ULTRAVIOLET ABSORPTION SPECTRUM OF METHYLCHLOROFORM IN THE VAPOR PHASE

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Abstract. Ultraviolet absorption cross sections of methylchloroform CH_3CCl_3 have been measured in the wavelength interval 180-240 nm and temperature range 210-295 K. Numerical values are given and compared with existing data at ambient temperature. Photodissociation coefficients have been calculated for altitudes between 20 and 45 km and appear to be significantly lower than generally considered. The substantial decrease in absorption cross sections observed at low temperatures and $\lambda > 210$ nm has only a minor influence on overall photodissociation coefficients. Relative contributions of photodissociation and reaction with OH radicals as potential sinks for methylchloroform at stratospheric altitudes are briefly discussed.

Introduction

Amongst the numerous chlorocompounds of industrial origin released to the atmosphere and considered as potentially harmful for stratospheric ozone, methylchloroform (1-1-1-trichloroethane, CH_3CCl_3), whose world production will probably reach 1 million tons by 1980, has been suggested to play an ever increasing role. Substantial destruction of this molecule occurs in the troposphere through reaction with OH radicals, but accurate assessment of mean tropospheric residence time is still in dispute.

Depending on the values adopted for the experimental rate constant of hydroxyl attack and time average hydroxyl concentration, the proposed residence time ranges from 3 to 7 years (Chang and Kaufman, 1977; Derwent and Eggleton, 1978). However, simultaneous consideration of global emissions figures for methylchloroform (Neely and Plonka, 1978) and recent monitoring data suggests a value as high as 8-11 years (Singh, 1977a,b, Chang and Penner, 1978).

In such conditions, a 10-15% penetration of ground released methylchloroform is to be expected at the tropopause level, and significant steady state ozone depletion values could be due to photodissociation of this compound (McConnell and Schiff, 1978).

The reliability of such predictions is strongly dependent on the photodissociation pattern adopted for methylchloroform. Until now, only two sets of measurements of absorption cross sections were available (Robbins, 1976; F.S. Rowland, unpublished data, 1977) : the proposed values disagree, in the whole wavelength range of stratospheric interest, by a factor close to two beyond 200 nm.

We report here a new investigation of the ultraviolet absorption spectrum of methylchloroform between 180-240 nm. Measurements have been completed down to 210 K, as it is now clearly established that in the case of halocarbons, a significant decrease of absorption cross sections may be observed in the range of stratospheric temperatures.

Experimental

The ultraviolet spectrum of methylchloroform in the 200 nm wavelength range has been studied as a function of temperature with a classical single beam equipment (deuterium light source, 1 m model 225 McPherson monochromator, absorption cell, photoelectric recording via a EMR type 542 P-09-18 multiplier tube). A complete description of the experimental device has been given previously by Wisemberg and Vanlaethem-Meurée (1978).

As condensation conditions can restrict the use of fairly high gas pressure at low temperatures and consequently the access to low absorption cross sections, a refrigerated stainless steel absorption cell with a 2 m optical path has been conceived. It can be evacuated down to 10^{-6} torrs by an ionic pump which prevents any contamination by organic materials. Temperature regulation down to 220 K is achieved by circulation of cooled methylcyclohexane through a double jacket. Thermic equilibrium is usually obtained after 3-4 hours, as revealed by a temperature gradient inferior to 2 K at 220 K between two thermic resistors placed on the inside walls, at the ends of the absorption tube.

Gas pressure is initially measured, and its decrease followed during a refrigeration process, by a capacitance manometer MKS Baratron directly coupled to the absorption cell. The actual gas temperature is assessed by considering both the conditions prevailing at the cell walls, and the value deduced from the pressure decrease, according to the perfect gases law.

Determination of the absorption cross section is made after several sequential recordings of the incident and absorbed fluxes measured in the same temperature conditions.

Methylchloroform was kindly provided by Solvay and Co., with a gas chromatography certified purity of better than 99%, and was used after thorough degassing, without further purification.

Results and discussion

At ambient temperature, measurements have been performed at working pressures ranging from 0.1 to 30 torr, and Beer's law was found to hold in all cases. In such conditions, appreciable absorption (more than 10%) is easily observed for wavelengths between 182 and 240 nm, so that absorption cross sections can be determined with good accuracy (± 2%).

As can be seen on fig. 1, our results are in fair agreement with those reported by Robbins (1976), but significantly lower than the values proposed by Rowland (unpublished data, 1977). Determinations have been extended to low temperature conditions (272 K, 252 K, 220 K) : as
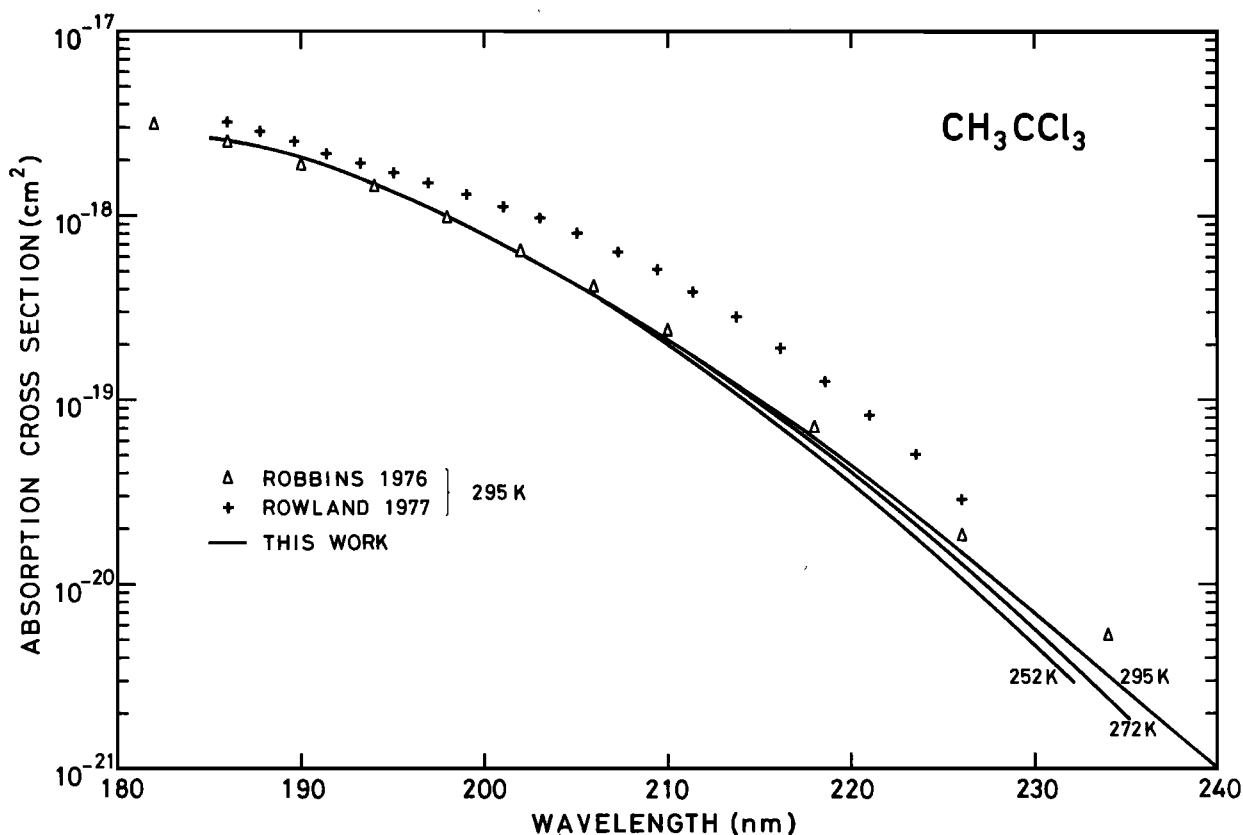
Fig. 1. Absorption cross sections of CH_3CCl_3 vs. wavelength, as a function of temperature.

already observed in the case of other halocarbons (Chou et al, 1977; Wisemberg et al., 1977) absorption cross sections decrease with decreasing temperature, the largest effect being detected near the absorption threshold. As temperature is given with a ± 2 K accuracy, the overall $\sigma(T)$ value is to be considered with a ± 4% confidence interval. At temperatures lower than 250 K, vapor pressure limitations considerably lower the maximum working pressure and prohibit direct determinations in the region of low absorption. However, the analysis of the absorption cross section vs. temperature relationship at a given wavelength shows an exponential decrease, so that interpolation for other temperatures and extrapolation down to 210 K can be reasonably made to determine numerical values at given temperatures.

Table 1 presents absorption cross-sections for 270, 250, 230 and 210 K and table 2 gives interpolated values at wavelengths corresponding to wavenumber intervals generally used in stratospheric photodissociation calculations. In both tables, blank space means that values at lower temperature are the same as those at 295 K.

At long wavelengths (230-240 nm) and low temperatures (210 K), absorption cross sections are reduced down to 20-30% of their 295 K values. However, in the region of high absorption, the temperature effect vanishes progressively and falls within the limits of experimental errors. In this case, absorption cross-sections have been deduced by linear extrapolation from values directly observed at longer wavelengths in order to provide a smooth transition with the temperature independent part of the absorption spectrum.

TABLE 1. Absorption cross section of CH_3CCl_3 $(10^{21}\ cm^2.molecule^{-1})$

$\lambda(nm)$	295 K	270 K	250 K	230 K	210 K
182	3150				
184	2800				
186	2500				
188	2200				
190	1920				
192	1635				
194	1400				
196	1180				
198	990				
200	810	810	810	810	810
202	658	655	650	645	640
204	520	510	502	495	487
206	400	387	379	370	360
208	308	295	284	274	265
210	240	227	216	207	198
212	168	156	147	139	132
214	120.0	110.0	102.0	95.0	88.5
216	86.0	77.5	71.5	66.0	61.0
218	60.0	54.0	50.0	46.0	42.5
220	41.5	37.4	34.2	31.2	29.0
222	29.5	25.7	23.0	20.6	18.6
224	20.5	17.4	15.3	13.5	11.8
226	14.8	12.2	10.4	8.90	7.60
228	10.2	8.35	7.10	6.05	5.15
230	7.00	5.60	4.70	3.95	3.30
232	4.90	3.65	2.90	2.30	1.82
234	3.35	2.42	1.87	1.45	1.12
236	2.30	1.58	1.17	0.87	0.64
238	1.53	1.01	0.73	0.51	0.36
240	1.02	0.64	0.48	0.34	0.24

TABLE 2. Absorption cross sections of CH_3CCl_3 $(10^{21}$ $cm^2.molecule^{-1})$.

λ(nm)	295 K	270 K	250 K	230 K	210 K
182.6	3050				
184.3	2780				
186.0	2500				
187.8	2250				
189.6	2000				
191.4	1750				
193.2	1520				
195.1	1290				
197.0	1080				
199.0	880				
201.0	725				
203.0	590				
205.1	460				
207.3	355	355	355	355	355
209.4	258	258	258	257	251
211.6	190	187	184	179	174
213.9	128	123	119	114	109
216.2	84.0	78.1	74.8	70.6	66.8
218.6	54.0	48.6	45.6	42.7	39.7
221.0	35.8	31.1	28.6	26.3	24.2
223.5	23.3	19.6	17.7	15.8	14.2
226.0	14.8	12.0	10.5	9.18	8.14
228.6	9.00	7.02	5.94	5.04	4.32
231.2	5.60	4.20	3.44	2.86	2.30
233.9	3.30	2.38	1.86	1.48	1.14
236.7	1.96	1.33	1.02	0.75	0.53
239.5	1.15	0.75	0.48	0.37	0.23

It is currently admitted that in the wavelength and pressure ranges of stratospheric interest, the only significant primary photolytic path for all halocarbons is the release of one Cl atom with a unitary quantum yield (Majer and Simons 1964)

$$CH_3CCl_3 + h\nu \quad CH_3CCl_2 + Cl \qquad (1)$$
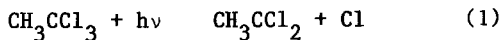
The immediate reaction of the CH_3CCl_3 radical with O_2 releases another Cl atom leaving CH_3CClO which in turn can be subject to photolysis. The ultimate fate of this radical in stratospheric conditions has not yet been considered in detail but it can be assumed that photodecomposition of methylchloroform results in the average production of more than two, if not three, Cl_x entities. Primary photodissociation coefficients J for a

TABLE 3. Photodissociation coefficient of CH_3CCl_3 vs. altitude.

Z(km)	J (s^{-1}) σ (295K)[a]	J (s^{-1}) σ = f(T)	J (s^{-1}) σ Rowland
20	$3.26 \ 10^{-10}$	$3.17 \ 10^{-10}$	$5.69 \ 10^{-10}$
25	$3.85 \ 10^{-8}$	$3.70 \ 10^{-8}$	$6.68 \ 10^{-8}$
30	$6.50 \ 10^{-7}$	$6.21 \ 10^{-7}$	$1.12 \ 10^{-6}$
35	$3.12 \ 10^{-6}$	$3.00 \ 10^{-6}$	$5.37 \ 10^{-6}$
40	$7.42 \ 10^{-6}$	$7.32 \ 10^{-6}$	$1.28 \ 10^{-5}$
45	$1.14 \ 10^{-5}$	$1.13 \ 10^{-5}$	$1.98 \ 10^{-5}$

[a]Temperature independant cross section.

TABLE 4. Destruction rates of CH_3CCl_3 by OH radicals vs. altitude.

Z(km)	T(K)	[OH] cm^{-3}	k_1[OH] s^{-1}	k_2[OH] s^{-1}
20	218	$0.15 \ 10^7$	$3.04 \ 10^{-9}$	$3.20 \ 10^{-8}$
25	227	$0.36 \ 10^7$	$1.99 \ 10^{-8}$	$1.03 \ 10^{-8}$
30	235	$0.67 \ 10^7$	$4.35 \ 10^{-8}$	$2.44 \ 10^{-8}$
35	252	$0.92 \ 10^7$	$9.12 \ 10^{-8}$	$5.36 \ 10^{-8}$
40	268	$1.0 \ 10^7$	$1.36 \ 10^{-7}$	$8.59 \ 10^{-7}$
45	274	$1.2 \ 10^7$	$1.82 \ 10^{-7}$	$1.18 \ 10^{-7}$

given altitude, have been computed by the product of the absorption cross section with the relevant solar flux based on the discussion published by Simon (1978) and integrated over the 180-240 nm wavelength interval.

Table 3 lists the values obtained for different altitudes, either for temperature independent or dependent absorption cross sections. Due to the significant increase of the solar flux absorption at longer wavelengths, the amplitude of the overall photodissociation coefficients between 20 and 35 km is mainly influenced by the 200-210 nm interval contribution. Consequently, consideration of temperature dependent cross sections only results, in the case of methylchloroform, in a reduction of a few percent of the photodissociation coefficients. More significant is the reduction of the values by a factor close to two, if the absorption cross sections obtained in this work are used instead of those proposed by Rowland (unpublished data, 1977).

As mentionned earlier, the only chemical sink for methylchloroform is due to reaction with OH radicals :

$$CH_3CCl_3 + OH \quad CH_2CCl_3 + H_2O \qquad (2)$$
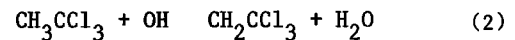
Two different expressions of the temperature-dependent rate constant for this reaction have been proposed until now :

$$k_1 = 1.95 \ 10^{-12} \ \exp \ [- \ 1331/T] \ cm^3.mol^{-1}.s^{-1}$$
(Chang and Kaufman, 1977)

$$k_2 = 3.72 \ 10^{-12} \ \exp \ [- \ 1627/T] \ cm^3.mol^{-1}.s^{-1}$$
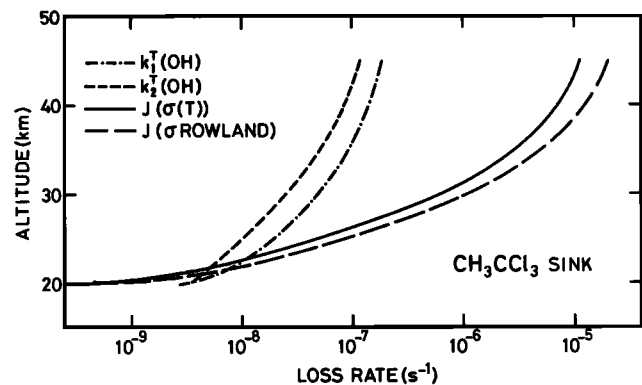(Watson et al, 1977)

Fig. 2. Contribution of photodissociation and reaction with OH to stratospheric destruction of CH_3CCl_3.

Destruction rates of CH_3CCl_3 due to this reaction have been evaluated for stratospheric conditions, on the basis of currently admitted concentration profiles of OH (Brasseur, 1976) and listed as k_1 [OH] and k_2 [OH] in table 4.

As can be seen on fig. 2, this mechanism provides an efficient sink for CH_3CCl_3 up to at least 25 km, while at higher altitudes, photo-dissociation - and consequently, Cl release- is the dominant process.

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