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Ultraviolet Absorption spectrum of Methylchloroform
in the Vapor Phase

by

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B E L G I S C H I N S T I T U U T V O O R R U I M T E - A E R O N O M I E

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ULTRAVIOLET ABSORPTION SPECTRUM OF METHYLCHLOROFORM

IN THE VAPOR PHASE

by

N. VANLAETHEM-MEUREE, J. WISEMBERG, and P.C. SIMON

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.

FOREWORD

The paper entitled "Ultraviolet Absorption Spectrum of Methylchloroform in the Vapor Phase" will be published in Geophysical Research Letters.

AVANT-PROPOS

Le travail intitulé "Ultraviolet Absorption Spectrum of Methylchloroform in the Vapor Phase" sera publié dans la revue Geophysical Research Letters.

VOORWOORD

De tekst getiteld "Ultraviolet Absorption Spectrum of Methylchloroform in the Vapor Phase" zal in Geophysical Research Letters gepubliceerd worden.

VORWORT

Der Text "Ultraviolet Absorption Spectrum of Methylchloroform in the Vapor Phase" wird in Geophysical Research Letters hergestellt worden.

Résumé

Les sections efficaces d'absorption dans l'ultraviolet du méthylchloroforme CH_3CCl_3 ont été mesurées pour des longueurs d'onde comprises entre 182 à 240 nm, et des températures variant de 210 à 295 K. Les valeurs numériques obtenues sont comparées avec celles proposées par d'autres auteurs à température ambiante. Les coefficients de photodissociation, calculés pour des altitudes comprises entre 20 et 45 km, présentent des valeurs inférieures à celles généralement considérées. L'importante diminution de section efficace d'absorption observée à température basse et aux longueurs d'onde supérieures à 210 nm ne provoque qu'un abaissement mineur du coefficient de photodissociation global. On discute brièvement des rôles respectifs de la photodissociation et de la réaction chimique avec les radicaux OH en tant que modes de destruction stratosphérique du méthylchloroforme.

Samenvatting

Het ultraviolette absorptiespectrum van methylchloroform CH_3CCl_3 werd bestudeerd van 182 tot 240 nm voor verscheidene temperaturen tussen 210 en 295 K. De werkzame absorptiedoorsneden worden vergeleken met deze bekomen door andere auteurs voor 295 K. Fotodissociatie coëfficiënten voor hoogtes tussen 20 en 45 km zijn kleiner dan de vroeger voorgestelde waarden. De vermindering van werkzame absorptiedoorsneden voor $\lambda > 210$ nm en $T = 210\text{-}230$ K beïnvloedt maar weinig totaal fotodissociatie coëfficiënten. De betekenis van fotodissociatie en chemische reactie met OH voor de vernieling van methylchloroform in de stratosfeer wordt kort besproken.

Zusammenfassung

Das Ultraviolette Absorptionsspektrum des Methylchloroform CH_3CCl_3 ist von 182 bis 240 nm für verschiedene Temperaturen (210-295 K) studiert worden. Absorptionsquerschnitte werden gegeben und verglichen mit Ergebnissen in anderen Werken aufgegeben. Photodissoziationskoeffizienten für Höhen zwischen 20 und 45 km sind kleiner als die frühere aufgebene Werte. Die Verkleinerung der Absorptionsquerschnitte für $\lambda > 210$ nm und $T = 210-230$ K ändert nur wenig den gesamten Photodissoziationskoeffizient. Die Bedeutung der Photodissoziation und der chemischer Reaktion mit OH für das Verschwinden des Methylchloroform in der Stratosphäre ist besprochen.

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, Rowland 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 Wisenberg and Vanlaethem (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 ($\pm 2\%$).

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 (1977).

Determinations have been extended to low temperature conditions (272 K, 252 K, 220 K) : as already observed in the case of other halocarbons (Chou et al 1977; Wisenberg 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 $\pm 4\%$ 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 extrapolation down to 210-230 K appears to be reasonable.

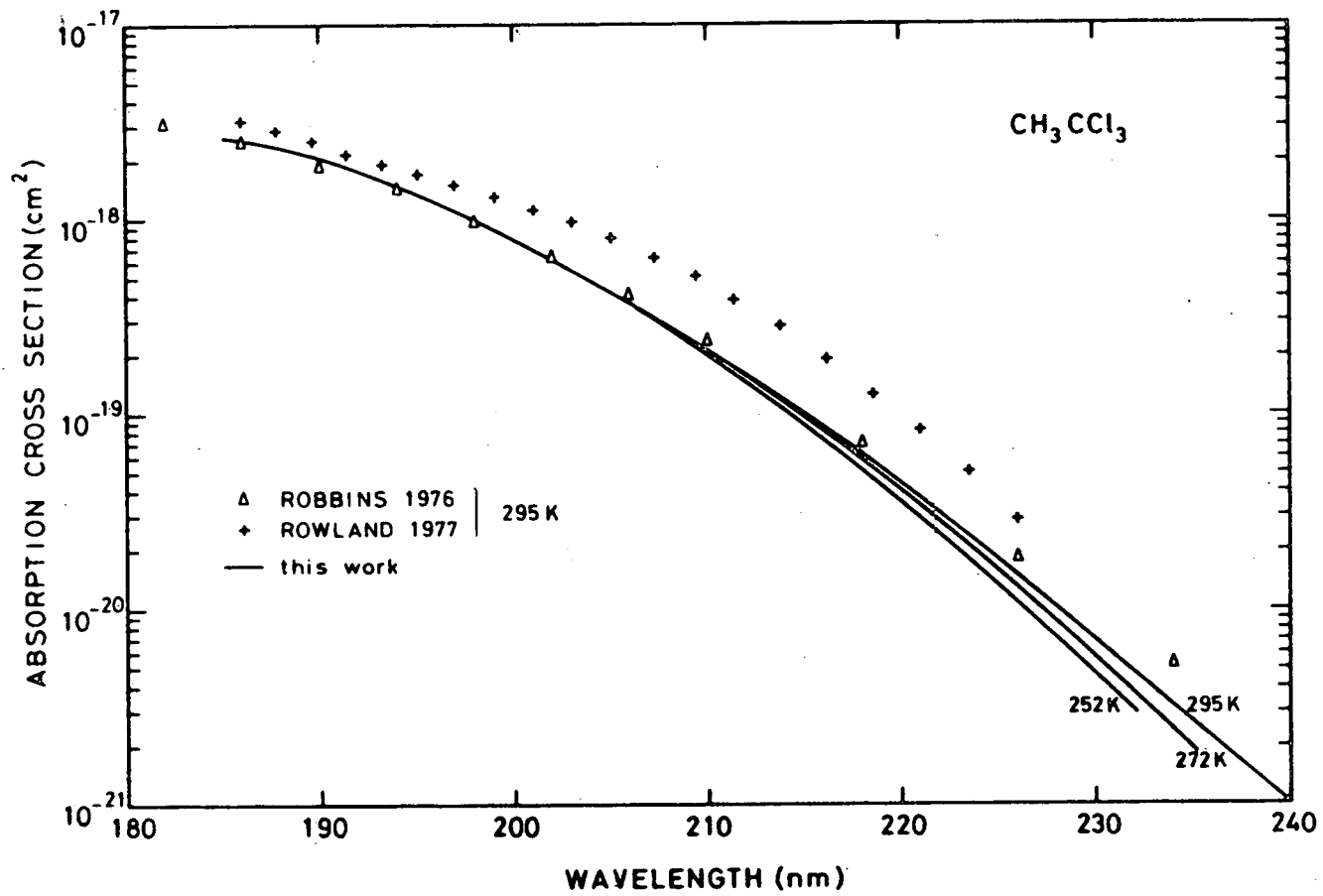
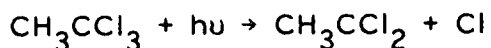


Fig. 1.- Absorption cross sections of CH₃CCl₃ vs. wavelength, as a function of temperature.

Numerical values of absorption cross sections for selected wavelengths and temperatures representative of stratospheric conditions are given in table 1 and 2.

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 : 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.

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)



The immediate reaction of the CH_3CCl_2 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 photo-decomposition of methylchloroform results in the average production of more than two, even not three, Cl_x entities.

Primary photodissociation coefficients J^Z for a 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

TABLE 1 : Absorption cross sections of CH_3CCl_3 ($10^{21} \text{ cm}^2 \cdot \text{molecule}^{-1}$)

$\lambda(\text{nm})$	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 ($10^{21} \text{ cm}^2 \text{ molecule}^{-1}$).

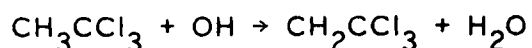
λ (nm)	$\Delta\nu$ (cm^{-1})	295 K	270 K	250 K	230 K	210 K
182.6	54500 - 55000	3050	3050			
184.3	54000 - 54500	2780				
186.0	53500 - 54000	2500				
187.8	53000 - 53500	2250				
189.6	52500 - 53000	2000				
191.4	52000 - 52500	1750				
193.2	51500 - 52000	1520				
195.1	51000 - 51500	1290				
197.0	50500 - 51000	1080				
199.0	50000 - 50500	880				
201.0	49500 - 50000	725				
203.0	49000 - 49500	590				
205.1	48500 - 49000	460				
207.3	48000 - 48500	355	355	355	355	355
209.4	47500 - 48000	258	258	258	257	251
211.6	47000 - 47500	190	187	184	179	174
213.9	46500 - 47000	128	123	119	114	109
216.2	46000 - 46500	84.0	78.1	74.8	70.6	66.8
218.6	45500 - 46000	54.0	48.6	45.6	42.7	39.7
221.0	45000 - 45500	35.8	31.1	28.6	26.3	24.2
223.5	44500 - 45000	23.3	19.6	17.7	15.8	14.2
226.0	44000 - 44500	14.8	12.0	10.5	9.18	8.14
228.6	43500 - 44000	9.00	7.02	5.94	5.04	4.32
231.2	43000 - 43500	5.60	4.20	3.44	2.86	2.30
233.9	42500 - 43000	3.30	2.38	1.86	1.48	1.14
236.7	42000 - 42500	1.96	1.33	1.02	0.75	0.53
239.5	41500 - 42000	1.15	0.75	0.48	0.37	0.23

TABLE 3 :

Z(km)	J (s ⁻¹) σ = cste	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

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 (1977).

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



Two different expressions of the temperature-dependent rate constant for this reaction have been proposed until now :

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

$$k_2 = 3.72 \cdot 10^{-12} \exp [- 1627/T] \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \text{ (Watson et al 1978)}$$

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 $k_1^T [\text{OH}]$ and $k_2^T [\text{OH}]$ 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, photodissociation - and consequently, Cl release- is the dominant process.

TABLE 4

Z (km)	T(K)	[OH] cm ⁻³	k ₁ ^T [OH] s ⁻¹	k ₂ ^T [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	4.53 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 ⁻⁸
45	274	1.2 10 ⁷	1.82 10 ⁻⁷	1.18 10 ⁻⁷

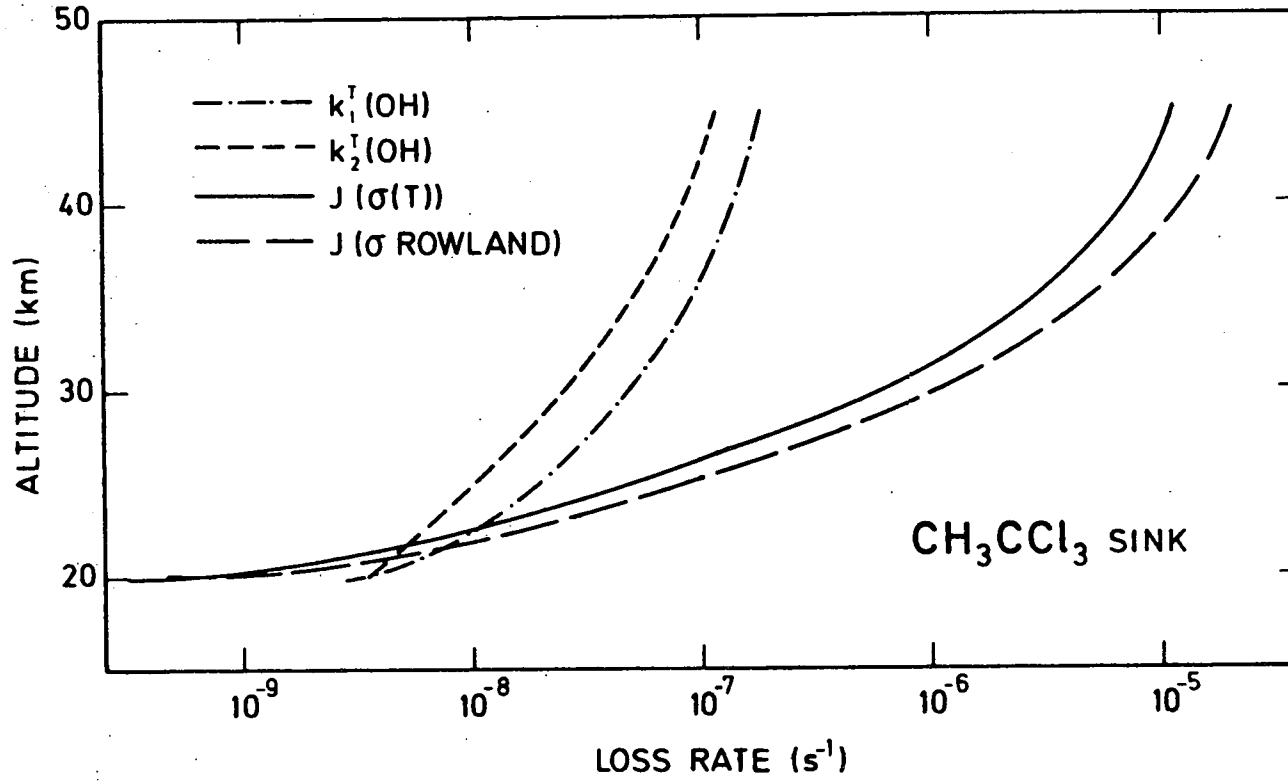


Fig. 2.- Contribution of photodissociation and reaction with OH to stratospheric destruction of CH₃CCl₃.

BIBLIOGRAPHY

- BRASSEUR, G. (1976) : L'action des oxydes d'azote sur l'ozone dans la stratosphère, Thèse de doctorat, Université Libre de Bruxelles, Aeronomica Acta A 173.
- CHANG J.S., KAUFMAN, F. (1977) : Kinetics of the reactions of hydroxyl radicals with some halocarbons : CHFCl_2 , CHF_2Cl , CH_3CCl_3 , C_2HCl_3 , C_2Cl_4 , J. Chem. Phys. 66, 4989.
- CHANG, J.S., PENNER, J.E. (1978) : Analysis of global budgets of halocarbons, Atm. Environment 12, 1867.
- CHOU, C.C., SMITH, W.S., VERA RUIZ, H., MOE, K., CRESCENTINI G., MOLINA, M., ROWLAND, F.S. (1977) : The temperature dependence of the UV absorption cross sections of CCl_2F_2 and CCl_3F and their stratospheric significance, J. Phys. Chem. 81, 286.
- DERWENT, R.G., EGGLETON, A.E.J. (1978) : Halocarbon lifetimes and concentration distributions calculated using a 2-D tropospheric model, Atm. Environ. 12, 1261.
- McCONNELL, J.C., SCHIFF, H.I. (1978) : Methylchloroform : Impact on stratospheric ozone, Science 199, 174.
- NEELY, W.B., PLONKA, J.H. (1978) : Estimation of time-averaged hydroxyl radical concentration in the troposphere, Environmental Science and Technology 12, 317.
- ROBBINS, D.E. (1976) : UV photoabsorption cross sections for halocarbons, Int. Conf. on the Stratosphere and related problems, Logan.
- ROWLAND, F.S. : unpublished data - given in Hudson 1977 : Chlorofluoromethanes and the stratosphere, NASA Ref. Pub. 1010.
- SIMON, P.C. (1978) : Irradiation solar flux measurements between 120 and 400 nm. Current Position and Future Needs, Planet. Space Science 26, 355.

- SINGH, H.B. (1977a) : Atmosphéric halocarbons : Evidence in favor of reduced average hydroxyl radical concentration in the troposphere, Geophys. Res. Letters 4, 101.
- SINGH, H.B. (1977b) : Preliminary estimation of average tropospheric HO concentrations in the northern and southern hemispheres, Geophys. Res. Letters 4, 453.
- WATSON, R.T., MACHADO, G., CONAWAY, B., WAGNER, S., DAVIS D.D. (1977) : A temperature dependent kinetics study of the reaction of OH with CH_2ClF , CHCl_2F , CHClF_2 , CH_3CCl_3 , $\text{CH}_3\text{CF}_2\text{Cl}$, $\text{CF}_2\text{ClCFCl}_2$, J. Phys. Chem. 81, 256.
- WISEMBERG, J., VANLAETHEM-MEUREE, N., SIMON, P.C. (1977) : Ultraviolet absorption measurements of halocarbons and other minor constituents of stratospheric interest : About the significance and consequences of temperature effects, IIIrd Conf. IAGA/IAMP, Seattle (USA).
- WISEMBERG, J., VANLAETHEM-MEUREE, N. (1978) : Mesure des sections efficaces d'absorption de constituants atmosphériques dans l'ultraviolet : description du système expérimental, Bull. Acad. Roy. Belgique, Cl. Sci. 64, 31.