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The ^{5}S State of Carbon

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The ^{5}S state of carbon is important in thermo-chemical theory, and its position has been the subject of much speculation. Evidence is here given that it is 33735.2 cm^{-1} above the ground state ^{3}P and combines with it to emit two lines at λ2965 and 2967.

In the theory of the chemical binding energies of carbon compounds, the sp^3 ^{5}S state of the carbon atom plays a large part. Because the tetravalent condition of carbon is ascribed to that state, the excitation energy of ^{5}S enters intimately into the calculations of the carbon-bond energies derived from observed reaction energies and from band spectra and, perhaps more important, it has been thought to be involved in the derivation of the heat of sublimation of carbon. This whole field has recently been discussed by Long and Norrish[1] in a paper on *The Thermochemistry of Carbon*, from which it is clear that there is serious disagreement on the value of ^{5}S between various workers in the field.

It is recognized that the well-developed theory of iso-electronic sequences has given quite accurate predictions of the positions of such terms as this ^{5}S. Using the means so provided, Edlen[2] predicted that ^{5}S should be about 32900 cm^{-1} above the ground state s^2p^2 ^{3}P of carbon. Bacher and Goudsmit[3] calculated 35,000 from a wave-mechanical theory, and Ufford,[4] also from the wave-mechanics, predicted 22,000 to 26,000. The value favored by Long and Norrish from the chemical data is in the range given by Ufford's theory and so falls considerably below the theoretical value of Bacher and Goudsmit and the extrapolation of Edlen. There is no doubt that Edlen's value would appeal to most spectroscopists because no radical exceptions have ever been found to the rules of iso-electronic sequences. It appears to have been assumed by spectroscopists, however, that the observations of the spectrum of the carbon arc made by Paschen and Kruger[5] were so complete that there was no hope of finding the absolute value of ^{5}S by actually observing its spectroscopic combinations.

Before the war when I was working on spectra which extend into the fluorite region, I found that there is in the literature a great lack of data on arc spectra in that region. This is due to the fact that most of the observations have been made with vacuum sources, which are notoriously poor emitters of arc lines. For that reason I had adopted the type of arc source first used by Selwyn,[6] and I had photographed with it the arcs of Cu, Ag, Au, Fe, Ni, Pt, and several other metals in nitrogen for myself and for Dr. Meggers at the Bureau of Standards. In those spectra the nitrogen lines always appeared, and, when carbon electrodes were used, the carbon arc and first

TABLE I.

λ(*A*)	Int.	ν(cm^{-1})	Δν	Assignment
1431.597	20	69852.1		$2s2p^3\,{}^5S_2-2s2p^23s\,{}^5P_3$
			24.8	
1432.105	15	69827.3		${}^5S_2-\quad{}^5P_2$
			20.7	
1432.530	10	69806.6		${}^5S_2-\quad{}^5P_1$

TABLE II. Evidence for correctness of assignment in Table I.

	Regular doublet law			$(\nu-RN^25/36)\times10^{-3}$	
	$\Delta\nu$	$(\Delta\nu)^{\frac{1}{4}}$	Diff.		Diff.
C *I*	45.5	2.695		54.61	
			.759		43.36
N *II*	126.6	3.354		97.97	
			.757		43.40
O *III*	285.6	4.111		141.37	
			.752		43.55
F *IV*	559.4	4.863		184.92	

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[1] L. H. Long and R. G. W. Norrish, Proc. Roy. Soc. **187A**, 337 (1946).

[2] B. Edlen, Nova Acta Regiae Soc. Sc. Upsala IV, **9**, No. 6 (1934).

[3] R. F. Bacher and S. Goudsmit, Phys. Rev. **46**, 948 (1934).

[4] C. W. Ufford, Phys. Rev. **53**, 569 (1938).

[5] F. Paschen and G. Kruger, Ann. d. Physik **5**, **7**, 1 (1930).

[6] E. W. H. Selwyn, Proc. Phys. Soc. **41**, 392 (1929); A. G. Shenstone, Trans. Roy. Soc. **A237**, 453 (1938).

TABLE III. Wave-lengths of multiplet at λ1656.

$\lambda(A)$	Int.	$\nu(\mathrm{cm}^{-1})$	$\Delta\nu$
1656.255	5	60377.18	27.08
1656.918	3	60353.02	
1656.998	10	60350.10	
1657.368	2	60336.63	27.11
1657.891	4	60317.60	
1658.113	5	60309.52	

TABLE IV. Wave-lengths and assignment of lines.

$\lambda(A)$	Int.	$\nu(\mathrm{cm}^{-1})$	Assignment
2964.846	2	33718.74	$2p^3P_1-2p'\,^5S_2$
		$\Delta\nu=27.02$	
2967.224	5	33691.72	$2p^3P_2-2p'\,^5S_2$
2582.901	5	38704.58	$2p^1S_0-3s^3P_1$

spark lines were observed. In the latter case there was always in addition a group of three lines at λ1432 which definitely associated themselves in character with the carbon lines and yet did not appear in any published wave-length lists. Their separations and position were incompatible with any unknown but predictable transition in C *I* or C *II*, except that from $2s2p^23s\,^5P$ down to $2s2p^3\,^5S$. Because I had many other spectra in hand and I knew of Professor B. Edlen's interest in the light atoms, I sent him these data in 1939 to use as he wished. He recently published the material given in Table I in Nature[7] and gave the following evidence for the correctness of my assignment of origin in Table II. The data in Tables I and II differ slightly from those originally given to Edlen because more recent measures have been included.

From the comparison with other spectra in the same iso-electronic sequence and from general familiarity with spectral relations, he estimated the position of the $sp^3\,^5S$ above the ground state at about 32,700±2 percent cm^{-1}. This prediction was questioned by Long and Norrish on the grounds that the evidence was insufficient and that the value was incompatible with the known thermochemical energy relations of carbon. It therefore seemed important to fix the position of the ^5S term definitely, by finding, if possible, the lines corresponding to the transition $s^2p^2\,^3P-sp^3\,^5S$. There should be two such lines with a separation corresponding to the separation $s^2p^2(^3P_1-^3P_2)$, those being the components of ^3P with which $^5S_2$ can combine without violation of the ΔJ rule. This separation is given in the literature as 27.5 cm^{-1} from measurements of unresolved multiplets in the Schumann region. I have recently obtained photographs of the $s^2p^2\,^3P-s^2ps\,^3P$ multiplet at λ1656 completely resolved, and I have made many measurements of the differences. Because of the scarcity of accurate standards, the wave-lengths may be in error by as much as ±0.02A but the differences should be much better, perhaps only ±0.002A. From these measurements I find the intervals to be:

$$s^2p^2\,^3P_{2,1,0}\quad 27.1 \text{ and } 16.4\pm0.1\ \mathrm{cm}^{-1},$$
$$sp^2s\,^3P_{2,1,0}\quad 40.6 \text{ and } 19.0\pm0.1\ \mathrm{cm}^{-1}.$$

The wave-lengths are given in Table III. The

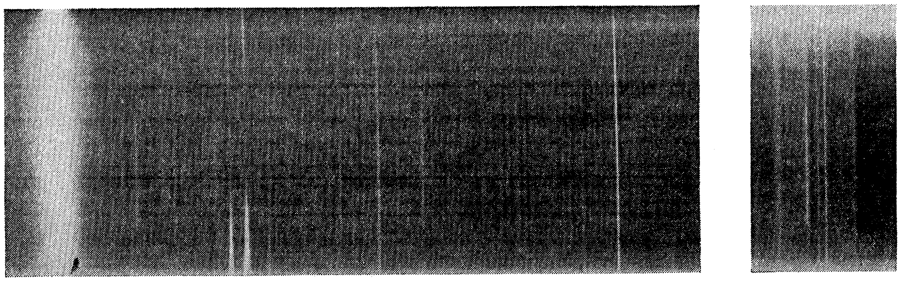

FIG. 1. Carbon arc in argon.
1. C *I* λ2479 $2p^1S_0-3s^1P_1$.
2. C *II* λ2509–12.
3. C *I* λ2583 $2p^1S_0-3s^3P_1$.
4. C *I* λ2964–7 $2p^3P_{1,2}-2p^1\,^5S_2$.

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[7] B. Edlen, Nature **159**, 129 (January 1947).

transition from the structure $2s2p^3$ to $2s^22p^2$ is of course an allowed one, being from odd to even, but the intensity of the inter-combination ^{3}P$-$^{5}S lines is zero in strict Russell-Saunders coupling. However, with a triplet width as large as 43.5 there is a sufficient departure from Russell-Saunders coupling to make one expect lines of intensity about 10^{-3} or 10^{-4} of the allowed lines.

Believing that the past failure to observe the desired transition was probably due to the very dense band spectrum which appears in the ordinary graphite arc, I tried the arc in nitrogen and in argon. Neither of these eliminates the band spectrum at all completely, but they both have the effect of lowering the temperature of the electrodes. The most obvious difference in the spectra is the almost complete disappearance of the ordinary impurities such as Ca and Mg when N_2 or A is used. This may be associated with the fact that the graphite burns away rapidly in air, more slowly in nitrogen, and scarcely at all in argon. The experimental arrangement was a simple enclosure of the arc in a glass bulb with an open neck toward the spectrograph. The gas was purified of oxygen by passage over hot copper turnings and was allowed to escape from the arc enclosure into the open air. The argon undoubtedly contained a percent or two of nitrogen. The arc was operated at about four amperes without any ballast resistance from a constant current source described elsewhere and was focussed on the spectrograph slit by a quartz-water achromatic lens. The potential across the electrodes was about 40–45 *V* in nitrogen, 55–60 *V* in argon, and 60–62 *V* in air, when the gap was about 3 mm. The rods were spectroscopic graphite ⅛ in. in diameter.

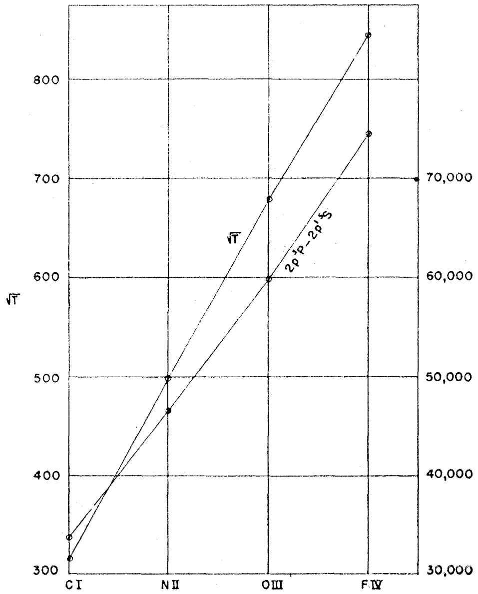


FIG. 2. Plot of $(T)^{\frac{1}{2}}$ and of $2p^3$P$-$$2p^5$S for iso-electronic sequence C *I* to F *IV*.

Figure 1 is a 6× enlargement of two sections of an exposure taken on a medium Hilger quartz spectrograph using an Eastman spectrum-analysis No. 1 plate. The shorter wave-length section exhibits the two known C *I* lines at λ2479 and λ2583, which stretch from one electrode to the other, and the C *II* lines at λ2509–11 which are very strong at the negative pole. The other line which stretches across the arc appears only occasionally. It is mercury λ2536. In the longer wave-length section of Fig. 1 the two marked lines have exactly the characteristics of the other C *I* lines and are the only ones observable on the whole plate which do. They can be photographed faintly in less than a second and then appear practically alone in that region of the spectrum. These two lines and λ2583 have been measured on several plates against copper and iron standards. The best values, obtained from a thirty-five minute exposure on a 21-ft. 30000 line grating, are given in Table IV. The lines at a dispersion of 1.25A per mm appear only slightly wider than the

TABLE V. Revision of term values.

Electron configuration	Name (Edlen's notation)	Value	
$2s^22p^2$	$2p^3P_0$	90880.5	16.4
	$2p^3P_1$	90864.1	27.1
	$2p^3P_2$	90837.0	
$2s^22p^2$	$2p^1S_0$	69232.1	
$2s2p^3$	$2p'\,^5S_2$	57145.3	
$2s^22p3s$	$3s^3P_0$	30546.5	19.0
	$3s^3P_1$	30527.5	40.6
	$3s^3P_2$	30486.9	
$2s2p^23s$	$3s'\,^5P_1$	-12661.3	20.7
	$3s'\,^5P_2$	-12682.0	24.8
	$3s'\,^5P_3$	-12706.8	

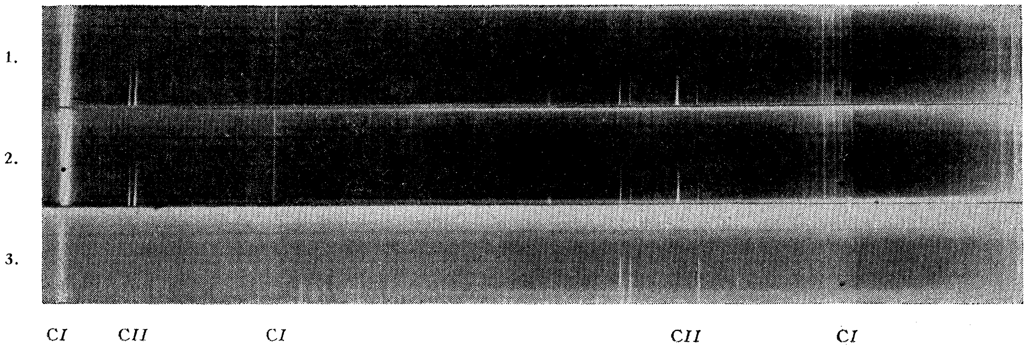


Fig. 3. Carbon arc in (1) argon, (2) nitrogen, and (3) air.

iron comparison lines. The consistency of the measurements indicates an accuracy of ±0.002A.

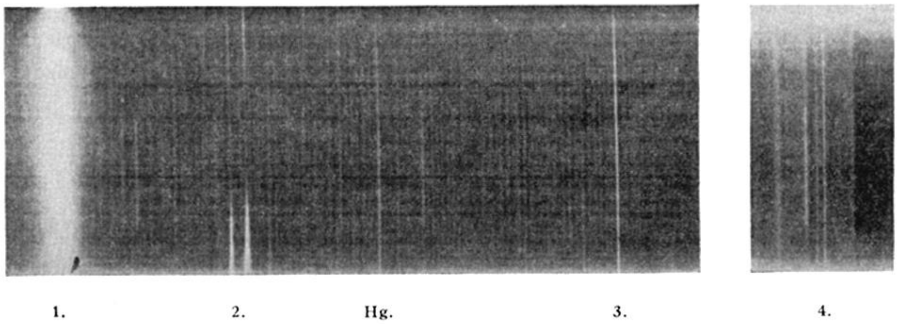
My assignment of the lines at λ2964 and 2967 as $2p^3P-2p'\,^5S$ is substantiated by the following positive evidence and a lack of any contrary evidence.

1. The two lines do not correspond to known lines of any element, and they are not band lines.
2. They are very close to the position predicted by Edlen.
3. They have the same character as other C *I* lines and are the only newly observed lines with such a character.
4. They have a wave-number separation which agrees within the small experimental error with the one found from Schumann region multiplets.
5. They have approximately the relative intensities to be expected in such a transition.
6. They have an absolute intensity of a reasonable order of magnitude, roughly 10^{-3} or 10^{-4} of λ2479.322 $2p^1S_0-3s^1P_1$ and of the same order as λ2583.65 $2p^1S-3s^3P_1$, which is the only other known inter-system line.
7. The plot of $(T)^{\frac{1}{2}}$ for ^5S for the iso-electronic sequence is very nearly a straight line, as is also the plot of $2p^3P-2p'\,^5S$, which illustrates the irregular doublet law. Both plots are given in Fig. 2.

Figure 3 exhibits the difference between arcs in air, nitrogen, and argon, and shows that the identification would have been possible, though with much more difficulty, in an arc in air. The three spectra are of about the same exposure time but the intensity of the air arc is strikingly greater corresponding to its greater visual brilliance. It should be noted that the polar C *II* lines are practically absent in the air arc and that the known C *I* lines are relatively weaker than in the other gases.

The use of the measurements here reported allows the following (Table V) revision of old term values and the addition of the new terms $2p'\,^5S$ and $3s'\,^5P$. This places ^5S at 33735.2 cm^{-1} above the ground state. Its excitation requires 4.16 ev or 96.4 kcal. per mole.

If one defines the resonance lines as those due to the transition to the lowest state from the first excited state of opposite parity, then the new lines here discussed are the resonance lines of carbon. It is odd that they are almost the last important lines of C *I* to be discovered. Their existence implies that ^5S can hardly be considered as a metastable state, and should not, therefore, enter in that role into thermochemical theory.



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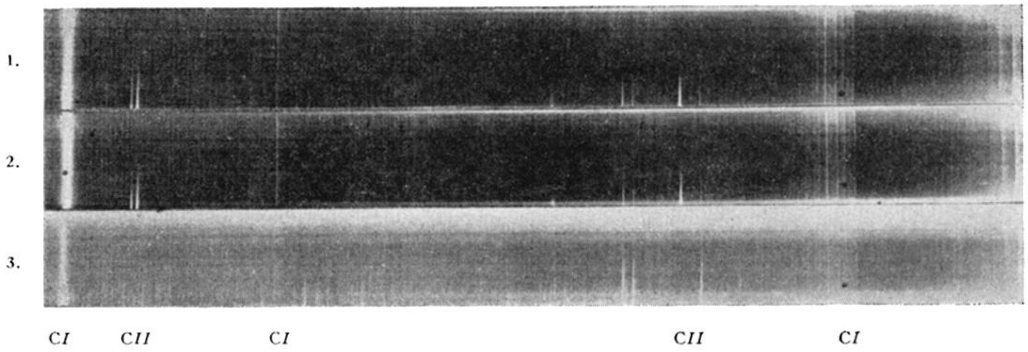

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