ULTRAVIOLET ABSORPTION CROSS-SECTIONS OF HALOCARBONS OF STRATOSPHERIC INTEREST

D. GILLOTAY and P.C. SIMON
Institut d'Aéronomie Spatiale de Belgique
Avenue Circulaire, 3, B-1180 Brussels, BELGIUM.

and

A. DE RUDDER
National Center for Atmospheric Research
Boulder, CO 80307, USA

1. Introduction.

The spectrometry laboratory of the "Institut d'Aéronomie Spatiale de Belgique" (IASB) is involved, since more than twenty years, in the measurements of ultraviolet absorption cross-sections of atmospheric constituents.

Measurements of temperature dependence of absorption cross-sections and calculations of photodissociation coefficients have been realised since 1977 for about thirty halocarbons of stratospheric interest. Recently, an updated compilation of the absorption cross-sections of halocarbons, entitled: "Ultraviolet Absorption Cross-sections of photoactive species of stratospheric interest, Part 1 : The Halocarbons." has been published by Gillotay and Simon (Aeronomica Acta A 356, 1990).

The purpose of this brief report is to present some recent results concerning absorption cross-sections measurements of halocarbons and to compare them with other available data. Recent values of Ozone Depletion Potential and lifetime calculated with a 1-D model will be also presented.

2. Experimental.

Absorption cross-sections are measured between 170 and 300 nm by means of a double beam experimental device equipped with thermostatic absorption cells of 20 and 200 cm. The experimental temperatures range from 210 to 295 K. A detailed description of the experimental system is given in Gillotay et al.,(Planet. Space Sci., 37, 1127-1140, 1989).

An error budget for the absorption cross-sections measurements is presented in table 1.

Table I. Error budget

(a) $T = 295$ K	%	%
Optical path (200 cm ± 0.1 cm)	0.05	
Pressure (in the range 10^3–2×10^{-3} torr)	0.1	
Impurities in the sample	0.1	
Temperature (± 0.1 K at 300 K)	0.03	
Absorbance $\ln(I_0/I)$ for $\tau = 1$	2.0	
Total r.m.s. error (2σ)	±2.00	
(b) $T = 210$ K		
Optical path (200 cm ± 0.1 cm)	0.05	
Pressure (in the range 10^3–2×10^{-3} torr)	0.1	
Impurities in the sample	0.1	
Temperature (± 2 K at 210 K)	1	
Cross-section dependence on temperature error	1	
Absorbance $\ln(I_0/I)$ for $\tau = 1$	2.0	
= 0.6 (min. value considered)		3.3
Total r.m.s. error (2σ)	±2.47	±3.62

(From Simon et al., J. Atmos. Chem., 7, 103-135, 1988)

3. Results.

Figure 1. represents the relative absorption cross-sections values obtained for CFC-11 by 6 different groups. The agreement between all the measurements is relatively good (within ± 10 %) up to 230 nm. A comparison of temperature dependence measurements show the same agreement.These conclusions are also valid for of CFC-12, CFC-113, CFC-114, CFC-115. (see Simon et al., J. Atmos. Chem., 7, 103-135, 1988; and Simon et al., Ann. Geophysicae, 6, 239-248, 1988)

Figure 2.1-2.3 represent a similar comparison for three alternative HCFC, the disagreement between the four sets of data is, in all cases, very large at room temperature and more important for absorption cross-sections values obtained at low temperature. (Gillotay and Simon, accepted by J. Atmos. Chem, 1990).

These two examples show the need for further and more accurate determinations of the photolytic parameters of photoactive atmospheric constituents.

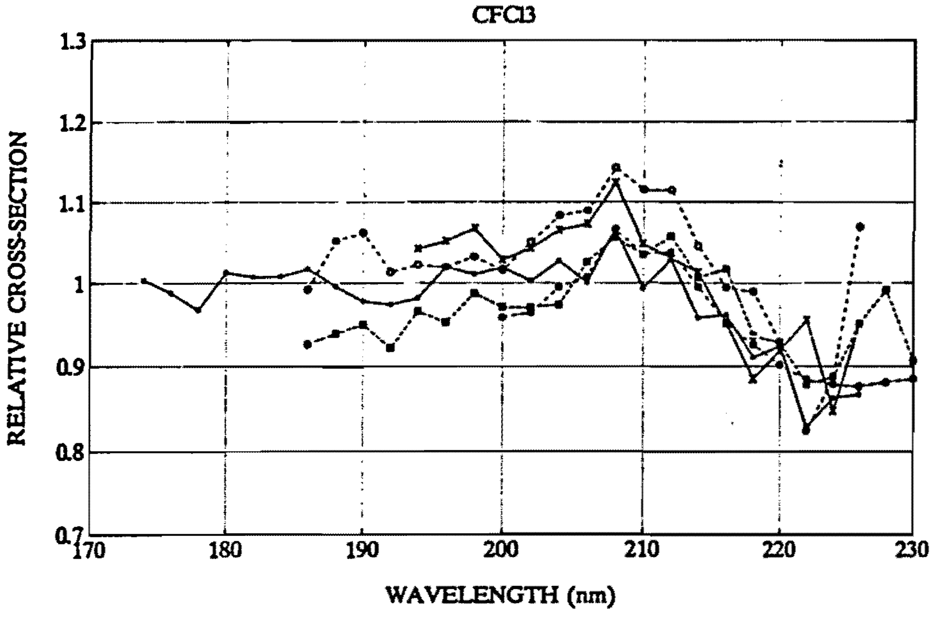

Figure 1 . Relative absorption cross-sections of $CFCl_3$ at room temperature, as a function of wavelength.

(——*——) : Robbins, 1976
(——x——) : Chou et al., 1977
(- -o- -) : Molina and Rowland, 1974
(--.-■---) : Bass and Ledford, 1976
(-.-●-.-) : Mérienne et al., 1990
Ref. : Simon et al., 1988a

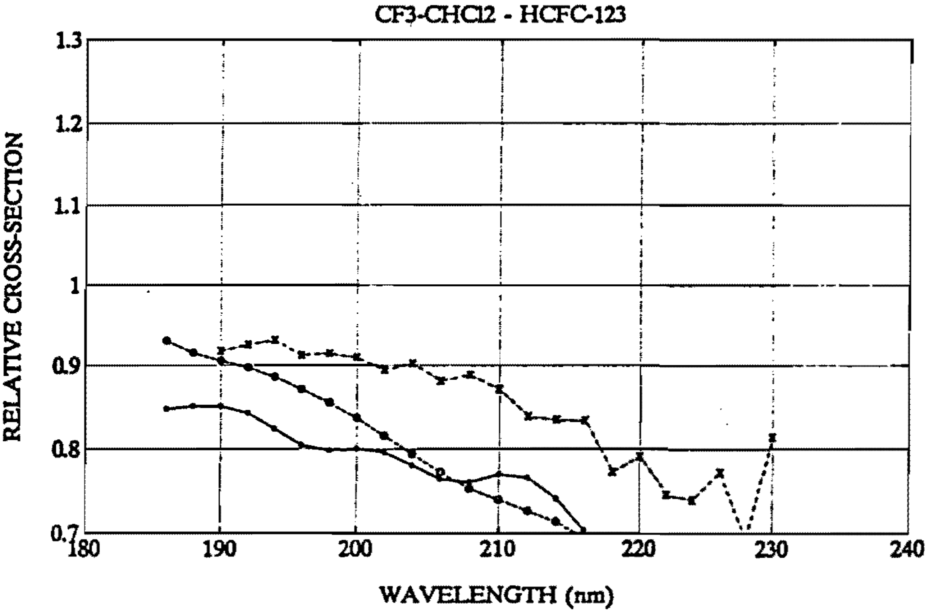

Figure 21. Relative absorption cross-sections of CF_3-$CHCl_2$ at room temperature, as a function of wavelength.

(——*——) : Allied-Signal Corporation, 1989
(---o---) : Molina and Molina, 1989
(-.-x-.-) : Orlando et al., 1990
Ref. : Gillotay and Simon, 1990

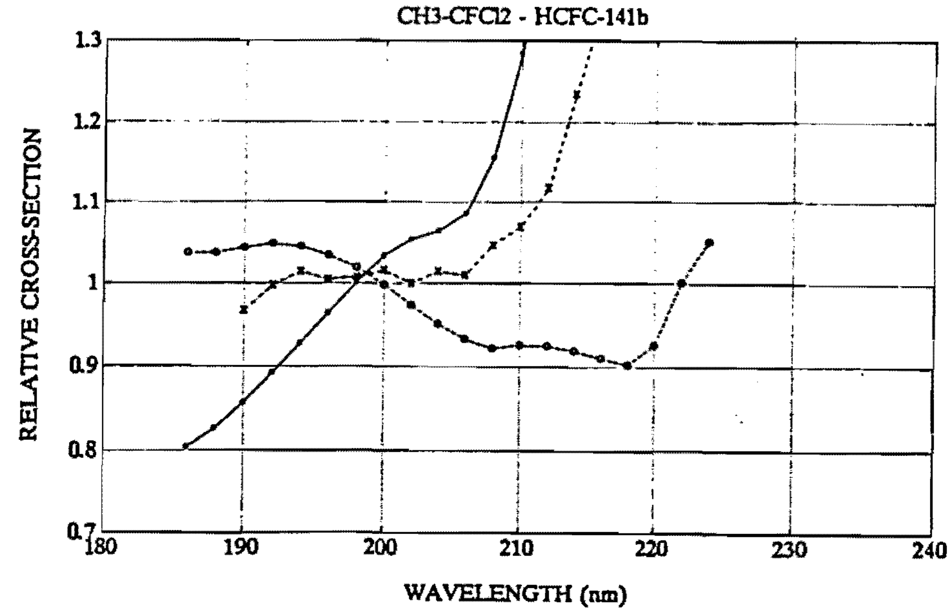

Figure 22. Relative absorption cross-sections of CH_3-$CFCl_2$ at room temperature, as a function of wavelength.

(——*——) : Allied-Signal Corporation, 1989
(---o---) : Molina and Molina, 1989
(-.-x-.-) : Orlando et al., 1990
Ref. : Gillotay and Simon, 1990

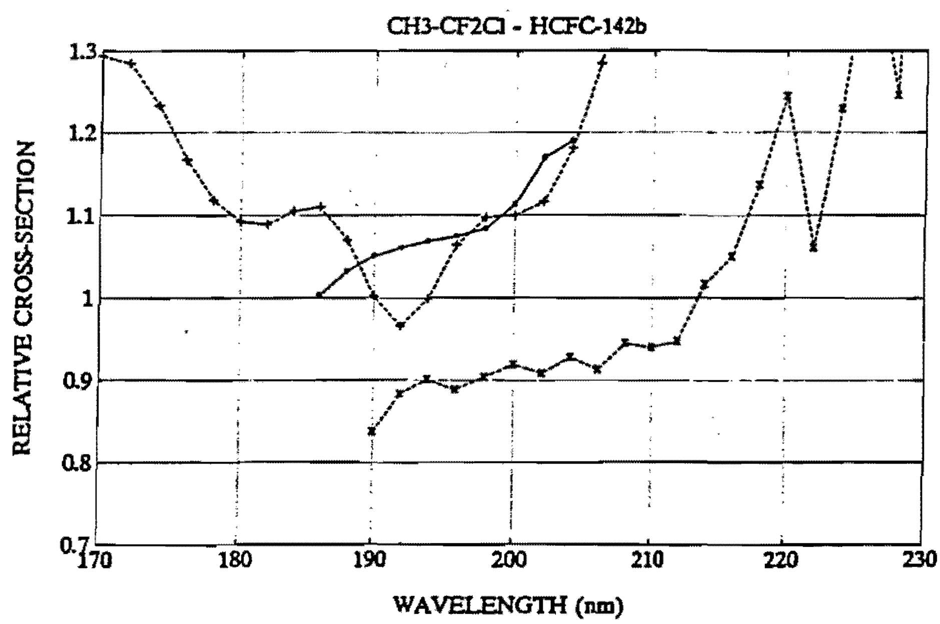

Figure 23. Relative absorption cross-sections of CH_3-CF_2Cl at room temperature, as a function of wavelength.

(——*——) : Allied-Signal Corporation, 1989
(---+---) : Hubrich and Stuhl, 1980
(-.-x-.-) : Orlando et al., 1990
Ref. : Gillotay and Simon, 1990

Finally, table 2 and 3 present respectively the Ozone Depletion Potential and the lifetime of photoactive halocarbons obtained with a 1-D model upon the absorption cross-sections measured at IASB. The parameters are compared with other determinations by 1-D an 2-D models.

Ozone Depletion Potentials.

	1-D Model						2-D Model			
	LLNL	AER	Du Pont	Montréal	Wuebbles	IASB	Oslo	LLNL	AER	Du Pont
CFC11 ($CFCl_3$)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
CFC12 (CF_2Cl_2)	1.0	0.92	1.0	1.0	1.03	0.93	0.92	0.87	0.88	0.89
CFC113 ($C_2F_3Cl_3$)	0.82	0.83	0.89	0.8	0.8	0.89	0.86	0.76		
CFC114 ($C_2F_4Cl_2$)	0.76	0.63	0.79	1.0	0.75	0.76	0.82	0.56		
CFC115 (C_2F_5Cl)	0.43	0.36	0.45	0.6	0.42	0.42	0.40	0.27	0.37	
HCFC21						0.012				
HCFC22	0.045	0.049	0.044			0.034	0.046	0.047	0.057	0.043
HCFC123	0.013	0.016	0.013			0.008	0.013	0.017	0.022	0.017
HCFC124	0.016	0.018	0.017				0.018	0.019	0.024	0.017
HCFC141b	0.069	0.078	0.069			0.041	0.089	0.089	0.11	0.088
HCFC142b	0.051	0.048	0.055			0.035	0.056	0.050	0.062	0.047
CCl_4	1.1	1.16	1.1			1.04	1.2	1.1	0.95	1.2
$CHCl_3$						0.005				
CH_2Cl_2						0.009				
CH_3CCl_3	0.094	0.12	0.092			0.057	0.14	0.13	0.16	0.149
C_3H_7Cl						0.006				
Halon 1211 (CF_2BrCl)	2.7			3.0	2.2	4.9				
Halon 1301 (CF_3Br)	11.4			10.0	13.2	8.8				
Halon 2402 ($C_2F_4Br_2$)				T.B.D.	6.2	6.9				
Halon 22b1 (CHF_2Br)						0.40				

Table 2. Ozone Depletion Potential of Halocarbons.
(adapted from WMO, 1990, report 20)

Lifetimes (years).

	1-D Model				2-D Model			
	LLNL	AER	Du Pont	IASB	Oslo	LLNL	AER	Du Pont
CFC11 ($CFCl_3$)	80	60	71	89	60	52	47	46
CFC12 (CF_2Cl_2)	154	125	154	158	105	101	95	118
CFC113 ($C_2F_3Cl_3$)	96	96	117	139	101	79		
CFC114 ($C_2F_4Cl_2$)	209	260	319	297	236	197		
CFC115 (C_2F_5Cl)	680	690	548	830	522	393	399	
HCFC21				1.6				
HCFC22	20	20	16	13	17	15	24	12.7
HCFC123	1.9	2.1	1.6	1.4	1.7	1.5	2.4	1.2
HCFC124	8.4	8.8	6.9		7.4	6.5	10	5.3
HCFC141b	8.9	9.4	7.8	6	8.0	6.9	11	5.8
HCFC142b	25	25	19	15	21	19	28	15.1
CCl_4	73	53	61	73	52.2	47	40	40
$CHCl_3$				0.5				
CH_2Cl_2				1.0				
CH_3CCl_3	7.4	7.4	6	5	6.3	5.8	7.9	4.7
C_3H_7Cl				1.4				
Halon 1211 (CF_2BrCl)	20			49				
Halon 1301 (CF_3Br)	90			86				
Halon 2402 ($C_2F_4Br_2$)				45				
Halon 22b1 (CHF_2Br)				20				
HFC125	37	37	25		27	43	19	
HFC134a	21	21	16		15	24	12.5	
HFC143a	54	52	42		40			
HFC152a	2.1	2.3	1.7		1.5	2.7	1.3	

Table 3. Lifetime of Halocarbons. (adapted from WMO, 1990, report 20)

where AER : Atmospheric and Environmental Research Inc.
Du Pont : Du Pont Central Research.
LLNL : Lawrence Livermore National Laboratory.
Oslo : University of Oslo.
IASB : Institut d'Aéronomie Spatiale de Belgique.

In conclusion, it is of fundamental importance to determine with a maximum of accuracy, the basic photolytic parameters of the photoactive atmospheric constituents in order to be able to determine the impact on ozone budget of these compounds with a maximum reliability and to reduce the uncertainties in the model predictions on ozone depletion.

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