THE SPECTRUM OF DOUBLY IONIZED CARBON, C_{III}

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Abstract

With new experimental data 54 lines of C_{III} have been classified. A large number of these lines involve terms in which both valence electrons are excited. The ionization potential deduced from this classification is 47.7 volts. The classification of a few additional C_{II} lines is also given. These analyses fix the relative position of the singlets and triplets in C_{III} and the doublets and quartets in C_{II}.

The spectrum of carbon was obtained with a vacuum spectrograph using as a source a vacuum spark between graphite electrodes. The electrodes were cut from graphite tubes that had been especially purified by the Acheson Graphite Company for Dr. King of the Mount Wilson Observatory. The particular sample used had been glowed out at a high temperature in the vacuum furnace by Dr. King. This treatment, Dr. King reports, gives material that is spectroscopically pure. The lines arising from the various stages of ionization were differentiated by varying the capacity and self induction in the spark circuit.

Table I. *Triplet lines in* C_{III}.

Int.	λ Vac.	ν	Series designation
0	319.24	313244	$2s2p\,^3P-2s7d\,^3D$
1	327.12	305698	$2s2p\,^3P-2s6d\,^3D$
3	341.14	293135	$2s2p\,^3P-2s5d\,^3D$
4	360.59	277323	$2s2p\,^3P-2p3p\,^3P$
2	363.81	274869	$2s2p\,^3P-2p3p\,^3S$
1	366.15	273112	$(2p)^2\,^3P-2p5d\,^3D$
2	369.40	270709	$2s2p\,^3P-2p3p\,^3D$
5	371.73	269012	$2s2p\,^3P-2s4d\,^3D$
5	389.05*	257036	$2s2p\,^3P-2s4s\,^3S$
0	397.85	251351	$(2p)^2\,^3P-2p4d\,^3P$
3	399.71	250181	$(2p)^2\,^3P-2p4d\,^3D$
7	459.532	217613	$2s2p\,^3P_{1,0}-2s3d\,^3D$
7	459.643	217560	$2s2p\,^3P_2-2s3d\,^3D$
4	493.49	202638	$(2p)^2\,^3P-2p3d\,^3P$
5	499.493	200203	$(2p)^2\,^3P-2p3d\,^3D$
7	538.108	185836	$2s2p\,^3P_{1,0}-2s3s\,^3S$
7	538.318	185764	$2s2p\,^3P_2-2s3s\,^3S$
3	609.00	164204	$(2p)^2\,^3P_{1,0}-2p3s\,^3P_{2,1}$
4	609.29	164125	$(2p)^2\,^3P_{2,1}-2p3s\,^3P_{2,1,0}$
0	818.18	122222	$(2p)^2\,^3P_2-2s3p\,^3P_2$
9	1174.922	85112.0	$2s2p\,^3P_1-(2p)^2\,^3P_2$
8	1175.261	85087.5	$2s2p\,^3P_0-(2p)^2\,^3P_1$
3	1175.577	85064.6	$2s2p\,^3P_1-(2p)^2\,^3P_1$
9	1175.711	85054.9	$2s2p\,^3P_2-(2p)^2\,^3P_2$
8	1175.988	85034.9	$2s2p\,^3P_1-(2p)^2\,^3P_0$
9	1176.359	85008.1	$2s2p\,^3P_2-(2p)^2\,^3P_1$
4	1426.50	70101.6	$2s3d\,^3D-2p3d\,^3P$
4	1427.89	70033.4	$2s3p\,^3P_{1,2}-2p3p\,^3P_2$
2	1428.23	70016.7	$2s3p\,^3P_{1,0}-2p3p\,^3P_1$
2	1428.56	70000.6	$2s3p\,^3P_{2,1}-2p3p\,^3P_{1,0}$
3	1477.70	67672.7	$2s3d\,^3D-2p3d\,^3D_{2,1}$
2	1478.21	67649.4	$2s3d\,^3D-2p3d\,^3D_3$
1	1480.03	67566.2	$2s3p\,^3P-2p3p\,^3S$
3	1576.48	63432.5	$2s3s\,^3S-2p3s\,^3P_2$
2	1577.28	63400.3	$2s3s\,^3S-2p3s\,^3P_1$
2	1577.95	63373.4	$2s3s\,^3S-2p3s\,^3P_0$
4	1619.98	61729.2	$2s3p\,^3P_{1,0}-2s4d\,^3D$
4	1620.62	61704.8	$2s3p\,^3P_2-2s4d\,^3D$
4	1922.98	52002.6	$2s3d\,^3D-2s4f\,^3F$
3	1923.33	51993.2	$2s3d\,^3D-2s4f\,^3F$
3	4648.70	21511.4	$2s3s\,^3S-2s3p\,^3P_2$
2	4651.46	21498.6	$2s3s\,^3S-2s3p\,^3P_1$
1	4652.65	21493.1	$2s3s\,^3S-2s3p\,^3P_0$

I. Analysis of Triplet Lines

A few of the triplet lines of C_{III} were classified by Bowen and Millikan.[1] It has however become evident that the 2297A line identified by them as $(2s)^2\,{}^1S-2s2p\,{}^3P_1$ is too intense to be classified in this way. Fowler and Selwyn[2] have also pointed out that the 1931A line identified as $2s3d\,{}^3D-2s4f\,{}^3F$ is in reality a C_I line and has suggested instead the line at 1923A for this transition.

The triplet lines which have been classified with the aid of the more complete data now available are given in Table I. The term values deduced from them are given in Table II. A surprising fact, that is brought out by this analysis, is the great strength of the lines involving terms in which both valence electrons are excited.

Table II. *Triplet term values in* C_{III}.

$2s3s\,{}^3S$	147896	$2s2p\,{}^3P_0$	333740	$2s3d\,{}^3D$	116100	$2s4f\,{}^3F$	64102
		$2s2p\,{}^3P_1$	333717				
$2s4s\,{}^3S$	76664	$2s2p\,{}^3P_2$	333660	$2s4d\,{}^3D$	64680		
		$2s3p\,{}^3P_0$	126402.9	$2s5d\,{}^3D$	40565		
		$2s3p\,{}^3P_1$	126397.4				
		$2s3p\,{}^3P_2$	126384.6	$2s6d\,{}^3D$	28002		
				$2s7d\,{}^3D$	20456		
		$2p3s\,{}^3P_0$	84523	$(2p)^2\,{}^3P_0$	248682	$2p3d\,{}^3P$	45998
		$2p3s\,{}^3P_1$	84496	$(2p)^2\,{}^3P_1$	248652		
		$2p3s\,{}^3P_2$	84464	$(2p)^2\,{}^3P_2$	248605	$2p3d\,{}^3D_{2,1}$	48427
						$2p3d\,{}^3D_3$	48451
				$2p3p\,{}^3S$	58827		
				$2p3p\,{}^3P_0$	56397		
				$2p3p\,{}^3P_1$	56383	$2p4d\,{}^3P$	−2708
				$2p3p\,{}^3P_2$	56357		
						$2p4d\,{}^3D$	−1538
				$2p3p\,{}^3D$	62991		
						$2p5d\,{}^3D$	−24469

II. Analysis of Singlet Lines

Unfortunately it has not been found possible to obtain as definite and clear cut an identification of many of the singlet lines as might be desired. However since not only the relative positions of the singlet and triplet terms of C_{III} but also the relationship between the terms of different multiplicity in C_{II} and C_I are dependent on the values of the singlet terms it seems wise to

Table III. *Singlet lines in* C_{III}.

Int.	λ Vac.	ν	Series designation	Int.	λ Vac.	ν	Series designation
5	386.20*	258933	$(2s)^2\,{}^1S-2s3p\,{}^1P$	6	1247.391	80167	$2s2p\,{}^1P-(2p)^2\,{}^1S$
2	409.30*	244320	$2s2p\,{}^1P-2s5d\,{}^1D$	2	1308.75*	76409	$(2p)^2\,{}^1S-2s3p\,{}^1P$
3	450.74*	221857	$2s2p\,{}^1P-2s4d\,{}^1D$	2	1531.74*	65285	$2s3p\,{}^1P-2s4d\,{}^1D$
5	574.287*	174129	$2s2p\,{}^1P-2s3d\,{}^1D$	10	2297.59	43524	$2s2p\,{}^1P-(2p)^2\,{}^1D$
2	884.52*	113055	$(2p)^2\,{}^1D-2s3p\,{}^1P$	4	5697.6*	17551.3	$2s3p\,{}^1P-2s3d\,{}^1D$
10	977.031	102351	$(2s)^2\,{}^1S-2s2p\,{}^1P$				

[1] Bowen and Millikan, Phys. Rev. **26,** 310 (1925).

[2] Fowler and Selwyn, Proc. Roy. Soc. **A118,** 40 (1928).

TABLE IV. *Singlet term values in* C_{III}.

$(2s)^2\,{}^1S$	386480	$2s2p\,{}^1P$	284129	$2s3d\,{}^1D$	110000
		$2s3p\,{}^1P$	127551	$2s4d\,{}^1D$	62266
				$2s5d\,{}^1D$	39809
				$(2p)^2\,{}^1S$	203962
				$(2p)^2\,{}^1D$	240605

make available the most probable identifications that can now be made. These lines are given in Table III and the terms fixed by them in Table IV.

Note added June 1, 1931. When the singlet lines were originally classified two possible arrangements of the lines were found. These were identical for the lines caused by transitions between the terms arising from the $(2s)^2$, $2s2p$ and $(2p)^2$ configurations but differed for the lines connecting these terms with higher terms. The first of these arrangements was discarded because of the very anomalous rations that it yielded for the separations between the terms of the $(2p)^2$ configuration of C_{III} and of the $(2p)^3$ configuration of C_{II} as discussed below.

Recently however Bengt Edlén (Nature **127** p. 744, 1931) using the exceedingly efficient grazing incidence spectrograph at Uppsala has been able to obtain these lines in N_{IV} and O_V as well as in C_{III}. The progression to these from the spectra of B_{II} already known, unambiguously shows that in spite of the anomalies mentioned above the first arrangement must be the correct one. The tables of lines and term values have been modified accordingly. All changes in the classification of lines have been marked with an asterisk.

III. ADDITIONAL LINES IN C_{II}

The doublets and quartets have been quite completely analysed by Fowler[3] by Bowen[4] and by Fowler and Selwyn.[5] The new experimental material now available makes it possible to identify a few additional lines that are of importance in fixing the relationships between the doublets and quartets. These lines are given Table V. The identification of the lines caused by

TABLE V. *Additional lines in* C_{II}.

Int.	λ Vac.	ν	Series designation	Int.	λ Vac.	ν	Series designation
1	516.8	193498	$2s(2p)^2\,{}^4P-2s2p6d\,{}^4D$	3	600.39	166558	$2s(2p)^2\,{}^4P-2s2p4s\,{}^4P$
3	531.91	188002	$2s(2p)^2\,{}^4P-2s2p5d\,{}^4P$	4	1065.89	93818.3	$2s(2p)^2\,{}^2D_3-(2p)^3\,{}^2P_2$
				4	1066.14	93796.3	$2s(2p)^2\,{}^2D_2-(2p)^3\,{}^2P_1$
3	532.75	187705	$2s(2p)^2\,{}^4P-2s2p5d\,{}^4D$				
				3	1720.37	58127.0	$2s(2p)^2\,{}^2P_1-(2p)^3\,{}^2P_2$
0	547.27	182725	$2s(2p)^2\,{}^4P-2s2p5s\,{}^4P$	3	1721.01	58105.4	$2s(2p)^2\,{}^2P_1-(2p)^3\,{}^2P_1$
				4	1721.67	58083.1	$2s(2p)^2\,{}^2P_2-(2p)^3\,{}^2P_2$
3	562.51	177775	$2s(2p)^2\,{}^4P-2s2p4d\,{}^4P$	2	1722.24	58063.9	$2s(2p)^2\,{}^2P_2-(2p)^3\,{}^2P_1$
					λ air		
5	564.63	177107	$2s(2p)^2\,{}^4P-2s2p4d\,{}^4D$	2	2885.47*	34646.3	$2s2p3p\,{}^4P_3-2s2p4d\,{}^4D_4$

* From Fowler and Selwyn[5].

[3] Fowler, Proc. Roy. Soc. **A105,** 299 (1924).
[4] Bowen, Phys. Rev. **29,** 231 (1927), and **34,** 534 (1929).
[5] Fowler and Selwyn, Proc. Roy. Soc. **A120,** 312 (1928).

transitions from terms of the $(2p)^3$ configuration, i.e., the ^2P term here fixed and the ^2D determined by Fowler and Selwyn, is very definite as shown by the irregular doublet law relationships indicated in Table IV. The classification of the lines involving the ^4S term of this same configuration is likewise confirmed by irregular doublet law considerations given in a previous paper.[4]

TABLE VI. *Irregular doublet law relationships confirming the identification of $(2p)^3$ configuration of C_{II}.*

$2s(2p)^2\,^2P_2-(2p)^3\,^2P_2$			$2s(2p)^2\,^2P_2-(2p)^3\,^2D_3$		
C_{II}	58083.1		C_{II}	[5]39796.46	
		26337.1			17289
N_{III}	[4]84420.2		N_{III}	[6]57085.7	
		23886			17344
O_{IV}	[4]108306		O_{IV}	74430	
$2s(2p)^2\,^2D_3-(2p)^3\,^2P_2$			$2s(2p)^2\,^2D-(2p)^3\,^2D$		
C_{II}	93818.3		C_{II}	[5] 75531.0	
		35564			26520
N_{III}	[4]129382.3		N_{III}	[6]102051	
		32711			26183
O_{IV}	[4]162093		O_{IV}	128234.1	

The additional quartet combinations here given determine longer series of terms than were available in previous analyses. When these are taken into account it indicates that the quartet term values given by Fowler and Selwyn should be decreased by about 500 cm^{-1}.

IV. Relationships between Terms of Different Multiplicity in C_{III} and C_{II}

As was pointed out above the identification of the singlet lines and in particular the higher series members on which the determination of series limits depends is rather uncertain. For this reason it is particularly important to obtain confirmatory evidence of the general correctness of the term values thus found.

One piece of evidence is found in the arrangement of the terms of the $(2p)^3$ configuration of C_{II}. If the C_{III} singlet terms are correctly fixed then the difference between $(2s)^{2\,1}S$ and $2s2p\,^3P_1$ is 52763 cm^{-1}. Since the known doublet series of C_{II} converge to the $(2s)^{2\,1}S$ term of C_{III} as a limit while the quartet terms are based on the $2s2p\,^3P$ term, the quartet term values should all be decreased by this difference to make them comparable to those of the doublets. When this shift is made, in addition to the correction of 500 cm^{-1} mentioned in the previous section, the ^4S term of the $(2p)^3$ configuration has a term value of 54525. Likewise the doublet identifications mentioned above fix the $^2P_2$ term of this configuration at 27909 while the $^2D_3$ term had previously been determined as 46196. This gives a ratio for $(^2D_3-{}^2P)/(^4S-{}^2D_3)=2.196$ as compared with 0.509 for the $(2s)^2(2p)^3$ configuration of O_{II} and 0.500 for N_I and 0.651 for S_{II}.

Similarly if we consider C_{III} directly and assume the correctness of the classification of the 2297A line and the 1247A line we find the ratio $(^1D-{}^1S)/(^3P_2-{}^1D)=4.580$ for the terms of the $(2p)^2$ configuration. This compares with 1.148 for the $(2s)^2(2p)^2$ configuration of O_{III} and 1.144 for N_{II}.

[6] Freeman, Proc. Roy. Soc. **A121**, 318 (1928).

As there are theoretical reasons for expecting these ratios to remain approximately constant it seems very unusual to find so anomalous values for these ratios in carbon. However the progressions found by Edlen are so convincing that it does not seem possible to arrive at any other values.

This fixes the ionization potential of C_{III} at 47.7 volts. The resonance potential of C_{III} is fixed at 6.51 volts with the resonance line $(2s)^2\,{}^1S-2s2p\,{}^3P_1$ occurring at $\nu=52763$ cm^{-1} or $\lambda=1895$A. Since the transition probability of this line is very small it should appear very faintly if at all. This coupled with the very large uncertainty in position will make it very difficult to locate. Similarly the resonance potential of C_{II} comes out of 5.32 volts and the resonance lines i.e. $(2s)^2 2p\,{}^2P-2s(2p)^2\,{}^4P$ should appear at $\nu=43111$ cm^{-1} or $\lambda=2320$A. Again the lines will be very faint and the positions uncertain.