ULTRAVIOLET ABSORPTION CROSS-SECTIONS OF SOME CARBONYL COMPOUNDS AND THEIR TEMPERATURE DEPENDENCE.

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ABSTRACT

Ultraviolet absorption cross-section of phosgene (CCl_2O), trichloroacetylchloride (CCl_3-CClO) and trichloroacetaldehyde (CCl_3-CHO) have been measured between 170 and 320 nm for temperature ranging from 210 to 295 K with a classical double beam equipment.

These data are compared with other available determinations performed at room temperature. Photodissociation coefficients are estimated and their temperature dependence is discussed. Impact of the photodissociation on the total atmospheric destruction of these compounds is illustrated.

I. INTRODUCTION.

Chemical degradation of alternative hydrochlorofluorocarbons in troposphere produces a series of carbonyl compounds like phosgene, halo-aldehydes or halo-ketones, which could themselves be removed in three ways : (1) Photodissociation by solar UV radiations to produce potential odd chlorine precursors,
(2) Reaction with H_2O and
(3) Reaction with OH.

In order to determine the lifetimes for the photolysis processes, an accurate knowledge of the UV absorption cross-sections is required as a function of wavelength and temperature.

II. EXPERIMENTAL.

Ultraviolet absorption cross sections of phosgene (CCl_2O), trichloroacetylchloride (CCl_3-CClO) and trichloroacetaldehyde (CCl_3-CHO) have been measured between 170 and 320 nm for temperature ranging from 210 to 295 K with a classical double beam equipment.(Gillotay et al., 1989). The purity of the three compounds is better than 99.5 % as determined by gas phase chromatography.

III. RESULTS.

Numerical values of absorption cross-sections for wavenumber intervals of 500 cm^{-1} are given in tables I-III. The absorption spectra are illustrated in Figures 1-3 for selected temperatures namely 295, 250 and 210 K and compared with other available data at 295 K.

In all cases, Beer-Lambert's law was verified for absorption ranging from 10 to 85 %. In such conditions, and according to the error budget previously published, (Simon et al., 1988), the absorption cross-sections reported here are determined with an accuracy of ± 2 % at room temperature and of ± 3 to ± 4 % at the lowest temperature.

Carbonyl compounds display a continuous absorption in the 170-335 nm range. The presence of two maxima and the temperature dependence observed near the maxima and for the longest wavelengths, seems to indicate that there are two continua, one corresponding to the absorption of the C-Cl bond, with a maximum around 170 nm and the other centred respectively at 240 nm for phosgene,around 260 nm for trichloroacetylchloride and at 290 nm for trichloroacetaldehyde, corresponding to the absorption of the C=O bond.

Absorption cross-sections values change with temperature by a factor, which depends on both the wavelength and the chemical composition of the compound. For each wavelength, an exponential dependence of the absorption cross-section versus temperature is clearly established, with a decrease of absorption cross-sections in the region of low absorptions (up to 80 % at 305 nm and 210 K in the case of CCl_2O) and a small increase near the maximum of absorption (up to 5 %). This effect is the most important at the lowest temperature.

Descrepancies observed between the different set of available data at room temperature have to be discussed in more details in terms of experimental conditions.

IV. DISCUSSION.

Photodissociation coefficients of the molecules have been calculated, neglecting the effects of multiple scattering, for given altitude (z), zenith angle (χ) and wavelengths intervals according to the relation :

$$J(z) = \sigma_\lambda q_\lambda(z) \quad ; \quad q_\lambda(z) = q_\lambda(\infty)\, e^{-\tau_\lambda(z)}$$

$$\tau_\lambda(z) = \int_z^\infty [n(O_2)\,\sigma_\lambda(O_2) + n(O_3)\,\sigma_\lambda(O_3) + n(air)\,\sigma_{scatt}]\,\sec\chi\, dz$$

where

z is the altitude,

σ are the absorption cross-sections,

q (z) and q (∞) are the solar irradiance at altitude z or extraterrestrial (z = ∞)

n is the number of particles per volume unit.

Calculations are made for solar zenith angle of 0° and 60° (sec = 1 and 2), taking into account the values of σ (O_2) and σ (O_3) from WMO and Kockarts (1976), σ_{scatt} from Nicolet (1984) and the values of q(∞) from WMO (1986) and by taking into account the actual values of cross-sections corresponding to the temperature conditions at each altitude.

These photodissociation coefficients are illustrated in Figures 4-6 and compared with those calculated with values of absorption cross-sections measured at room temperature.

Stratospheric photodissociation coefficients (for altitude ranging from 15 to 50 km) calculated the temperature dependent absorption cross-sections, are smaller than those calculated with the room temperature values in the 20-35 km region, due to the decrease in the absorption cross-sections in the 200 nm region and the influence of the wavelengths longer than 280nm in the low stratosphere.

Tropospheric photodissociation coefficients for phosgene are very low (between 10^{-9} and 10^{-11} sec $^{-1}$) and are reduced down to 20 % of their room temperature values, using the temperature dependent cross-sections. For the two other compounds, tropospheric photodissociation coefficients are relatively high (ebetwen 10^{-7} and 10^{-4} sec^{-1}) and show a small temperature dependence. Photolysis is, for these two molecules, a non negligible mechanism for their tropospheric removal.

In conclusion, this work presents a new set of experimental data on the absorption cross-sections of carbonyl compounds in atmospheric temperature conditon and highlights a non negligible temperature dependence of their photolysis.

V. REFERENCE.

CHOU, C.C., G. CRECENTINI, H. VERA-RUIZ, W.S. SMITH, and F.S. ROWLAND, 1977, Stratospheric photochemistry of CF_2O, CClFO and CCl_2O, 173rd American Chemical Society Meeting, New Orleans.

GILLOTAY D., A. JENOUVIER, B. COQUART, M.F. MERIENNE, and P.C. SIMON, 1898, Ultraviolet absorption cross-sections of Bromoform in the temperature range 295-240 K., Planet. Space Sci., 37, 1127-1140.

KOCKARTS G., 1976, Absorption and photodissociation in the Schumann-Runge bands of molecular oxygen in terrestrial atmosphere., Planet. Space Sci., 24, 589-604

NICOLET M., 1984, On the molecular scattering in the terrestrial atmosphere : an empirical formula for calculation in the homosphere., Planet. Space Sci., 32, 1467-1468.

RATTINGAN G., and R.A. COX, Spectra and photochemistry of degradation products of hydrochlorofluorocarbons and hydrofluorocarbons, 1991, report to SPA-AFEAS, INC.

SIMON P.C., D. GILLOTAY, N. VANLAETHEM-MEUREE, and J. WISEMBERG, 1988, Ultraviolet absorption cross-sections of chloro and chlorofluoromethanes at stratospheric temperatures., J. Atmos. Chem., 7, 107-1345.

WMO, Atmospheric ozone 1985, WMO global ozone research and monitoring project, Report 14, 1986.

ZABEL, F. et al., 1992, Private communication.

Table I PHOSGENE (CCl_2O)

$\sigma(\lambda) \times 10^{21}$ (cm^2 molec.$^{-1}$)

N°	(nm)	295K	270K	250K	230K	210K
42	166.7-169.5	3010	3600	4160	4810	5560
43	169.5-172.4	4330	4760	5130	5530	5960
44	172.4-175.9	4930	5160	5360	5560	5770
45	175.2-175.4	5030	5150	5240	5330	5430
46	175.4-177.0	4890	4910	4920	4940	4950
47	177.0-178.6	4540	4490	4460	4420	4380
48	178.6-180.2	4040	3960	3900	3850	3790
49	180.2-181.8	3470	3390	3330	3270	3210
50	181.8-183.5	2890	2820	2760	2710	2660
51	183.5-185.2	2340	2280	2240	2200	2150
52	185.2-186.9	1860	1820	1790	1760	1730
53	186.9-188.7	1460	1440	1410	1390	1370
54	188.7-190.5	1160	1140	1120	1110	1090
55	190.5-192.3	903	888	876	865	854
56	192.3-194.2	715	698	685	673	660
57	194.2-196.1	524	509	498	487	476
58	196.1-198.0	399	386	376	367	357
59	198.0-200.0	312	302	293	285	277
60	200.0-202.0	252	243	236	229	223
61	202.0-204.1	209	202	196	191	185
62	204.1-206.2	179	173	168	163	159
63	206.2-208.3	158	153	149	145	141
64	208.3-210.5	143	139	136	132	129
65	201.5-212.8	133	129	127	124	121
66	212.8-215.0	126	124	121	119	117
67	215.0-217.4	123	121	119	117	115
68	217.4-219.8	122	120	119	117	116
69	219.8-222.2	122	121	120	119	118
70	222.2-224.7	124	124	123	121	122
71	224.2-227.3	127	127	127	127	127
72	227.3-229.9	131	131	131	131	132
73	229.9-232.6	134	134	135	135	135
74	232.6-235.3	136	137	137	137	137
75	235.3-238.1	131	132	132	133	133
76	238.1-241.0	125	125	126	126	127
77	241.0-243.9	116	116	117	117	118
78	243.9-246.9	105	106	106	106	106
79	246.9-250.0	93.1	92.9	92.8	92.7	92.5
80	250.0-253.2	80.5	79.8	79.3	78.8	78.2
81	253.2-256.4	66.5	65.3	64.4	63.4	62.5
82	256.4-259.7	53.4	51.8	50.6	49.4	48.2
83	259.7-263.2	40.3	38.4	37.0	35.7	34.4
84	263.2-266.7	28.9	27.1	25.8	24.5	23.2
85	266.7-270.3	19.8	18.1	16.9	15.8	14.7
86	270.3-274.0	12.6	11.3	10.3	9.45	8.64
87	274.0-277.8	7.36	6.39	5.71	5.10	4.55
88	277.8-281.7	3.92	3.29	2.86	2.48	2.16
89	281.7-285.7	1.93	1.56	1.31	1.11	0.933
90	285.7-289.9	0.831	0.643	0.524	0.426	0.347
91	289.9-294.1	0.316	0.233	0.183	0.143	0.112
92	294.1-298.5	0.105	0.0732	0.0549	0.0413	0.0310
93	298.5-303.0	0.0288	0.0190	0.0136	0.00970	0.00694
94	303.0-307.7	0.00491	0.00298	0.00200	0.00134	0.000899

Table III TRICHLOROACETYLCHLORIDE (CCl_3CClO)

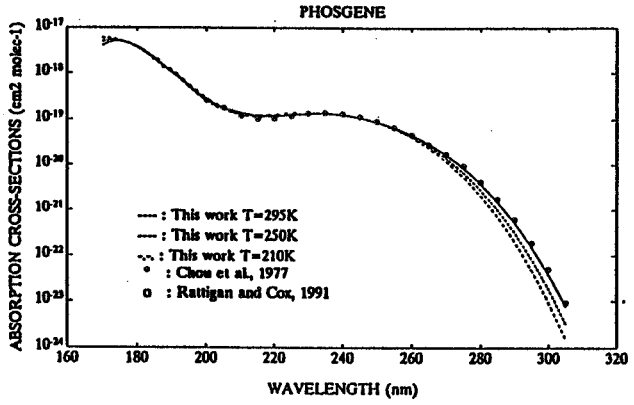
$\sigma(\lambda) \times 10^{21}$ (cm^2 molec.$^{-1}$)

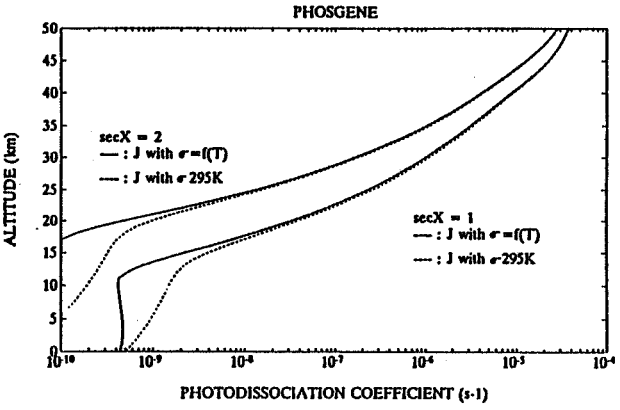
N°	(nm)	295K	270K	250K	230K	210K
42	166.7-169.5	6710	6710	6700	6690	6690
43	169.5-172.4	6990	6910	6840	6780	6720
44	172.4-173.9	7120	7000	6900	6810	6710
45	173.2-175.4	7160	7020	6910	6800	6690
46	175.4-177.0	7170	7010	6890	6770	6650
47	177.0-178.6	7140	6970	6840	6710	6580
48	178.6-180.2	7060	6890	6750	6620	6490
49	180.2-181.8	6940	6770	6640	6510	6380
50	181.8-183.5	6770	6610	6480	6360	6240
51	183.5-185.2	6550	6410	6290	6180	6060
52	185.2-186.9	6300	6160	6060	5960	5860
53	186.9-188.7	5990	5880	5790	5710	5620
54	188.7-190.5	5670	5580	5500	5430	5360
55	190.5-192.3	5280	5210	5150	5100	5050
56	192.3-194.2	4870	4830	4790	4750	4710
57	194.2-196.1	4450	4420	4400	4370	4350
58	196.1-198.0	4020	4000	3990	3980	3970
59	198.0-200.0	3580	3580	3580	3580	3580
60	200.0-202.0	3140	3150	3160	3170	3170
61	202.0-204.1	2720	2730	2740	2750	2770
62	204.1-206.2	2310	2330	2340	2250	2370
63	206.2-208.3	1940	1950	1960	1980	1990
64	208.3-210.5	1600	1610	1620	1620	1630
65	210.5-212.8	1290	1290	1290	1300	1300
66	212.8-215.0	1020	1020	1020	1020	1010
67	215.0-217.4	789	783	776	772	767
68	217.4-219.8	595	584	575	566	557
69	219.8-222.2	440	426	415	404	393
70	222.2-224.7	318	302	289	278	266
71	224.2-227.3	258	243	232	222	212
72	227.3-229.9	219	207	198	189	181
73	229.9-232.6	195	186	178	171	164
74	232.6-235.3	183	175	168	162	156
75	235.3-238.1	179	172	166	161	155
76	238.1-241.0	181	174	170	165	160
77	241.0-243.9	187	182	178	174	170
78	243.9-246.9	197	193	189	186	183
79	246.9-250.0	209	205	203	200	197
80	250.0-253.2	218	216	213	211	210
81	253.2-256.4	223	221	220	218	217
82	256.4-259.7	226	223	221	219	217
83	259.7-263.2	223	220	218	215	213
84	263.2-266.7	211	208	205	203	200
85	266.7-270.3	191	188	185	183	181
86	270.3-274.0	166	163	160	158	156
87	274.0-277.8	137	134	132	130	128
88	277.8-281.7	107	105	104	102	100
89	281.7-285.7	81.4	79.5	78.0	76.5	75.0
90	285.7-289.9	58.6	56.9	55.6	54.4	53.1
91	289.9-294.1	40.3	38.9	37.8	36.8	35.7
92	294.1-298.5	26.7	25.5	24.6	23.7	22.8
93	298.5-303.0	16.8	15.8	15.1	14.4	13.7
94	303.0-307.7	9.21	8.48	7.93	7.42	6.95
95	307.7-312.5	6.05	5.46	5.03	4.64	4.27
96	312.5-317.5	3.39	2.96	2.65	2.38	2.14
97	317.5-322.5	1.88	1.57	1.37	1.19	1.03
98	322.5-327.5	1.04	0.830	0.693	0.579	0.484
99	327.5-332.5	0.578	0.436	0.347	0.277	0.221
100	332.5-337.5	0.326	0.230	0.173	0.131	0.0998

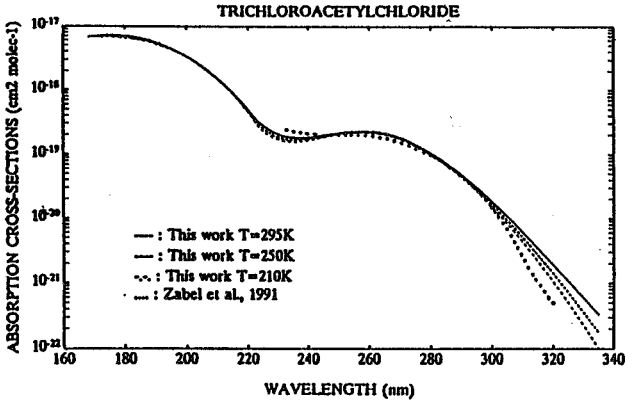
Table II TRICHLOROACETALDEHYDE (CCl_3CHO)

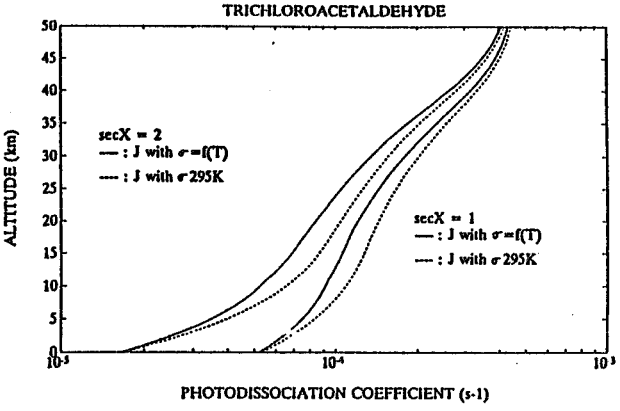
$\sigma(\lambda) \times 10^{21}$ (cm^2 molec.$^{-1}$)

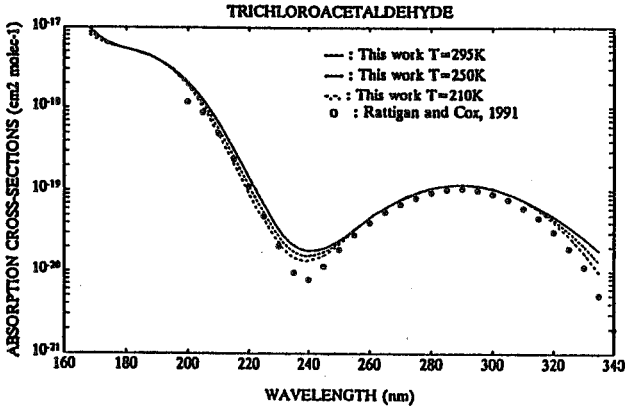
N°	(nm)	295K	270K	250K	230K	210K
42	166.7-169.5	9880	9310	8880	8470	8070
43	169.5-172.4	7850	7540	7310	7080	6860
44	172.4-173.9	6890	6710	6570	6430	6300
45	173.2-175.4	6420	6300	6210	6120	6030
46	175.4-177.0	6040	5980	5920	5870	5820
47	177.0-178.6	5730	5700	5680	5660	5630
48	178.6-180.2	5480	5480	5470	5470	5470
49	180.2-181.8	5250	5270	5290	5300	5320
50	181.8-183.5	5030	5070	5090	5120	5150
51	183.5-185.2	4820	4850	4880	4920	4950
52	185.2-186.9	4590	4620	4650	4680	4710
53	186.9-188.7	4330	4360	4390	4410	4430
54	188.7-190.5	4070	4080	4100	4110	4120
55	190.5-192.3	3740	3740	3740	3740	3740
56	192.3-194.2	3400	3390	3360	3350	3330
57	194.2-196.1	3030	2990	2960	2930	2900
58	196.1-198.0	2650	2600	2550	2510	2460
59	198.0-200.0	2270	2200	2140	2090	2040
60	200.0-202.0	1890	1810	1750	1700	1640
61	202.0-204.1	1540	1450	1390	1330	1280
62	204.1-206.2	1210	1130	1080	1020	967
63	206.2-208.3	936	865	812	762	715
64	208.3-210.5	703	642	596	554	515
65	210.5-212.8	511	461	424	390	359
66	212.8-215.0	366	326	298	271	248
67	215.0-217.4	257	227	205	186	168
68	217.4-219.8	176	155	139	126	113
69	219.8-222.2	121	106	95.3	85.7	77.0
70	222.2-224.7	83.5	73.2	65.9	59.4	53.5
71	224.2-227.3	57.9	51.3	46.5	42.1	38.2
72	227.3-229.9	39.4	35.2	32.1	29.4	26.8
73	229.9-232.6	28.3	25.3	23.2	21.2	19.4
74	232.6-235.3	22.3	20.1	18.4	17.0	15.6
75	235.3-238.1	19.2	17.4	16.1	14.9	13.8
76	238.1-241.0	17.9	16.4	15.4	14.3	13.4
77	241.0-243.9	18.0	16.8	15.8	14.9	14.1
78	243.9-246.9	19.4	18.3	17.5	16.7	15.9
79	246.9-250.0	22.1	21.2	20.5	19.8	19.2
80	250.0-253.2	26.2	25.5	24.9	24.4	23.8
81	253.2-256.4	32.5	32.0	31.6	31.3	30.9
82	256.4-259.7	40.4	40.2	40.1	39.9	39.8
83	259.7-263.2	50.9	51.0	51.0	51.1	51.2
84	263.2-266.7	60.9	60.6	60.3	60.0	59.7
85	266.7-270.3	72.7	72.0	71.5	71.0	70.4
86	270.3-274.0	84.6	83.7	83.0	82.3	81.6
87	274.0-277.8	96.0	95.1	94.3	93.5	92.8
88	277.8-281.7	106	105	104	104	103
89	281.7-285.7	112	112	111	111	111
90	285.7-289.9	116	116	116	116	116
91	289.9-294.1	115	115	116	116	116
92	294.1-298.5	110	111	111	112	112
93	298.5-303.0	101	102	102	103	103
94	303.0-307.7	87.0	87.1	87.1	87.2	87.3
95	307.7-312.5	76.2	75.8	75.4	75.0	74.6
96	312.5-317.5	61.5	60.1	59.1	58.0	57.0
97	317.5-322.5	47.7	45.5	43.9	42.3	40.7
98	322.5-327.5	35.6	32.8	30.8	28.9	27.1
99	327.5-332.5	25.7	22.6	20.5	18.5	16.8
100	332.5-337.5	17.9	14.9	12.9	11.1	9.61

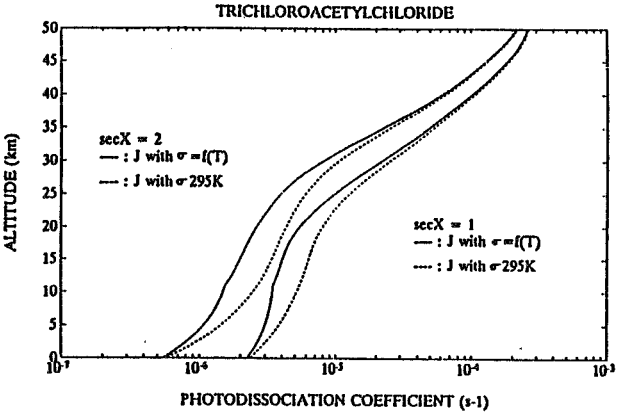












Figures 1-3 : Ultraviolet absorption cross-sections at 295 K, 250 K and 210 K.

Figures 4-6 : Photodissociation coefficients as a function of altitude.