TEMPERATURE DEPENDENCE OF ULTRAVIOLET ABSORPTION CROSS SECTIONS OF BROMINATED METHANES AND ETHANES

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ABSTRACT

Absorption cross-sections of five brominated methanes (CH_3Br, CH_2Br_2, CF_3Br, CF_2Br_2 and CF_2BrCl), and of two brominated ethanes (CF_2Br-CF_2Br and CF_3-$CHBrCl$) have been measured between 172 and 300 nm with a classical single beam system, for temperature ranging from 210 to 295 K. These data are compared with previous determinations made at room temperature (Robbins, 1976 and Molina et al., 1982).

Numerical values of absorptions cross-sections are given and the temperature effects on the photodissociation coefficients of these molecules discussed.

1. INTRODUCTION

Recent studies (Prather et al., 1984; Rodriguez et al., 1986; Yung et al., 1980) show that brominated compounds can play a significantly role in the ozone catalytic destruction in the stratosphere. RBr species concentrations have been measured in the atmosphere by several authors (Fabian et al., 1981; Lal et al., 1985; Cicerone et al., 1988; Berg et al., 1984; Penkett et al., 1985; Class et al., 1986) confirming their possible impact on the ozone layer.

The reliability of models is strongly dependent on the photodissociation pattern adopted for these bromocarbons. Until now, one set of measurements of absorption cross-sections is available at room temperature for most of the bromocarbons (Molina et al., 1982), a second set of data being available for CH_3Br (Robbins, 1976). The purpose of this paper is to report a new investigation of ultraviolet absorption cross-sections of five brominated methanes (CH_3Br, CH_2Br_2, CF_3Br, CF_2Br_2 and CF_2BrCl), and of two brominated ethanes (CF_2Br-CF_2Br and CF_3-$CHBrCl$) measured between 172 and 300 nm, for temperatures between 295 and 210 K. Temperature dependence of absorption cross-section is clearly demonstrated. Photodissociation coefficients are calculated and their temperature dependence is discussed.

2. EXPERIMENTAL

The absorption measurements has been performed by means of a single beam experimental device previously discribed in Gillotay and Simon, (1988), including a Deuterium or a Tungsten filament light source, a 1 m McPherson 225 monochromator, a 2 m thermostatic absorption cell and a EMR type 542 P-09-18 solar blind photomultiplier. The temperature is regulated down to 210 K by circulation of cooled methylcyclohexane through double jacket around the absorption cell and is determined with a precision better than 1% at 210 K. The pressures ranging from 2×10^{-3} to 1000 torr are measured with three capacitance manometers MKS Baratron with a precision better than 0.1%.

Determination of absorption cross-sections is made after at least fifteen sequential recordings of the incident and absorbed fluxes measured for identical temperature conditions, using the Beer-Lambert's law.

3. RESULTS

Numerical values of absorption cross-sections for selected wavelengths between 168 and 304 nm (2 nm intervals) are given in Tables 2-8. The absorption spectra are illustrated in Figures 1 for the bromo-methanes.

Measurements have been performed at working pressures given in Table 1. In all cases, Beer-Lambert's law was verified for absorptions ranging from 10 to 85%. In such conditions, and according to the error budget recently published (Simon et al., 1988), the absorption cross- sections given in Tables 2-8 are determined with an accuracy of $\pm$ 2% at room temperature and of $\pm$ 3 to $\pm$ 4% at the lowest temperature.

Brominated compounds display a continuous absorption in the 172-300 nm range, with absorption cross-sections ranging from 10^{-17} to 10^{-25} cm^2 $molecule^{-1}$, with a maximum around 200 nm for the monobrominated carbons and around 225 nm for the dibrominated ones. The results are compared with the previous available values (Molina et al., 1982; Robbins, 1976). Disagreements up to 20% are observed between our set of measurements and the values proposed by Molina et al., (1982), the latter being lower than ours mainly in the region of high absorption.

Absorption cross-section 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 shown, with a decrease of absorption cross-sections in the region of low absorptions (up to 80% at 310 nm and 210 K) and an increase (up to 20% at 210 K) near the maximum of absorption.

OZONE IN THE ATMOSPHERE
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TABLE 1. : PRESSURE RANGES FOR ABSORPTION CROSS-SECTIONS MEASUREMENTS.

Compound \ Temp. (K)	PRESSURE (torr) 295 K	255 K	210 K
CF_3Br (*)	722 - 6×10^{-1}	597 - 6×10^{-1}	384.6 - 2×10^{-2}
CF_2Br_2 (*)	234 - 3×10^{-2}	67 - 1×10^{-1}	3.4 - 2×10^{-2}
CF_2BrCl (*)	453 - 1×10^{-1}	80 - 8×10^{-2}	10.3 - 9×10^{-2}
CH_3Br (**)	22 - 4×10^{-2}	19 - 7×10^{-2}	9.6 - 9×10^{-2}
CH_2Br_2	36 - 4×10^{-2}	1 - 5×10^{-2}	
$C_2F_4Br_4$	80 - 2×10^{-2}	67 - 5×10^{-2}	11.2 - 2×10^{-2}
C_2F_3HBrCl	147 - 4×10^{-2}	20 - 4×10^{-2}	9×10^{-1}-4×10^{-2}

(*) : Gillotay and Simon, 1988a.
(**) : Gillotay and Simon, 1988b.

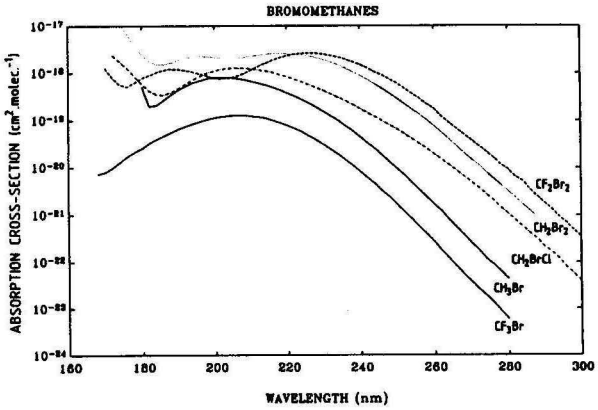

Fig. 1. Ultraviolet absorption cross-sections of bromomethanes with respect to wavelength at 295 K.

TABLE 2. ABSORPTION CROSS-SECTIONS [$\sigma(\lambda) \times 10^{21}$ (cm^2 molec.$^{-1}$)] OF CH_3Br (Gillotay and Simon, 1988b)

λ(nm)	295K	270K	250K	230K	210K
180	500	500	500	500	500
182	198	198	198	198	198
184	208	208	208	208	208
186	271	271	271	271	271
188	346	346	346	346	346
190	439	439	439	439	439
192	529	529	529	529	529
194	620	620	620	620	620
196	691	691	691	691	691
198	760	760	760	760	760
200	791	791	791	791	791
202	797	797	797	797	797
204	793	793	793	793	793
206	767	767	767	767	767
208	727	727	727	727	727
210	666	666	666	666	666
212	614	613	613	613	613
214	557	557	556	556	556
216	493	493	492	492	492
218	440	438	436	434	432
220	378	374	372	369	367
222	325	321	318	316	313
224	278	273	268	264	260
226	231	226	222	218	214
228	190	187	184	181	179
230	155	152	149	147	144
232	125	122	120	117	115
234	99.2	96.1	93.7	91.3	89.0
236	77.3	74.2	71.7	69.3	67.1
238	59.7	56.6	54.3	52.0	49.9
240	44.6	42.7	41.0	39.4	37.9
242	33.3	31.6	30.2	28.9	27.7
244	25.1	23.3	22.0	20.8	19.6
246	18.2	16.9	15.9	15.0	14.1
248	13.0	12.0	11.2	10.5	9.81
250	9.57	8.65	7.98	7.37	6.80
252	6.89	6.09	5.52	5.01	4.54
254	4.83	4.26	3.85	3.48	3.14
256	3.39	2.93	2.61	2.32	2.07
258	2.40	2.02	1.75	1.52	1.32
260	1.70	1.43	1.24	1.07	0.932
262	1.23	0.946	0.800	0.678	0.573
264	0.810	0.638	0.529	0.439	0.364
266	0.557	0.429	0.348	0.282	0.229
268	0.384	0.287	0.227	0.180	0.142
270	0.255	0.191	0.147	0.114	0.0875
272	0.183	0.127	0.0953	0.0713	0.0533
274	0.118	0.0847	0.0614	0.0444	0.0322
276	0.0880	0.0567	0.0394	0.0275	0.0193
278	0.0616	0.0375	0.0253	0.0170	0.0114
280	0.0434	0.0251	0.0162	0.0104	0.00672

TABLE 3. ABSORPTION CROSS-SECTIONS [$\sigma(\lambda) \times 10^{21}$ (cm^2 molec.$^{-1}$)] OF CH_2Br_2

λ(nm)	295K	270K	250K	230K	210K
174	11709				
176	6624	6352	6143	5940	5744
178	3772	3594	3458	3326	3200
180	2410	2331	2270	2211	2153
182	1784	1714	1660	1608	1557
184	1544	1469	1412	1357	1303
186	1535	1487	1450	1414	1379
188	1661	1646	1634	1623	1611
190	1870	1879	1887	1894	1902
192	2093	2115	2133	2151	2170
194	2225	2270	2306	2343	2381
196	2283	2322	2354	2387	2419
198	2260	2291	2317	2342	2368
200	2201	2209	2216	2223	2230
202	2143	2133	2126	2119	2111
204	2101	2087	2075	2064	2052
206	2112	2101	2092	2084	2075
208	2175	2186	2195	2205	2214
210	2269	2307	2339	2370	2402
212	2428	2530	2614	2702	2792
214	2548	2706	2839	2979	3126
216	2622	2825	2998	3182	3377
218	2647	2879	3080	3294	3524
220	2621	2868	3082	3311	3558
222	2547	2792	3005	3234	3481
224	2430	2659	2859	3073	3304
226	2276	2479	2656	2844	3046
228	2094	2264	2411	2566	2732
230	1893	2026	2140	2261	2388
232	1682	1779	1861	1946	2035
234	1470	1533	1585	1639	1695
236	1264	1297	1324	1352	1380
238	1070	1079	1086	1094	1101
240	892	883	876	868	861
242	733	711	694	678	662
244	594	565	542	521	500
246	475	442	417	394	372
248	375	342	317	294	273
250	293	261	238	217	197
252	226	197	176	158	141
254	172	147	129	114	100
256	130	109	93.9	81.2	70.1
258	97.8	79.7	67.7	57.5	48.8
260	72.7	58.0	48.5	40.5	33.8
262	53.7	42.0	34.5	28.3	23.2
264	39.4	30.2	24.4	19.7	15.9
266	28.8	21.6	17.2	13.7	10.9
268	20.9	15.4	12.1	9.47	7.42
270	15.2	11.0	8.46	6.55	5.06
272	11.0	7.81	5.95	4.53	3.45
274	7.93	5.55	4.17	3.14	2.36
276	5.73	3.95	2.93	2.18	1.62
278	4.15	2.82	2.07	1.52	1.12
280	3.01	2.02	1.47	1.07	0.773
282	2.19	1.45	1.04	0.750	0.539
284	1.60	1.05	0.747	0.532	0.379
286	1.18	0.764	0.540	0.381	0.269
288	0.877	0.562	0.393	0.275	0.193
290	0.656	0.416	0.290	0.201	0.140

TABLE 4. ABSORPTION CROSS-SECTIONS [$\sigma(\lambda) \times 10^{21}$ (cm^2 molec.$^{-1}$)] OF CF_3Br (Gillotay et al., 1988a)

λ(nm)	295 K	270K	250K	230K	210K
168	5.17	5.09	5.04	4.98	4.93
170	6.96	6.89	6.84	6.79	6.73
172	9.28	9.24	9.21	9.17	9.14
174	12.2	12.3	12.3	12.3	12.3
176	16.0	16.1	16.2	16.3	16.4
178	20.5	20.8	21.1	21.3	21.6
180	26.1	26.6	27.1	27.5	28.0
182	32.6	33.5	34.3	35.0	35.8
184	40.2	41.6	42.7	43.9	45.1
186	48.8	50.8	52.4	54.1	55.9
188	58.2	60.9	63.2	65.5	67.9
190	68.4	71.9	74.8	77.8	81.0
192	78.8	83.2	86.9	90.7	94.7
194	89.3	94.6	99.0	104	108
196	99.4	105	110	116	121
198	109	115	121	127	133
200	116	123	129	136	142
202	122	130	136	142	149
204	126	133	139	146	152
206	128	134	140	146	152
208	127	132	137	142	148
210	123	128	132	136	140
212	117	121	124	127	130
214	110	112	114	116	118
216	101	102	102	103	104
218	90.6	90.3	90.1	89.9	89.7
220	79.9	78.6	77.6	76.6	75.6
222	69.2	67.1	65.4	63.8	62.3
224	58.8	56.1	54.1	52.1	50.1
226	49.1	46.1	43.8	41.6	39.5
228	40.3	37.1	34.7	32.5	30.5
230	32.4	29.3	27.0	25.0	23.0
232	25.7	22.8	20.7	18.8	17.1
234	20.0	17.4	15.6	13.9	12.4
236	15.3	13.1	11.5	10.1	8.88
238	11.6	9.66	8.35	7.22	6.24
240	8.62	7.04	5.98	5.09	4.33
242	6.33	5.06	4.23	3.54	2.96
244	4.59	3.59	2.95	2.43	2.00
246	3.28	2.52	2.04	1.65	1.33
248	2.32	1.75	1.39	1.11	0.881
250	1.63	1.20	0.941	0.738	0.579
252	1.13	0.818	0.632	0.489	0.378
254	0.777	0.554	0.422	0.322	0.246
256	0.530	0.373	0.281	0.212	0.160
258	0.360	0.250	0.186	0.139	0.104
260	0.243	0.167	0.123	0.0911	0.0674
262	0.164	0.111	0.0817	0.0600	0.0440
264	0.110	0.0742	0.0542	0.0396	0.0290
266	0.0736	0.0496	0.0362	0.0264	0.0192
268	0.0494	0.0333	0.0243	0.0177	0.0129
270	0.0331	0.0225	0.0164	0.0120	0.00882
272	0.0223	0.0153	0.0112	0.00829	0.00611
274	0.0151	0.0105	0.00779	0.00580	0.00432
276	0.0103	0.00725	0.00547	0.00414	0.00313
278	0.00706	0.00509	0.00392	0.00301	0.00232
280	0.00489	0.00363	0.00286	0.00225	0.00177

TABLE 5. ABSORPTION CROSS-SECTIONS [$\sigma(\lambda) \times 10^{21}$ (cm^2 molec.$^{-1}$)] OF CF_2Br_2 (Gillotay et al., 1988a)

λ(nm)	295 K	270 K	250 K	230 K	210 K
170	1245	1108	1000	891	782
172	781	696	629	560	493
174	553	551	550	549	548
176	495	523	546	568	590
178	603	641	671	700	730
180	750	791	824	857	890
182	866	939	997	1058	1114
184	1009	1086	1148	1210	1272
186	1118	1204	1272	1341	1409
188	1180	1262	1327	1392	1458
190	1168	1252	1319	1387	1454
192	1109	1185	1246	1306	1366
194	1022	1085	1135	1185	1235
196	920	973	1016	1058	1100
198	825	869	905	941	976
200	748	792	827	862	898
202	716	758	791	825	858
204	735	778	812	846	880
206	810	853	887	921	955
208	936	989	1033	1078	1119
210	1110	1173	1223	1273	1323
212	1431	1408	1466	1525	1583
214	1586	1670	1738	1806	1873
216	1841	1935	2011	2086	2162
218	2081	2186	2270	2353	2437
220	2281	2394	2482	2577	2676
222	2477	2585	2675	2767	2863
224	2540	2643	2729	2817	2909
226	2545	2640	2718	2800	2883
228	2493	2577	2646	2717	2790
230	2390	2461	2519	2578	2639
232	2246	2302	2347	2394	2442
234	2068	2109	2143	2177	2212
236	1869	1897	1918	1941	1964
238	1659	1674	1686	1698	1710
240	1448	1452	1455	1459	1463
242	1243	1238	1235	1232	1229
244	1050	1039	1031	1023	1015
246	875	860	848	836	825
248	718	701	687	674	661
250	582	564	549	535	521
252	466	447	433	419	406
254	369	351	337	325	312
256	289	272	260	248	237
258	224	209	198	189	178
260	172	159	150	141	132
262	130	119	112	104	97.3
264	98.7	89.6	82.9	76.7	71.0
266	74.0	66.5	61.0	56.0	51.3
268	55.1	48.9	44.5	40.6	36.8
270	40.8	35.9	32.3	29.1	26.3
272	30.1	26.1	23.3	20.8	18.6
274	22.1	18.9	16.7	14.8	13.1
276	16.1	13.7	12.0	10.5	9.17
278	11.7	9.81	8.51	7.38	6.39
280	8.52	7.04	6.04	5.18	4.44
282	6.17	5.03	4.27	3.62	3.08
284	4.47	3.59	3.02	2.53	2.13
286	3.23	2.56	2.13	1.77	1.47
288	2.34	1.83	1.50	1.23	1.01
290	1.69	1.30	1.06	0.856	0.695
292	1.22	0.928	0.744	0.596	0.478
294	0.876	0.663	0.525	0.415	0.329
296	0.645	0.474	0.370	0.290	0.226
298	0.470	0.340	0.262	0.202	0.156
300	0.343	0.244	0.186	0.142	0.108
302	0.252	0.176	0.132	0.0993	0.0746
304	0.185	0.1274	0.0944	0.0699	0.0518

TABLE 6. ABSORPTION CROSS-SECTIONS [$\sigma(\lambda) \times 10^{21}$ (cm^2 molec.$^{-1}$)] OF CF_2BrCl (Gillotay et al. 1988a)

λ(nm)	295 K	270 K	250 K	230 K	210 K
170	3230	3200	3180	3160	3150
172	2342	2300	2265	2250	2227
174	1760	1720	1680	1660	1660
176	1208	1180	1175	1170	1160
178	847	840	834	830	825
180	581	580	579	579	578
182	419	419	418	418	418
184	350	353	356	359	362
186	341	347	353	359	366
188	389	405	420	437	456
190	474	500	524	548	573
192	584	626	666	707	748
194	722	768	816	868	922
196	845	919	974	1020	1078
198	990	1041	1090	1139	1190
200	1197	1244	1284	1324	1366
202	1230	1283	1328	1374	1422
204	1244	1302	1350	1400	1452
206	1239	1299	1350	1402	1457
208	1216	1277	1325	1381	1435
210	1177	1237	1286	1337	1391
212	1124	1180	1227	1276	1326
214	1060	1111	1154	1198	1245
216	986	1032	1070	1110	1151
218	907	947	980	1014	1049
220	824	858	885	914	943
222	741	768	790	813	836
224	659	680	697	714	732
226	580	595	608	620	633
228	505	516	524	533	541
230	436	442	447	452	457
232	373	376	378	380	382
234	316	316	316	316	316
236	266	264	262	260	259
238	222	218	215	212	210
240	183	179	175	172	168
242	150	145	141	136	134
244	123	117	113	109	106
246	99.2	94.0	90.0	86.1	82.5
248	79.7	74.7	70.9	67.3	63.9
250	63.7	59.0	55.5	52.2	49.1
252	50.5	46.2	43.1	40.2	37.5
254	39.8	36.0	33.3	30.7	28.3
256	31.2	27.9	25.5	23.3	21.3
258	24.3	21.4	19.4	17.5	15.9
260	18.8	16.4	14.7	13.1	11.7
262	14.5	12.4	11.0	9.73	8.61
264	11.1	9.39	8.21	7.18	6.28
266	8.46	7.05	6.09	5.26	4.54
268	6.42	5.26	4.49	3.83	3.26
270	4.84	3.90	3.29	2.77	2.33
272	3.63	2.88	2.39	1.99	1.65
274	2.71	2.11	1.73	1.42	1.16
276	2.01	1.54	1.24	1.00	0.810
278	1.48	1.11	0.887	0.706	0.562
280	1.09	0.803	0.629	0.493	0.386
282	0.798	0.576	0.444	0.342	0.264
284	0.579	0.410	0.311	0.236	0.179
286	0.419	0.290	0.216	0.161	0.120
288	0.301	0.204	0.149	0.109	0.0802
290	0.215	0.143	0.103	0.0737	0.0530
292	0.153	0.0990	0.0698	0.4927	0.0348
294	0.108	0.0683	0.0472	0.0327	0.0226
296	0.0761	0.0468	0.0317	0.0215	0.0146
298	0.0532	0.0318	0.0211	0.0140	0.00929
300	0.0369	0.0215	0.0139	0.00905	0.00587
302	0.0255	0.0144	0.00914	0.00579	0.00367

TABLE 7. ABSORPTION CROSS-SECTIONS [$\sigma(\lambda) \times 10^{21}$ (cm^2 molec.$^{-1}$)] OF $C_2F_4Br_2$

λ(nm)	295K	270K	250K	230K	210K
170	509	539	564	590	618
172	564	594	620	646	674
174	623	653	678	705	732
176	685	715	740	765	791
178	751	779	802	826	851
180	818	844	866	888	911
182	886	909	929	949	969
184	953	973	990	1007	1024
186	1018	1035	1048	1062	1076
188	1080	1092	1102	1112	1122
190	1135	1143	1149	1155	1161
192	1184	1186	1188	1190	1192
194	1223	1221	1219	1217	1214
196	1252	1245	1238	1233	1227
198	1269	1257	1247	1237	1228
200	1273	1257	1244	1231	1218
202	1264	1244	1228	1212	1197
204	1241	1218	1200	1182	1165
206	1205	1180	1160	1141	1122
208	1157	1131	1110	1090	1070
210	1099	1072	1051	1030	1010
212	1031	1004	983	963	943
214	957	931	910	890	871
216	877	852	833	814	795
218	795	772	753	735	718
220	712	690	673	657	641
222	630	611	595	580	566
224	551	534	520	506	493
226	477	461	449	437	425
228	408	394	383	372	362
230	345	332	323	314	305
232	288	278	269	261	253
234	239	229	222	215	208
236	195	187	181	175	169
238	158	151	146	140	135
240	127	121	116	111	107
242	101	95.5	91.3	87.4	83.6
244	79.5	74.8	71.2	67.8	64.5
246	62.1	58.0	54.9	52.0	49.2
248	48.1	44.5	41.9	39.4	37.1
250	37.0	33.9	31.6	29.5	27.6
252	28.2	25.6	23.7	21.9	20.3
254	21.4	19.2	17.6	16.1	14.7
256	16.1	14.2	12.9	11.7	10.6
258	12.1	10.5	9.38	8.38	7.49
260	9.04	7.70	6.77	5.96	5.24
262	6.72	5.61	4.85	4.20	3.63
264	4.98	4.06	3.45	2.93	2.49
266	3.69	2.93	2.43	2.02	1.68
268	2.73	2.10	1.71	1.39	1.13
270	2.01	1.50	1.19	0.942	0.745
272	1.49	1.07	0.825	0.634	0.488
274	1.10	0.763	0.569	0.424	0.316
276	0.816	0.542	0.390	0.281	0.203
278	0.607	0.385	0.267	0.185	0.129
280	0.454	0.273	0.182	0.121	0.0809

TABLE 8. ABSORPTION CROSS-SECTIONS [$\sigma(\lambda) \times 10^{21}$ (cm^2 molec.$^{-1}$)] OF CF_3-$CHBrCl$

λ(nm)	295K	270K	250K	230K	210K
170	7026	7014	7005	6996	6987
172	6146	6058	5988	5919	5851
174	4968	4849	4756	4665	4575
176	3798	3682	3592	3504	3418
178	2811	2715	2640	2567	2496
180	2061	1988	1932	1877	1823
182	1533	1481	1441	1401	1363
184	1184	1148	1120	1093	1067
186	971	948	929	912	894
188	866	853	842	832	822
190	906	905	903	902	901
192	985	988	991	994	997
194	1052	1061	1069	1078	1084
196	1105	1120	1132	1145	1157
198	1143	1153	1160	1197	1214
200	1164	1190	1210	1232	1253
202	1169	1199	1223	1247	1272
204	1156	1190	1217	1244	1272
206	1132	1166	1194	1223	1253
208	1092	1127	1156	1186	1216
210	1041	1076	1104	1134	1164
212	981	1014	1042	1070	1099
214	913	945	971	998	1025
216	842	871	894	919	944
218	768	794	815	837	859
220	694	716	734	753	773
222	621	640	655	671	687
224	551	566	579	592	605
226	484	496	508	518	527
228	422	431	439	447	454
230	365	372	377	383	388
232	313	318	321	325	329
234	267	269	272	274	276
236	226	227	228	229	230
238	190	190	190	190	190
240	159	158	157	156	155
242	132	130	129	128	126
244	109	107	105	103	102
246	89.2	86.9	85.1	83.4	81.7
248	72.7	70.4	68.5	66.8	65.0
250	58.9	56.6	54.8	53.1	51.4
252	47.5	45.3	43.6	42.0	40.4
254	38.1	36.1	34.5	33.0	31.6
256	30.4	28.6	27.2	25.8	24.5
258	24.2	22.5	21.2	20.1	18.9
260	19.1	17.6	16.5	15.5	14.6
262	15.0	13.7	12.8	11.9	11.1
264	11.7	10.6	9.85	9.12	8.45
266	9.11	8.21	7.55	6.94	6.38
268	7.05	6.30	5.75	5.26	4.80
270	5.42	4.81	4.36	3.96	3.59
272	4.16	3.65	3.29	2.97	2.68
274	3.17	2.76	2.47	2.21	1.98
276	2.40	2.07	1.85	1.64	1.46
278	1.80	1.55	1.37	1.21	1.07
280	1.35	1.15	1.01	0.892	0.785
282	1.01	0.852	0.746	0.652	0.571
284	0.745	0.627	0.545	0.475	0.413
286	0.548	0.458	0.397	0.344	0.298
288	0.401	0.333	0.287	0.247	0.213
290	0.291	0.240	0.206	0.177	0.152

4. DISCUSSION

Photodissociation coefficients of these molecules have been calculated, neglecting effects of multiple scattering, for given altitude (z), zenith angle (χ) and wavelength interval according to the relations :

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

$$\tau_\lambda(z) = \int_z^\infty [n(O_2)\,\sigma_\lambda(O_2) + n(O_3)\,\sigma_\lambda(O_3) + n(air)\sigma_{scatt}] \sec\chi \, dz \qquad (1)$$

where

z is the altitude,
σ_λ are the absorption cross-sections,
$q_\lambda(z)$ and $q_\lambda(\infty)$ are the solar irradiance at altitude z or extraterrestrial ($z = \infty$),
n is the number of particles per volume unit,
for solar zenith angles of 0° and 60° ($\sec\chi = 1$ and 2),
taking into account the values of $\sigma_\lambda(O_2)$ and $\sigma_\lambda(O_3)$ from WMO and Kockarts (1976), σ_{scatt} from Nicolet (1984) and the values of $q_\lambda(\infty)$ from WMO (1985) and taking into account the actual values of cross-sections corresponding to the temperatures conditions at each altitude. Stratospheric photodissociation coefficients (for altitude ranging from 15 to 50 km) calculated with the temperature dependent absorption cross-sections, are about 15% greater than those calculated with the room temperature values in the 20-35 km region, due to the increase in the absorption cross-sections in the 200 nm region. The photodissociation coefficients of CH_3Br and $C_2F_4Br_2$ seem to be temperature independent. Tropospheric photodissociation coefficients for all these molecules are very low (between 10^{-8} and 10^{-11} sec^{-1}) and are reduced down to 20% of their room temperature values, using the temperature dependent cross- sections values. Therefore, the theoretical tropospheric residence times are increased, and the production of Br radicals in the troposphere by photodissociation of brominated species may be considered as negligible.

In conclusion, this work presents a new set of experimental data on the absorption cross-sections of brommocarbons in atmospheric temperature conditions and also highlights the non negligible temperature dependence for stratospheric studies.

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