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Stratospheric pollution
related ultraviolet radiation phenomena

by

M. ACKERMAN

FOREWORD

This article has been written at the request of the organizers of the Vth International Conference on Vacuum Ultraviolet Radiation Physics which will be held in Montpellier (France) in September 1977. It will be published in "Journal de Physique".

AVANT-PROPOS

Cet article a été écrit à la demande des organisateurs du "Vth International Conference on Vacuum Ultraviolet Radiation Physics" qui aura lieu à Montpellier (France) en septembre 1977. Il sera publié dans le Journal de Physique.

VOORWOORD

Dit artikel werd geschreven op aanvraag van de organisatoren van "Vth International Conference on Vacuum Ultraviolet Radiation Physics" die zal plaats grijpen te Montpellier (Frankrijk) gedurende de maand september 1977. Het zal vervolgens gepubliceerd worden in Journal de Physique.

VORWORT

Diese Arbeit wurde geschrieben auf Verlangen der Organisatoren des "Vth International Conference on Vacuum Ultraviolet Radiation Physics" das in September 1977 in Montpellier (France) stattfinden wird. Sie wird in Journal de Physique heraugegeben werden.

STRATOSPHERIC POLLUTION RELATED ULTRAVIOLET RADIATION PHENOMENA

by

M. ACKERMAN

Abstract

A short review of ultraviolet phenomena related to stratospheric pollution is presented. Its purpose is to highlight major aspects with recent examples. The new data obtained on the solar ultraviolet radiation since seven years are emphasized.

Résumé

Une revue concise des phénomènes ultraviolets qui jouent un rôle dans la pollution stratosphérique est présentée. Son but est de mettre en évidence les aspects principaux par des exemples récents. L'accent est placé sur les nouvelles données obtenues depuis sept ans au sujet du rayonnement ultraviolet solaire.

Samenvatting

Er wordt een kort overzicht gegeven van de ultraviolette verschijnselen die verband houden met de bezoedeling van de stratosfeer. Het is de bedoeling met behulp van recente voorbeelden de voornaamste aspecten van dit probleem in het daglicht te stellen. Een speciale nadruk wordt gelegd op de gedurende de laatste zeven jaren bekomen gegevens in verband met de ultraviolet straling van de zon.

Zusammenfassung

Ein kurzer Uberblick der ultravioletten Phänomenen, die eine Rolle in der Pollution der Stratosphäre spielt, wird vorgestellt. Die wichtigste Punkten werden mit Hilfe frischen Beispiele erklärt. Die Ergebnisse über ultravioletten Sonnenstrahlung, die seit sieben Jahr erreicht wurden, werden klargestellt.

INTRODUCTION

Solar ultraviolet radiation plays a fundamental role in the formation of the stratosphere itself since it leads to the ozone photochemical formation from oxygen molecules dissociated below 242 nm. Ozone in turn maintains the positive stratospheric temperature gradient versus altitude by absorbing solar energy in the ultraviolet in the upper stratosphere and earth energy in the infrared in the lower stratosphere. The combination of these delicate energy transfer processes associated with those related with carbon dioxyde and water vapor leads to the existence of the very characteristic stratospheric layer. This stable layer,not only limits the exchange of matter with the troposphere below but also limits by its ozone content the penetration of ultraviolet solar radiation of wavelengths smaller than 290 nm to the troposphere, down to the ground, protecting living organisms from too harsh radiations.

The spectral distribution of the number of photons available at various altitudes is governed by the atmospheric absorbers : molecular oxygen and ozone itself. The various photochemical processes proceed at various rates depending on the altitude and on the characteristic spectral response of the molecular species involved of which a survey has recently been published by Nicolet (1). The photochemical processes have variable efficiencies depending on wavelength but also on temperature.

At wavelengths larger than 290 nm, Rayleigh scattering and earth albedo effects play a role in the intensity spectral distribution of radiation available for photochemical processes in the troposphere and in the stratosphere, and also at ground level where its effects on living organisms is evident already in the visible range of the solar spectrum from the blue color of the sky.

Eventually ultraviolet radiation is used in the study of the stratosphere itself for remote sensing or in situ determinations of molecular species of which the ultraviolet spectra offer unique opportunities to measure them.

These various aspects of ultraviolet radiation phenomena will be briefly reviewed.

THE SOLAR FLUX

Since the solar ultraviolet radiation is not observable from the ground at wavelengths shorter than 290 nm it has not been determined before the use of large balloons, rockets or satellites. In earlier times aeronomers had to use solar physics data based on observations at longer wavelengths to estimate the ultraviolet solar flux. Solar flux data based on rocket observations and published in 1961 by Detwiler, Garrett, Purcell and Tousey (2) for the wavelength range from 85 nm to 260 nm have been widely used thereafter. Satellite measurements performed by Parkinson and Reeves (3) showed that the flux from 140 nm to 180 nm has been previously overestimated. On the other hand Bonnet obtained evidence from rocket stigmatic spectra (4) for the abrupt change in limb darkening of the sun around 200 nm concurrent with an abrupt intensity change. This was confirmed by solar flux measurements performed from a balloon platform (5) in the 200 nm atmospheric window. This lead in 1971 to the publication of a new listing (6) of solar flux values from 116.3 nm to 730 nm presented in wavelength intervals compatible with the variation with wavelength of oxygen and ozone absorption cross sections.

Much effort has been devoted since five years to the improvement of our knowledge of the solar spectrum which deserves to be taken into account. The various experimental data sets are indicated in table 1. Extensive reviews on solar physics have also appeared (19, 20).

The solar flux values listed in reference 6 and mostly based on various Naval Research Laboratory data except for a narrow region around 200 nm are shown in figure 1 by the solid histogram. Part of them have been updated on the basis of ref. 15 from 137 to 210.5, of ref. 17 from 210.5 to 227.3, of ref. 7 from 227.3 to 307.7 and on ref. 21 from 307.5 to 735.0. The new values are also shown on figure 1 and are presented in table 2 where their ratios to the previous values are also given.

If some differences appear from 300 nm to 200 nm the largest changes occur at smaller wavelengths. It should be kept in mind that here the basic observations (15), which are in general agreement with all relevant work indicated in table 1, were performed selectively on a non-active region of the sun. They are thus likely to represent minimum values.
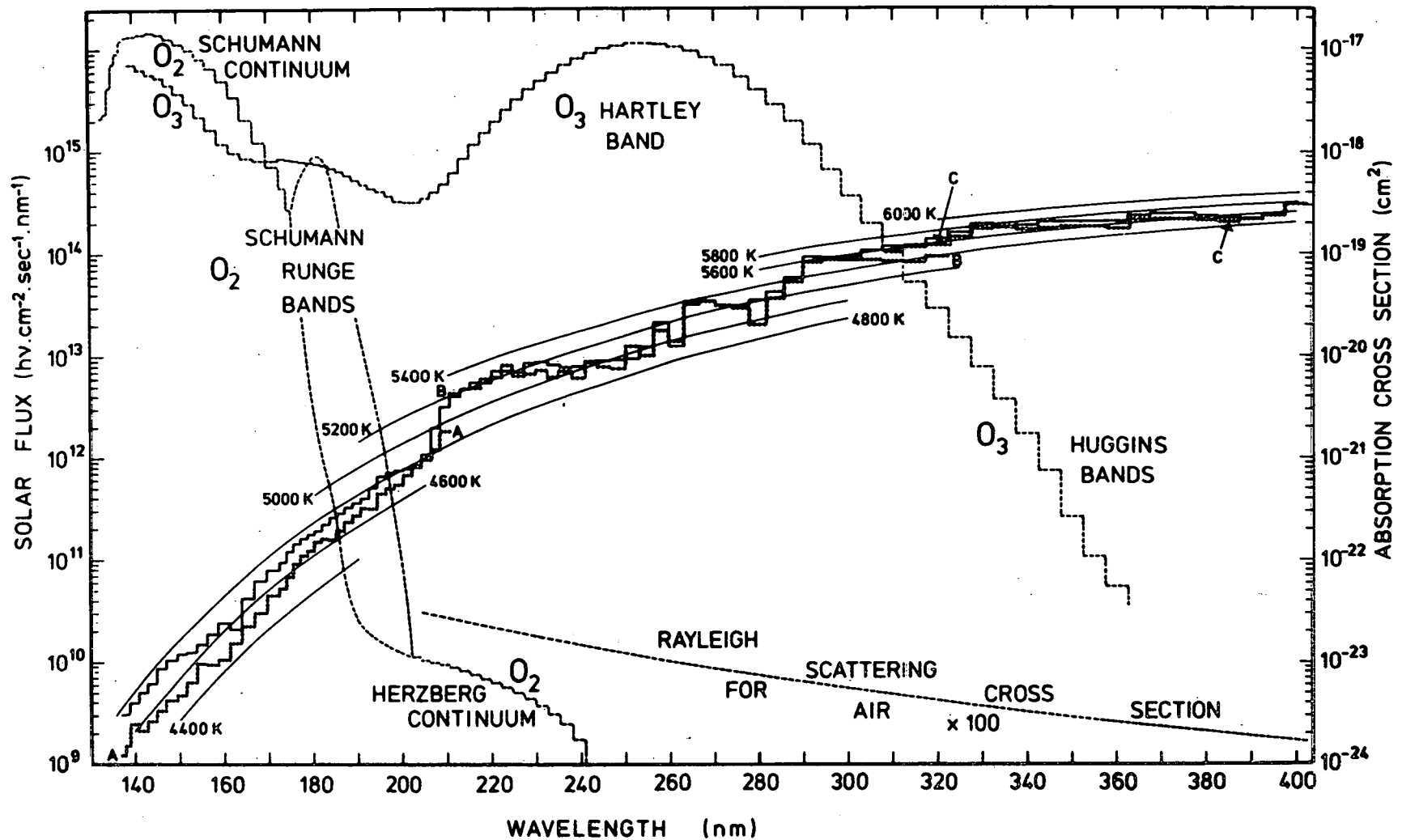
Fig. 1.- Ultraviolet solar flux from 140 nm to 400 nm based on the measurements performed by Kjeldseth Moe *et al* (15), Broadfoot (7) and Arvesen *et al.* (21) which are respectively represented by the dotted histograms marked A, B and C. The measurements made by Simon (17) in the 200 nm atmospheric window and taken into account in table 2 are not represented here for the sake of clarity. The values published by Ackerman in 1971 (6) are represented by the continuous histogram for the sake of comparison. Solar black body temperatures are indicated from 4400 K to 6000 K. The absorption cross sections of O_2 on O_3 are also shown with the Rayleigh scattering cross section for air.

The visible part of the spectrum contributes the most to the solar constant. The last discussion on the subject has been recent by published (22) giving a value equal to 1.972 cal cm^{-2} min^{-1}.

ATTENUATION OF SOLAR RADIATION

Molecular oxygen

The O_2 molecules are attenuating the solar ultraviolet radiation and photodissociate leading to atomic oxygen and subsequently to ozone. Two spectral regions have to be considered in the stratosphere. From the dissociation limit at 242 nm to 200 nm the Herzberg continuum is now rather well known (23, 24, 25) as well as the absorption by O_4 (26). At wavelengths shorter than 200 nm the predissociated lines of the Schumann-Runge bands add some complexity to the atmospheric models due to the large variations of the absorption cross section from the center to the wings of the lines.

The most recent spectroscopic measurements of the bands have been performed in 1970 (27) in absorption and in 1975 in emission in this latter case up to v" levels = 28 have been involved in the observed spectra (28). Several theoretical studies have appeared since then on their fine structure (29), the knowledge of which could still be improved by new high resolution measurements. Their predissociation has been extensively studied (30) and many aspects remain unclear indicating there also the possibilities of new measurements on various isotopic combinations. Very recently, an ab initio vibrational analysis has lead to the conclusion that predissociation of all Schumann-Runge bands from 0-0 to 13-0 as deduced from experimental work (23) could be theoretically explained (31).

The attenuation of solar ultraviolet radiation by O_2 in the S-R bands is of crucial importance for atmospheric modelling since many species are photodissociated in their wavelength range in addition to O_2 itself : NO, H_2O, CO_2, HCl, HNO_3, halocarbons etc. The most accurate procedure to determine the dissociation coefficients is to compute line by line the absorption versus altitude, taking into account, the atmospheric temperature, the

solar elevation angles depending on times of the day, seasons and latitudes. This has been done in a few cases and only for simplified geometries by Kockarts (32) for O_2 and H_2O and by Cieslik and Nicolet (33) for NO. In this latter case where predissociated NO bands interfere with the S-R bands the problem becomes rather heavy to be treated, particularly if the high resolution solar spectrum is considered (16). Due to the complexity of the computations in atmospheric models where chemical kinetics rate constants and air motion have to be dealt with, several authors have attempted to parametrize the attenuation in the S-R bands of atmospheric O_2 (34, 35, 36, 37, 38, 39).

At wavelengths shorter than 175 nm, molecular oxygen absorbs the solar radiation in the thermosphere at altitudes larger than 90 kilometers. At the maximum of the Schumann continuum (about 144 nm) and at the stratopause (50 km) an optical depth about equal to unity is reached over a pathlength of 3 meters.

Ozone

A measurable (40, 41, 42) ozone absorption begins below 360 nm in the ultraviolet. The Huggins bands are followed by the Hartley band below 310 nm with a maximum at 255 nm. A minimum of absorption appears at 202 nm. This broad structure, combined with the absorption by O_2 in the S-R bands leads to the formation of an atmospheric window letting the solar ultraviolet photons to reach the middle stratosphere (30 km) while a unit vertical optical depth occurs at 45 km at 255 nm.

Air

Even if Rayleigh scattering cross sections (43) are small (figure 1), the redistribution of the ultraviolet photons by scattering plays a role on the photochemical processes taking place at wavelengths as short as 200 nm in the atmosphere as well as on the total amount of radiation reaching the ground near 300 nm. In the latter case, if ozone absorption in the Huggins bands is the controlling factor aerosols intervene in the processes. The problem has

been schematically illustrated (16) and has been studied in detail by various authors (44, 45) due to its importance on biological effects of solar ultraviolet radiation reaching the ground.

The earth albedo has also to be taken into account as well as in the evaluation of the photodissociation coefficients of various chemically active molecules when Rayleigh scattering is considered. In this case detailed evaluations are due to several authors (46, 47. 48) and show that the accuracy of model calculations of the stratospheric composition relies on the consideration of scattering effects on the photodissociation of NO_2, O_3, N_2O, HNO_3 etc.

PHOTODISSOCIATION

A basic term in stratospheric photochemical modelling is the photodissociation coefficient j which can be expressed in photon.molecule^{-1} sec^{-1} by

$$ j = q'_z \; \varphi \; \sigma $$

q'_z being the number of solar photon available at one moment and one geographic location per cm^2 and per second at an altitude z, σ the absorption cross section expressed in cm^2 molecule^{-1} and φ the quantum yield for the process under consideration.

The determination of σ implies most of the time to measure the strength of continua. Even if this task does not look very appealing, new measurements often give surprising results since the data usually available have been obtained several decades ago and since the techniques and the availability of very pure substances have been both greatly improved. As an example, recent measurements of the absorption cross section of N_2O (49) have shown that contrarily to the indication by older experiments the molecule does not absorb below 320 nm but below 260 nm. The implication of this observation on the nitrogen cycle is remarkable since photodissociation of nitrous oxyde in the troposphere at 300 nm has been up to now the only sink considered for this molecule.

A more recent example concerns CH_4. Methane was considered to present appreciable absorption at least up to 165 nm while new measurements (50) indicate a cross section value 200 times smaller than previously published at 147 nm with practically no absorption at wavelengths larger than 155 nm. This finding combined with new methane measurements (51) showing a very low abundance of CH_4 in the upper stratosphere indicates that this species is totally under chemical control in the earth atmosphere without any direct action of the solar UV radiation.

Temperature variations of absorption cross section may have some importance when band absorption is under consideration. This aspect is important for the Schumann-Runge bands (23). The NO_2 extinction coefficient is an other example (52). The ozone absorption cross section is also known to vary with temperature (41).

The quantum yield for photodissociation is usually taken equal to unity. However, at the energy threshold of a specific process and particularly when the molecule involved is capable of storing and exchanging appreciable amounts of internal energy within the reaction path, important effects occur. This is the case for the formation of O ^{1}D atoms by photolysis of ozone. In this case the quantum yield can vary from 0.25 to 0.5 at 313 nm over the stratospheric temperature range (53).

The halocarbons, many of which have apparently no sink in the troposphere, are photodissociated in the stratosphere, generating chlorine atoms capable of modifying the ozone balance (54). Such substances absorb UV solar radiation at wavelengths shorter than 300 nm being protected by ozone in the low stratosphere. For many of them the knowledge of the penetration of the solar radiation in the Schumann-Runge bands of O_2 has to be determined and in addition their absorption cross section is sensitive to temperature variations (55).

STRATOSPHERIC SPECIES ANALYSIS IN THE ULTRAVIOLET

Stratospheric atoms and molecules are detected and their abundances measured on the basis of their molecular spectra. Ozone is routinely measured by the method developped by

Dobson and Goetz (see ref. 56 and several articles in the same volume) which is based on differential absorption measurements in the Huggins bands. The observation from satellites take place since several years on the basis of the observation of the backscattered U.V. radiation from 255 to 340 nm (57).

The 306 nm OH band has been used by several groups to measure this radical: by means of a fluorescence chamber dropped from a balloon gondola at 40 km altitude (58) and of lasers operated from an aircraft (59). The total atmospheric content of OH has also been measured from the ground by the observation (60) of the absorption spectrum using the sun as a source. Absorption measurement with a tunable dye laser have also lead to OH determinations in the troposphere (61, 62). Again by excitation and observation of the fluorescence in a falling chamber atomic oxygen has been observed in the stratosphere at the ^3P - ^3S transition à 130.4 nm (63). On the basis of the same atomic resonance fluorescence method, Cl atoms have been observed in the stratosphere at 118.8 nm as well as ClO through the formation of Cl by in situ stimulated reaction with NO (64).

CONCLUSION

It is obvious, even from a non comprehensive review as this one, that much progress has been made in recent years on stratospheric research on the basis of the investigation and of the application of ultraviolet phenomena. The large amount of work devoted to the stratosphere has been largely stimulated by the environmental concerns about the possibility of the artificial modification of the ozone balance. The consciousness of the wealth and of the importance of the natural phenomena occuring in the stratosphere has greatly benefitted from this effort which has also indicated that much remains to be done.

TABLE 1.- Solar ultraviolet measurements published since 1972.

Authors	Wavelengths covered (nm)	Vehicle	Reference
Broadfoot	210 to 320	Rocket	7
Carver et al.	143 to 162	id.	8
Ackerman-Simon	121.6, 145 and 171	id.	9
Nishi et al.	155 to 195	id.	10
Rottman	115 to 195	id.	11
Heroux-Swirbalus	123 to 194	id.	12
Brueckner et al.	175 to 210	id.	13
Samain-Simon	150 to 210	id.	14
Kjeldseth Moe et al.	135 to 210	id.	15
Ackerman	182 and 191	Balloon + Rocket	16
Simon	196 to 230	Balloon	17
DeLuisi	298.1 to 400.0	Ground	18

TABLE II.- Solar flux, q' (137 nm - 730 nm), at one astronomical unit per wavelength intervals and comparison with Ref. 6.

Interval number (Ref. 6)	Wavelength interval (nm)	q' ($h\nu.cm^{-2}.sec^{-1}$)	Ratio q'/q (Ref. 6)
28	137.0 - 137.9	1.09×10^9	0.398
29	137.9 - 138.9	1.51×10^9	0.487
30	138.9 - 140.8	4.69×10^9	0.617
31	140.8 - 142.8	4.20×10^9	0.416
32	142.8 - 144.9	5.49×10^9	0.422
33	144.9 - 147.0	6.97×10^9	0.383
34	147.0 - 149.2	9.33×10^9	0.400
35	149.2 - 151.5	1.08×10^{10}	0.406
36	151.5 - 153.8	1.45×10^{10}	0.500
37	153.8 - 156.2	2.31×10^{10}	0.642
38	156.2 - 158.7	2.38×10^{10}	0.501
39	158.7 - 161.3	2.74×10^{10}	0.428
40	161.3 - 163.9	4.01×10^{10}	0.730
41	163.9 - 166.7	6.39×10^{10}	0.537
42	166.7 - 169.5	8.48×10^{10}	0.482
43	169.5 - 172.4	1.31×10^{11}	0.565
44	172.4 - 173.9	7.83×10^{10}	0.544
45	173.9 - 175.4	1.04×10^{11}	0.568
46	175.4 - 177.0	1.45×10^{11}	0.620
47	177.0 - 178.6	1.75×10^{11}	0.668
48	178.6 - 180.2	1.96×10^{11}	0.681
49	180.2 - 181.8	2.42×10^{11}	0.771
50	181.8 - 183.5	2.75×10^{11}	0.722
51	183.5 - 185.2	2.70×10^{11}	0.609
52	185.2 - 186.9	3.33×10^{11}	0.673
53	186.9 - 188.7	4.29×10^{11}	0.722
54	188.7 - 190.5	4.92×10^{11}	0.752
55	190.5 - 192.3	5.82×10^{11}	0.802

TABLE II.- (continued).

Interval number (Ref. 6)	Wavelength interval (nm)	q' (hν.cm^{-2}.sec^{-1})	Ratio q'/q (Ref. 6)
56	192.3 - 194.2	6.04×10^{11}	0.613
57	194.2 - 196.1	8.38×10^{11}	0.660
58	196.1 - 198.0	9.53×10^{11}	0.686
59	198.0 - 200.0	1.09×10^{12}	0.712
60	200.0 - 202.0	1.37×10^{12}	0.856
61	202.0 - 204.1	1.82×10^{12}	1.046
62	204.1 - 206.2	2.03×10^{12}	0.879
63	206.2 - 208.3	2.54×10^{12}	0.605
64	208.3 - 210.5	4.10×10^{12}	0.562
65	210.5 - 212.8	7.12×10^{12}	0.756
66	212.8 - 215.0	9.23×10^{12}	0.871
67	215.0 - 217.4	8.42×10^{12}	0.628
68	217.4 - 219.8	1.20×10^{13}	0.909
69	219.8 - 222.2	1.22×10^{13}	0.705
70	222.2 - 224.7	1.77×10^{13}	0.983
71	224.7 - 227.3	1.60×10^{13}	0.973
72	227.3 - 229.9	1.77×10^{13}	0.783
73	229.9 - 232.6	1.97×10^{13}	0.821
74	232.6 - 235.3	1.70×10^{13}	0.756
75	235.3 - 238.1	2.00×10^{13}	0.905
76	238.1 - 241.0	1.77×10^{13}	0.763
77	241.0 - 243.9	2.58×10^{13}	1.032
78	243.9 - 246.9	2.35×10^{13}	0.861
79	246.9 - 250.0	2.35×10^{13}	0.816
80	250.0 - 253.2	2.28×10^{13}	0.755
81	253.2 - 256.4	3.24×10^{13}	0.816
82	256.4 - 259.7	5.83×10^{13}	0.818
83	259.7 - 263.2	4.89×10^{13}	1.119
84	263.2 - 266.7	1.19×10^{14}	1.063

TABLE II.- (continued).

Interval number (Ref. 6)	Wavelength interval (nm)	q' (hν.cm^{-2}.sec^{-1})	Ratio q'/q (Ref. 6)
85	266.7 - 270.3	1.27 x 10^{14}	1.016
86	270.3 - 274.0	1.17 x 10^{14}	1.009
87	274.0 - 277.8	1.11 x 10^{14}	0.933
88	277.8 - 281.7	7.85 x 10^{13}	0.569
89	281.7 - 285.7	1.48 x 10^{14}	0.871
90	285.7 - 289.9	2.23 x 10^{14}	0.907
91	289.9 - 294.1	3.43 x 10^{14}	0.879
92	294.1 - 298.5	3.37 x 10^{14}	0.845
93	298.5 - 303.0	3.12 x 10^{14}	0.808
94	303.0 - 307.7	5.08 x 10^{14}	1.000
95	310.0 (± 2.5)	5.15 x 10^{14}	0.870
96	315.0	5.80 x 10^{14}	0.959
97	320.0	6.05 x 10^{14}	0.872
98	325.0	7.30 x 10^{14}	0.899
99	330.0	8.65 x 10^{14}	0.891
100	335.0	8.60 x 10^{14}	0.959
101	340.0	8.56 x 10^{14}	0.907
102	345.0	8.77 x 10^{14}	0.868
103	350.0	9.16 x 10^{14}	0.889
104	355.0	9.11 x 10^{14}	0.885
105	360.0	8.88 x 10^{14}	0.854
106	365.0	1.06 x 10^{15}	0.898
107	370.0	1.07 x 10^{15}	0.870
108	375.0	1.07 x 10^{15}	0.863
109	380.0	1.06 x 10^{15}	0.906
110	385.0	1.02 x 10^{15}	0.919
111	390.0	1.08 x 10^{15}	0.991
112	395.0	1.20 x 10^{15}	1.008
113	400.0	1.55 x 10^{15}	1.006

TABLE II.- (continued).

Interval number (Ref. 6)	Wavelength interval (nm)	q' ($h\nu.cm^{-2}.sec^{-1}$)	Ratio q'/q (Ref. 6)
114	405.0 ($\pm$ 2.5)	1.80×10^{15}	0.947
115	410.0	1.89×10^{15}	0.950
116	415.0	1.96×10^{15}	0.985
117	420.0	1.96×10^{15}	0.970
118	425.0	1.88×10^{15}	0.935
119	430.0	1.81×10^{15}	0.933
120	435.0	1.92×10^{15}	0.970
121	440.0	2.13×10^{15}	0.947
122	445.0	2.25×10^{15}	0.941
123	450.0	2.33×10^{15}	0.940
124	455.0	2.41×10^{15}	0.968
125	460.0	2.44×10^{15}	0.984
126	465.0	2.43×10^{15}	0.972
127	470.0	2.45×10^{15}	0.961
128	475.0	2.52×10^{15}	0.966
129	480.0	2.54×10^{15}	0.981
130	485.0	2.42×10^{15}	0.984
131	490.0	2.42×10^{15}	0.992
132	495.0	2.49×10^{15}	0.984
133	500.0	2.47×10^{15}	0.996
134	505.0	2.50×10^{15}	1.004
135	510.0	2.53×10^{15}	1.012
136	515.0	2.48×10^{15}	1.021
137	520.0	2.42×10^{15}	0.996
138	525.0	2.49×10^{15}	0.988
139	530.0	2.56×10^{15}	0.992
140	535.0	2.57×10^{15}	0.973
141	540.0	2.57×10^{15}	0.963
142	545.0	2.59×10^{15}	0.959

TABLE II.- (continued).

Interval number (Ref. 6)	Wavelength interval (nm)	q' (hν.cm^{-2}.sec^{-1})	Ratio q'/q (Ref. 6)
143	550.0 (± 2.5)	2.61 x 10^{15}	0.974
144	555.0	2.59 x 10^{15}	0.974
145	560.0	2.58 x 10^{15}	0.970
146	565.0	2.62 x 10^{15}	0.981
147	570.0	2.66 x 10^{15}	0.996
148	575.0	2.70 x 10^{15}	1.004
149	580.0	2.75 x 10^{15}	1.015
150	585.0	2.73 x 10^{15}	1.007
151	590.0	2.72 x 10^{15}	1.004
152	595.0	2.71 x 10^{15}	0.996
153	600.0	2.71 x 10^{15}	0.996
154	605.0	2.72 x 10^{15}	1.004
155	610.0	2.74 x 10^{15}	1.015
156	615.0	2.71 x 10^{15}	1.004
157	620.0	2.69 x 10^{15}	0.996
158	625.0	2.69 x 10^{15}	1.000
159	630.0	2.70 x 10^{15}	1.007
160	635.0	2.69 x 10^{15}	1.007
161	640.0	2.69 x 10^{15}	1.011
162	645.0	2.66 x 10^{15}	1.004
163	650.0 (± 5.0)	3.95 x 10^{15}	1.000
164	660.0	5.52 x 10^{15}	1.057
165	670.0	5.33 x 10^{15}	1.029
166	680.0	5.37 x 10^{15}	1.045
167	690.0	5.18 x 10^{15}	1.018
168	700.0	5.29 x 10^{15}	1.050
169	710.0	5.11 x 10^{15}	1.024
170	720.0	5.04 x 10^{15}	1.020
171	730.0	5.03 x 10^{15}	1.027

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