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ULTRAVIOLET PHOTODISSOCIATION OF METHYLCHLOROFORM

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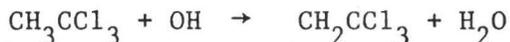
Abstract

Ultraviolet absorption cross sections of methylchloroform  $\text{CH}_3\text{CCl}_3$  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 pertinent to stratospheric conditions are deduced and briefly discussed in relation with the chlorine stratospheric budget.

It is currently admitted that the use of nontoxic chemical solvents with tropospheric residence time of about one year is a desirable goal from the point of view of air pollution. Such compounds are unreactive enough to limit photochemical pollution but are nevertheless mostly destroyed before significant diffusion up to stratospheric altitudes may occur.

Until recently, it was considered that methyl chloroform  $\text{CH}_3\text{CCl}_3$  presented the desired characteristics and could be regarded as a good alternative to widely used oxydants such as perchlorethylene or trichlorethylene which are now subject to stringent regulation. Consequently, the world production of methylchloroform increased considerably during the last few years and will probably reach 1 million tons by 1980<sup>(1)</sup>. This increase, as well as the availability of recent measurements of average tropospheric mixing ratios<sup>(2)</sup>, led people concerned with potential depletion of stratospheric ozone via the chlorine cycle, to reconsider the case of methyl chloroform.

The main tropospheric sink for methyl chloroform is due to reaction with OH radicals :



According to NASA recommendations<sup>(3)</sup>, the rate constant is given by the temperature-dependent expression

$$k = 3,5 \cdot 10^{-12} e^{-1562/T} \text{ (cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}\text{)}$$

A corresponding residence time of about 5 years is deduced by Derwent and Eggleton<sup>(4)</sup> who use two-dimensional modelling techniques and a seasonal-altitudinal latitudinal distribution of OH radicals.

This result is substantiated by the study of the global budget and hemispheric distribution of methyl chloroform : it has been shown that a

global average residence time of about 8 years best fits the observational data. Undoubtedly, the originally proposed value of 1-2 years was underestimated.

In such conditions, a significant fraction of released methyl chloroform could survive and reach the stratosphere where photodissociation leading to chlorine atoms production ought to be considered.

As in the case of all other halocarbons, the UV spectrum of methyl chloroform in the wavelength range of stratospheric interest (170-240 nm) has a continuous character and corresponds to the less energetic band of the electronic spectrum<sup>(5)</sup>.

Absorption cross sections data have been given by Robbins<sup>(6)</sup> and Rowland<sup>(7)</sup>: these two sets of measurements disagree, in the whole wavelength range, by a factor close to two beyond 200 nm. Furthermore, only room temperature values are available, while it is now clearly established that in the case of halocarbons a significant decrease may be observed in the range of stratospheric temperatures<sup>(8,9,10)</sup>.

In the present work, determinations of absorption cross sections have been performed as a function of pressure, wavelength and temperature, using a 2 m refrigerated absorption cell.

This device allows accurate determination of fairly low absorption cross sections, even when the working pressure has to be reduced because of vapor pressure limitations. A complete description of the experimental device (light source, monochromator, absorption cell, detection circuit) as well as operation conditions has been published previously<sup>(11)</sup>.

At ambient temperatures, measurements have been performed between 0.1 and 30 torrs: as can be seen on figure 1, absorption cross sections show a fair agreement with Robbin's values while Rowland's ones seem to have been overestimated.

As already observed in the case of other halocarbons, absorption cross sections decrease with decreasing temperature, the largest effect being detected near the absorption threshold.

Vapor pressure limitations prohibit direct determinations at temperatures lower than 250 K. However, the analysis of the absorption cross section vs. temperature relationship at a given wavelength shows an exponential decrease, so that extrapolation down to 210-230 K appears to be reasonable (fig. 2).

Numerical values of absorption cross sections for selected wavelengths and temperatures representative of stratospheric conditions are given in table 1.

The amplitude of the temperature effect is most easily visualized by considering relative absorption cross sections  $\sigma_T/\sigma_{295K}$  (fig. 3) : the reduction factor can amount up to 3, at long wavelengths and low temperatures.

In the region of high absorption, the temperature effects vanishes progressively : reasonable values of absorption cross sections have been assumed in order to provide a smooth transition with the temperature independent part of the absorption spectrum.

Photodissociation coefficients  $J_\lambda^Z$ , for a given wavelength interval and altitude, have been computed by the product of the absorption cross section with the relevant solar flux<sup>(12)</sup>, assuming a unitary quantum yield :

$$J_\lambda^Z = \sigma_\lambda q_\lambda^Z$$

Overall photodissociation coefficients are then obtained by integration over the relevant wavelength interval :

$$J^Z = \int_{\lambda = 180 \text{ nm}}^{\lambda = 240 \text{ nm}} J_\lambda^Z d\lambda$$

Table 1 : Absorption cross sections  $\sigma \times 10^{21} \text{ cm}^2/\text{molecule}$ .

$\lambda$ (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	990.0				
200	810.0				
202	658.0				
204	520.0				
206	400.0				
208	308.0				
210	240.0	240.0	240.0	235.0	229.0
212	168.0	165.0	161.0	156.0	151.0
214	120.0	115.0	111.0	107.0	103.0
216	86.0	80.0	76.5	72.7	68.8
218	60.0	54.6	51.0	48.0	45.0
220	41.5	36.5	34.0	31.3	29.0
222	29.5	25.4	23.0	20.9	19.2
224	20.5	17.1	15.4	12.6	12.3
226	14.8	12.0	10.5	9.18	8.07
228	10.2	8.06	6.88	5.86	5.10
230	7.00	5.35	4.48	3.74	3.11
232	4.90	3.63	2.94	2.40	1.91
234	3.35	2.41	1.88	1.47	1.14
236	2.30	1.59	1.22	0.92	0.67
238	1.53	1.02	0.76	0.55	0.37
240	1.02	0.65	0.47	0.34	0.20

Table 2

	$J_{\sigma}$ Rowland ( $s^{-1}$ )	$J_{\sigma} = \text{cste}$ ( $s^{-1}$ )	$J_{\sigma} = f(T)$ ( $s^{-1}$ )	$k_T$ [OH] $s^{-1}$
20	5.69 $10^{-10}$	3.26 $10^{-10}$	3.17 $10^{-10}$	3.5 $10^{-9}$
25	6.68 $10^{-8}$	3.85 $10^{-8}$	3.70 $10^{-8}$	1.20 $10^{-8}$
30	11.2 $10^{-7}$	6.50 $10^{-7}$	6.21 $10^{-7}$	3.10 $10^{-8}$
35	5.38 $10^{-6}$	3.12 $10^{-6}$	3.00 $10^{-6}$	6.60 $10^{-8}$
40	1.28 $10^{-5}$	7.42 $10^{-6}$	7.32 $10^{-6}$	1.04 $10^{-7}$
45	1.98 $10^{-5}$	1.14 $10^{-5}$	1.13 $10^{-5}$	1.40 $10^{-7}$

Table 2 lists the values obtained for different altitudes either for Rowland's values, or our own temperature independent and dependent absorption cross sections. Photodissociation coefficients appear significantly lower than originally considered.

Due to the particular shape of the solar flux vs. wavelength relationship, the amplitude of photodissociation coefficients between 20 and 35 km is mainly influenced by the 190-210 nm interval contribution; consequently, values including the temperature effect in the case of methylchloroform are only reduced by a few percent. Consideration of destruction rates of methyl chloroform via the attack by stratospheric OH (listed as  $k_T[\text{OH}]$  in table 2) shows that this mechanism provides an alternative and efficient sink up to at least 25 km.

At higher altitudes, photodissociation appears to be the dominant process.

Assuming a tropospheric residence time of 5-8 years, a 10-15% penetration of ground released methyl chloroform is to be expected at the tropopause level.

In such conditions, reasonable projections for the release schedule of methyl chloroform would lead to steady state ozone depletion values due to photodissociation of this compound, about 20% as large as those resulting from the continuous release of  $\text{CF}_2\text{Cl}_2$  and  $\text{CFCl}_3$  at the 1973 rates<sup>(13)</sup>. This estimate, based on the photodissociation pattern proposed by Rowland, ought to be reconsidered in the light of the new experimental data above mentioned.

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LEGEND FOR FIGURES

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Fig. 1 : Experimental absorption cross sections vs. wavelength for different temperatures.

Fig. 2 : Absorption cross sections vs. temperature for different wavelengths.

Fig. 3 : Relative absorption cross sections  $\frac{\sigma_T}{\sigma_{295K}}$  vs. wavelength for different temperatures.

FIG. 1

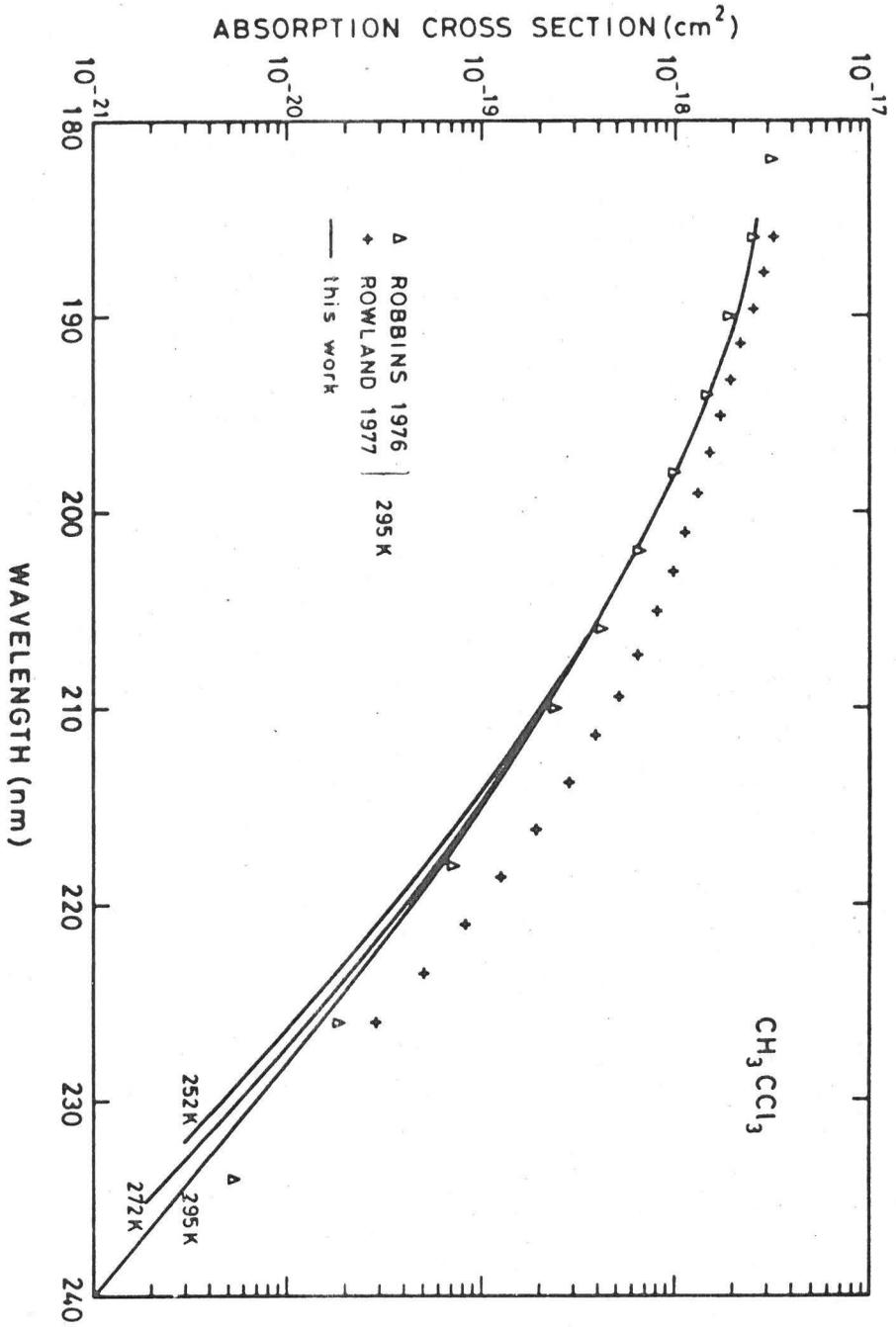


FIG. 2

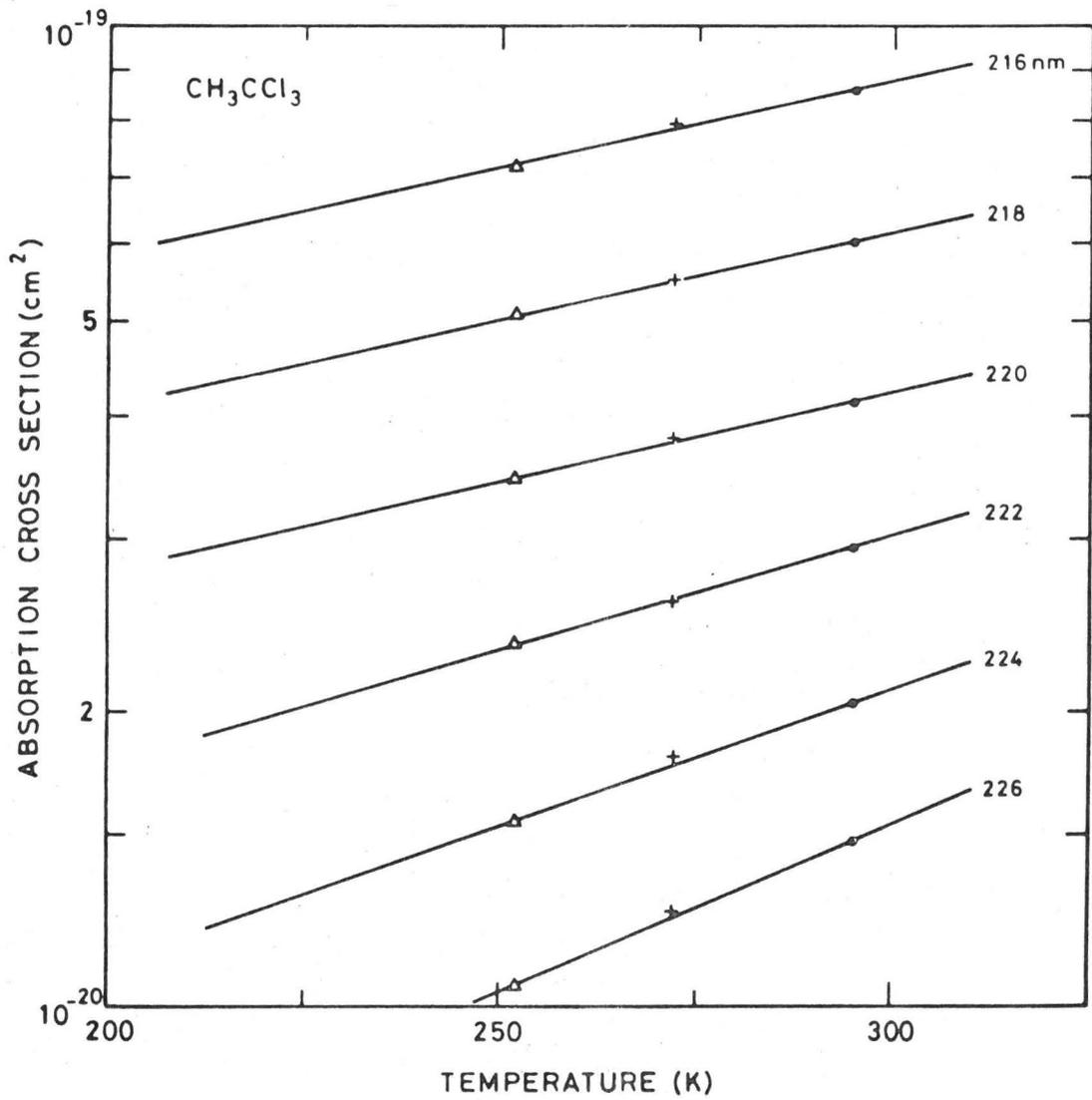


FIG. 3

