The different units of this equipment are : (fig. 1)

- a light source (S)
- a monochromator (M)
- a thermostatic absorption cell (C)
- a pressure measurement unit (P)
- a photomultiplier tube as detector (PM)
- a gas handling and supply system (G)

Light source

A deuterium lamp type Hamamatsu L656K 40 W was used. It can be operated under vacuum or under nitrogen flushing at the entrance slit of the monochromator. It produces a continuous spectrum with a maximum of intensity around 250 nm and a stability of a few percent per day.

Monochromator

The monochromator is a McPherson model 225 of 1 m focal length, which can be pumped down to 10^{-7} torrs. Hydrocarbon contaminations are avoided by using a 450 l s^{-1} turbomolecular pump « Alcatel-Riber ».

A 1200 l mm^{-1} grating « Baush and Lomb » gives a maximum resolution of 0.015 nm in the first order for

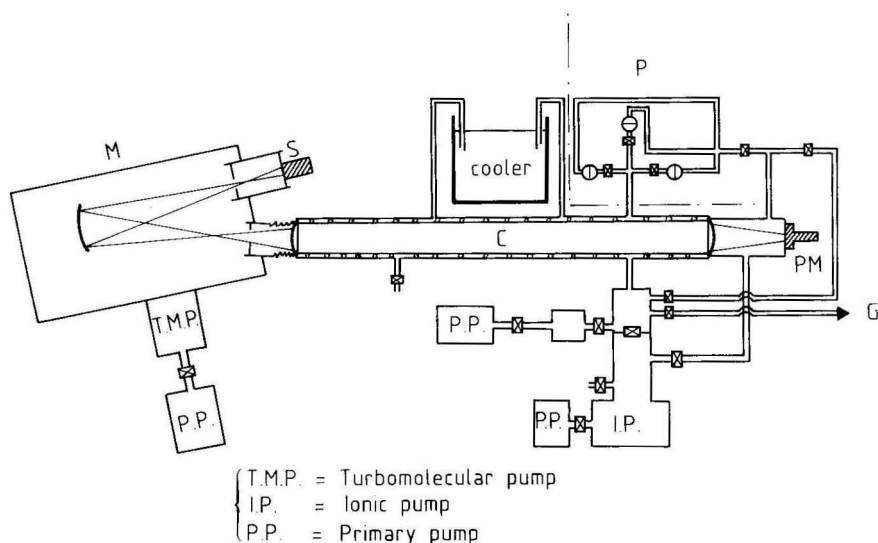


Figure 1
Experimental U.V. single beam absorption equipment.

10 μm slits. Wavelength scanning with speeds from 0.01 to 100 nm min^{-1} are obtained by means of a stepping motor.

Absorption cell

As condensation conditions of gases studied can restrict the use of fairly high gas pressure at low temperature and then, to access to low absorption cross-sections, a refrigerated stainless steel absorption cell with a 2 m optical path is used.

It can be evacuated down to 10^{-7} torrs by a 100 l s^{-1} ionic pump « Riber P.I. 100 » which prevents any contamination by organic materials. Temperature regulation down to 210 K is achieved by circulation of cooled methylcyclohexane through a double jacket of the cell. Thermic equilibrium is obtained usually after 3-4 h with a temperature gradient inferior to 2 K at 220 K between 3 thermic resistors placed inside the cell at the medium and the ends.

The optic path is limited by 2 plan convex quartz « suprasil » lenses which provide the parallelism of the light beam through the optical cell and its focalization on the photodetector. The 9 cm diameter of the internal cell prevents any internal reflection of the light.

Pressure measurement unit

The absorption cell is directly coupled with 3 differential capacitance manometers « MKS Baratron » which enable the measurement of a 4 decades pressure range up to 1, 10 or 1000 torrs with a precision better than 0.1 %. The reference level is taken as the pressure reached in the absorption cell before the introduction of gases ($\sim 10^{-7}$ torrs). Each manometer can be stabilized in temperature to limit the fluctuations during the measurements. The capacitive method also prevents the risks of contamination existing with other conventional manometers like oil, mercury or sulfuric acid manometers.

At low temperature, the actual gas temperature can also be deduced from the pressure decrease according to the perfect gases law.

Photoelectric detector

The light beam is focused on a solar blind photomultiplier « EMR 542 P.09.18 » with a front MgF_2 window and a CsTe photocathode sensitive to radiations ranging from 120 to 320 nm. The dark current is of a few picoamperes for an operating voltage of 2500 V. The output current is measured by means of a picoammeter « Keithley model 417 ».

Gas supply system

The gas supply system is made of pyrex glass, allowing distillations under vacuum and purification under vacuum of gases. A Hg diffusion pump with a N_2 trap pumps the gas handling system down to 10^{-5} torrs, measured by a Penning gauge. The samples are stocked under vacuum at low temperature (solid CO_2 or liquid N_2).

CH_3Br provided by Matheson is of analytical grade (99.5 %) and is used after vacuum distillation and thorough outgassing.

The determination of absorption cross-sections is made after several sequential recordings of the incident and absorbed fluxes measured in the same temperature conditions using Beer-Lambert's law :

$$I(\lambda) = I_0(\lambda) \exp(-\sigma(\lambda) nd) \quad (1)$$

where $I_0(\lambda)$ and $I(\lambda)$ are respectively the incident and transmitted fluxes, n is the number of molecules per volume unit and d the optical path.

RESULTS

At ambient temperature, measurements have been performed at working pressures ranging from $4 \cdot 10^{-2}$ to 22 torrs, and Beer-Lambert's law was found to hold in all cases. In such conditions, appreciable absorption (more than 15 %) is easily observed for wavelength between 182 nm and 260 nm so that absorption cross-sections can be determined with good accuracy (± 2 %). CH_3Br displays continuous absorption in the 182-260 nm region, with absorption cross-section rang-

ing from 10^{-21} to $8 \cdot 10^{-19}$ $\text{cm}^2 \text{molec}^{-1}$ with a maximum at 202 nm and a band structure below 182 nm. Figure 2 and table 1 show our results which

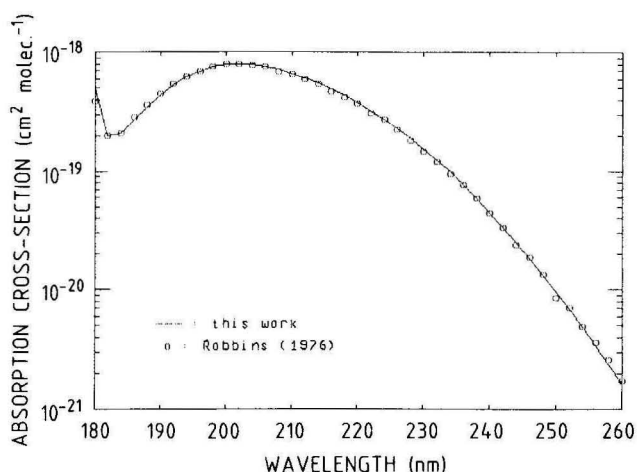


Figure 2
Absorption cross-sections of CH_3Br with respect of wavelength between 180 and 260 nm, at 295 K.

are in close agreement (within 5% in average) with those published by Robbins (1976), and Molina *et al.* (1982), the maximum of divergence being 13% at 1 wavelength (250 nm).

Measurements were extended to low temperature conditions (255 K, 227 K, 209 K). The working pressures are given in table 2 and are in all cases largely below the condensation conditions. The Beer-Lambert law was verified in all pressure and temperature range used in this work. The experimental results are presented in table 1. The analysis of the cross-sections *versus* temperature dependence for a given

Table 2

Experimental conditions for the measurement of absorption cross-sections at low temperatures.

Temperature (K)	Pressure range (torr)
295 K	$21.6 \rightarrow 4.2 \cdot 10^{-2}$
255 K	$19.4 \rightarrow 7.7 \cdot 10^{-2}$
227 K	$16.4 \rightarrow 9.0 \cdot 10^{-2}$
209 K	$9.6 \rightarrow 8.9 \cdot 10^{-2}$

Table 1

CH_3Br absorption cross-sections : experimental values at 295 K, 255 K, 227 K and 209 K compared with the values of Robbins (1976) and of Molina *et al.* (1982).

λ (nm)	σ (λ) 10^{21} (cm molec. ⁻¹)				Robbins (1976)	Molina <i>et al.</i> (1982)
	This work 295K	This work 255K	This work 227K	This work 209K		
180	500	500	500	500	391	
182	198	198	198	198	197	
184	208	208	208	208	211	
186	271	271	271	271	284	
188	346	346	346	346	358	
190	439	439	439	439	447	441
192	529	529	529	529	544	
194	620	620	620	620	626	
196	691	691	691	691	692	
198	760	760	760	760	768	
200	791	791	791	791	796	785
202	797	797	797	797	797	
204	793	793	793	793	778	
206	767	767	767	767	757	
208	727	727	727	727	695	
210	666	666	666	666	657	649
212	614	613	613	613	597	
214	559	558	558	556	547	
216	493	495	494	490	476	
218	442	436	434	433	420	
220	377	374	369	366	375	360
222	324	321	315	312	310	
224	276	275	261	259	270	
226	230	228	213	216	223	
228	188	188	181	177	182	
230	154	151	146	144	146	145
232	124	121	118	114	121	
234	98.7	95.2	90.8	88.6	96.1	
236	76.5	73.4	69.9	65.8	76.4	
238	59.5	55.2	51.6	49.7	58.7	
240	44.7	41.7	39.0	37.9	44.2	41.1
242	33.5	30.2	28.9	27.6	33.0	
244	25.0	22.5	20.7	19.4	23.8	
246	18.2	16.2	14.7	14.2	18.7	
248	13.1	11.3	10.4	9.80	13.4	
250	9.57	8.13	7.31	6.75	8.48	9.49
252	6.86	5.68	4.99	4.47	7.04	
254	4.87	3.88	3.43	3.15	4.95	
256	3.36	2.72	2.32	2.02	3.58	
258	2.35	1.90	1.49	1.29	2.60	
260	1.64	1.37	1.08	0.88	1.72	1.63

wavelength, shows an exponential decrease as shown in figure 3. Numerical values can be extrapolated for selected temperatures (295 K, 270 K, 250 K, 230 K and 210 K) which cover all stratospheric conditions. The RMS uncertainties for these values are estimated

to be $\pm 2\%$ for values larger than to $2 \cdot 10^{-21} \text{ cm}^2 \text{ molecule}^{-1}$ and, $\pm 3\%$ for values lower than $2 \cdot 10^{-21} \text{ cm}^2 \text{ molecule}^{-1}$. The extrapolated data are given in table 3 and represented for 3 temperatures in figure 4.

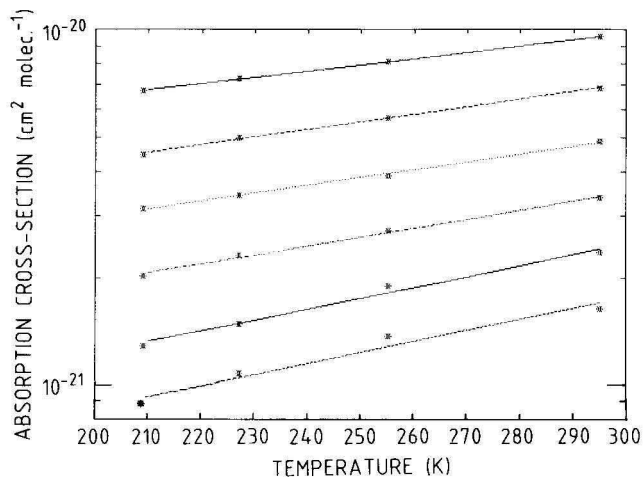


Figure 3
Absorption cross-sections of CH_3Br versus temperature at six wavelengths (250-260 nm).

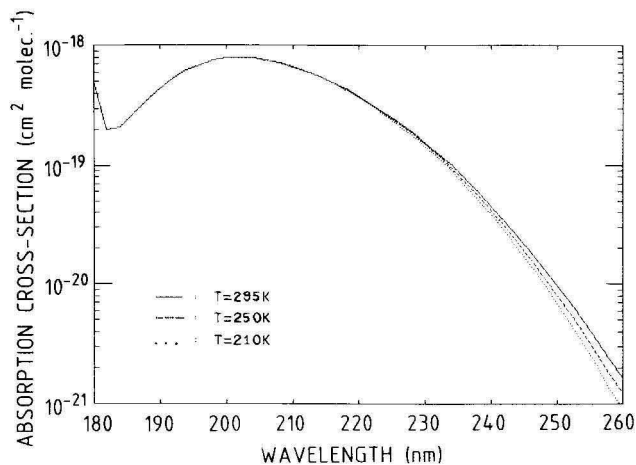


Figure 4
Absorption cross-sections of CH_3Br versus wavelength as a function of temperature.

Table 3
 CH_3Br absorption cross-sections at selected temperatures (295 K, 270 K, 250 K, 230 K, 210 K).

λ (nm)	σ (λ) 10^{-21} (cm ² molec. ⁻¹)				
	295K	270K	250K	230K	210K
180	500	500	500	500	500
182	198	198	198	198	198
184	208	208	208	208	208
186	271	271	271	271	271
188	346	346	346	346	346
190	439	439	439	439	439
192	529	529	529	529	529
194	620	620	620	620	620
196	691	691	691	691	691
198	760	760	760	760	760
200	791	791	791	791	791
202	797	797	797	797	797
204	793	793	793	793	793
206	767	767	767	767	767
208	727	727	727	727	727
210	666	666	666	666	666
212	614	613	613	613	613
214	557	557	556	556	556
216	493	493	492	492	492
218	440	438	436	434	432
220	378	374	372	369	367
222	325	321	318	316	313
224	278	273	268	264	260
226	231	226	222	218	214
228	190	187	184	181	179
230	155	152	149	147	144
232	125	122	120	117	115
234	99.2	96.1	93.7	91.3	89.0
236	77.3	74.2	71.7	69.3	67.1
238	59.7	56.6	54.3	52.0	49.9
240	44.8	42.7	41.0	39.4	37.9
242	33.3	31.6	30.2	28.9	27.7
244	25.1	23.3	22.0	20.8	19.6
246	18.2	16.9	15.9	15.0	14.1
248	13.0	12.0	11.2	10.5	9.81
250	9.57	8.65	7.98	7.37	6.80
252	6.89	6.09	5.52	5.01	4.54
254	4.83	4.26	3.85	3.48	3.14
256	3.39	2.93	2.61	2.32	2.07
258	2.40	2.02	1.75	1.52	1.32
260	1.70	1.43	1.24	1.07	0.932

DISCUSSION AND CONCLUSIONS

The absorption cross-sections of CH_3Br can be represented by an empirical function of temperature for each wavelength according to the following expression :

$$\log_{10} \sigma(\lambda) = A(\lambda) + B(\lambda) \cdot T. \quad (2)$$

The A and B parameters were determined by a polynomial fitting of the available experimental data with respect of temperature and wavelength by means of a least squares computer software (PC.MATLAB — The Math Works Inc).

The most efficient result is :

$$\begin{aligned} \log_{10} \sigma(\lambda, T) = & A_0 + A_1 \lambda + A_2 \lambda^2 + \\ & + A_3 \lambda^3 + A_4 \lambda^4 + (T - 273) \\ & \times (B_0 + B_1 \lambda + B_2 \lambda^2 + B_3 \lambda^3 + B_4 \lambda^4) \quad (3) \end{aligned}$$

with

$$\begin{aligned} A_0 = & 46.520 & B_0 = & 9.3408 \cdot 10^{-1} \\ A_1 = & -1.4580 & B_1 = & -1.6887 \cdot 10^{-2} \\ A_2 = & 1.1469 \cdot 10^{-2} & B_2 = & 1.1487 \cdot 10^{-4} \\ A_3 = & -3.7627 \cdot 10^{-5} & B_3 = & -3.4881 \cdot 10^{-7} \\ A_4 = & 4.3264 \cdot 10^{-8} & B_4 = & 3.9945 \cdot 10^{-10} \end{aligned}$$

for a λ range of 200-260 nm and a T range of 210-300 K.

The computed values represent all the experimental data with an accuracy of $\pm 2.5\%$ expected for the lowest one ($< 2 \cdot 10^{-21} \text{ cm}^2 \text{ molecule}^{-1}$) where the differences may increase to $\pm 4\%$.

In conclusion, this work presents a new set of experimental data about absorption cross-sections of methyl bromide in stratospheric conditions, which present a non negligible temperature dependence above 210 nm and can be easily computed by a fairly simple relationship of wavelength and temperature.

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