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Term Values in Carbon*

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The energies of the terms of the normal state of C I, $1s^2\,2s^2\,2p^2$, and of the excited state, $1s^2\,2s\,2p^3$, are calculated with one-electron functions for a self-consistent field. The effect of the interaction of $1s^2\,2s^2\,2p^2$ and $1s^2\,2p^4$ is also included. Tables are given of the radial integrals, of the absolute energies of the terms, and of the separations of the terms. $1s^2\,2s\,2p^3\;{}^5S$ is found 3.16 volts above the ground state $2p^2\;{}^3P$.

THE energies of the terms of the normal state of C I, $1s^2\,2s^2\,2p^2$, and of the excited state, $1s^2\,2s\,2p^3$, are here calculated from Torrance's[1] values of the one-electron functions for a self-consistent field. The method is that used by Hartree and Black.[2] The values of the radial integrals F, G, and I are given in Table I. The I and F^0 integrals were checked by the method of H and B. The G integrals and F^2 were checked by calculating the difference between pairs of integrals, e.g., excited state minus normal state. Thus let Δ represent the difference of a function obtained by subtracting the function for the normal state from that for the excited state. Then in the notation of H and B,

$$\Delta\rho(\alpha\beta|r)=P_0(\alpha|r)\Delta P_0(\beta|r)+P_0(\beta|r)\Delta P_0(\alpha|r)+\Delta P_0(\alpha|r)\Delta P_0(\beta|r) \qquad (1)$$

and

$$\Delta I_k(\alpha\beta:\gamma\delta)=\int_0^\infty r^{-1}\{\Delta\rho(\alpha\beta|r)\,Y_k(\gamma\delta|r)+[\rho(\alpha\beta|r)+\Delta\rho(\alpha\beta|r)]\Delta Y_k(\gamma\delta|r)\}dr, \qquad (2)$$

where $P_0(\alpha|r)$, $P_0(\beta|r)$, $\rho(\alpha\beta|r)$ and $Y_k(\gamma\delta|r)$ are the functions belonging to the normal state; and $\Delta Y_k(\alpha\beta|r)$ is calculated by replacing $\rho(\alpha\beta|r)$ by $\Delta\rho(\alpha\beta|r)$ in (13) and (14) of H and B. The errors in the integrals computed in this way are given in Table I.

Fried working with Shortley[3] has found $F^2(2p,\,2p)=0.2137$ independently for the normal state by numerical integration of the differential equations given in H and B. This agrees well with the value given in Table I considering the different method used.

The term values were found from the radial integrals by Slater's[4] method. The coefficients of the integrals for $1s^2\,2s^2\,2p^2$ are given in Table IV of H and B. The energies of $1s^2\,2s\,2p^3$ are[5]

$$2I(1s)+I(2s)+3I(2p)+F^0(1s,\,1s)+2F^0(1s,\,2s)+6F^0(1s,\,2p)+3F^0(2s,\,2p)+3F^0(2p,\,2p)-G^0(1s,\,2s)$$
$$-G^1(1s,\,2p)+\left\{\begin{array}{llll} {}^1P & 0 & {}^3P & -\tfrac{2}{3}G^1(2s,\,2p) \\ {}^1D & -\tfrac{6}{25}F^2(2p,\,2p) & {}^3D & -\tfrac{6}{25}F^2(2p,\,2p)\;-\tfrac{2}{3}G^1(2s,\,2p) \\ {}^3S & -\tfrac{15}{25}F^2(2p,\,2p)+\tfrac{1}{3}G^1(2s,\,2p) & {}^5S & -\tfrac{15}{25}F^2(2p,\,2p)-G^1(2s,\,2p) \end{array}\right\}$$

Table II gives the energy values of the terms. The term values are also given when allowance is made for the approximate value of the interaction of $1s^2\,2s^2\,2p^2$ with $1s^2\,2p^4$ as calculated by the method of Hartree and Swirles.[6] Here the integrals used in finding the terms of $1s^2\,2p^4$ are

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* Presented at the Washington meeting of the American Physical Society, April 1937: Phys. Rev. **51**, 1020A (1937). Small errors in the values given there are corrected here.

[1] C. C. Torrance, Phys. Rev. **46**, 388 (1934). I am grateful to Dr. Torrance for letting me have these functions before publication.

[2] D. R. Hartree and M. M. Black, Proc. Roy. Soc. **A139** 311 (1933). This paper will be referred to as H and B. In Table V, p. 331, for O II $2s^2\,2p^3\;{}^4S$ observed, 1.301 should be 1.290 which improves the agreement with the calculations and gives differences varying in the same way as those of O III and O.

[3] I am grateful to Dr. G. H. Shortley for sending me this unpublished result.

[4] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[5] Cf. Condon and Shortley: *Theory of Atomic Spectra* (Cambridge 1935) p. 199. The sign of G_1 in ${}^3S$ should be reversed. Also M. H. Johnson, Jr., Phys. Rev. **39**, 209 (1932).

[6] D. R. Hartree and Bertha Swirles, Proc. Camb. Phil. Soc. **33**, 240 (1937).

TABLE I. *Values of the radial integral I, F and G for* C I.

	NORMAL STATE $1s^2\,2s^2\,2p^2$	ERROR	EXCITED STATE $1s^2\,2s\,2p^3$	ERROR
$I(1s)$	-17.9324	8×10^{-5}	-17.9359	14×10^{-5}
$I(2s)$	$-\ 3.7239$	2	$-\ 3.7381$	5
$I(2p)$	$-\ 3.2430$	28	$-\ 3.2839$	44
$F^0(1s, 1s)$	3.5050		3.5110	
$F^0(1s, 2s)$	0.7666	2	0.7708	1
$F^0(1s, 2p)$	0.7131	3	0.7250	1
$F^0(2s, 2s)$	0.5477		0.5516	
$F^0(2s, 2p)$	0.5134	4	0.5212	4
$F^0(2p, 2p)$	0.4844		0.4954	
$F^2(2p, 2p)$	0.2134	6	0.2197	6
$G^0(1s, 2s)$	0.0412	0	0.0416	0
$G^1(1s, 2p)$	0.0532	21	0.0547	21
$G^1(2s, 2p)$	0.3154	0	0.3217	0

TABLE II. *Absolute term values in* C I. *Atomic units.*

	NORMAL STATE $1s^2\,2s^2\,2p^2$	WITH INTERACTION $1s^2\,2s^2\,2p^2-1s^2\,2p^4$	EXCITED STATE $1s^2\,2s\,2p^3$	
^3P	-37.6599	-37.6756	^5S -37.5590	^3S -37.1301
^1D	-37.6087	-37.6244	^3D -37.3727	^1D -37.1582
^1S	-37.5319	-37.5945	^3P -37.3200	^1P -37.1055

TABLE III. *Term values of* C I. *Wave numbers measured from* $1s^2\,2s^2\,2p\ ^2P_{\frac{1}{2}}$.

		CALCULATED*	WITH INTERACTION* $1s^2\,2s^2\,2p^2-1s^2\,2p^4$	OBSERVED	BACHER AND GOUDSMIT
$1s^2\,2s^2\,2p^2$	^3P	91965	91284	90786	88155
	^1D	80727	80047	80622	77910
	^1S	63872	73485	69167	71431
$1s^2\,2s\,2p^3$	^5S	69820	65694	58000†	55894
	^3D	28931	24805	26727	26053
	^3P	17365	13239	15560	17827
	^1D	−18146	−22272	− 7000†	−14027
	^3S	−24313	−28439	−14984	−24412
	^1P	−29712	−33838	−29000†	−22326

* The absolute positions of the calculated values have been adjusted by least squares to agree with the observed values below the ionization potential. The differences only of the terms are theoretically significant. To determine their absolute position relative to $1s^2\,2s^2\,2p\ ^2P_{\frac{1}{2}}$, the energy of the latter would have to be calculated.

† The observed value of ^5S is estimated by Edlén, reference 7, from the irregular doublet law. The values of ^1D and ^1P are estimated from the irregular doublet law and comparison with O III and N II. No combinations are observed for these levels.

taken from $1s^2\,2s\,2p^3$ instead of from $1s^2\,2s^2\,2p^2$. The separations of the terms together with the observed values of Edlén[7] and the values calculated by Bacher and Goudsmit[8] are given in Table III. The lowest term ^5S of $1s^2\,2s\,2p^3$, which has not been observed. is calculated to be 3.16 volts above the ground state $2p^2\ ^3P$.

It is also interesting to compare these calculations with those of Van Vleck[9] done empirically by the use of Johnson's formulas,[5] and with those of Beardsley[10] who used approximate wave functions. The radial integrals of Table I are not greatly different from those found by Van Vleck and Beardsley. The terms of $2s\,2p^3$ are similar to those obtained by them, except that ^5S falls somewhat higher than the rather low value found by Beardsley.

The interaction of $1s^2\,2s^2\,2p^2$ with $1s^2\,2p^4$ is seen to be in the right direction for all the terms below the ionization potential. The correction introduced is, however, too large except in the case of $2p^2\ ^3P$ and $2s\,2p^3\ ^5S$. It is also too large for the interval ratio in $1s^2\,2s^2\,2p^2$ as was the case in O III[6].

C I: $(^1D-{}^1S)/(^3P-{}^1D)$, Slater 1.50, interaction 0.59, observed 1.13, and Bacher and Goudsmit 0.63.

Interaction also improves slightly the value of the ionization potential of the normal state of C I. Ionization potential: calculated 1019.66 volts, with interaction $1s^2\,2s^2\,2p^2-1s^2\,2p^4$ 1020.09 volts, and observed 1024.84 volts.[7] Were it possible to include the interaction of all configurations, good agreement between theory and experiment might be expected.

I am grateful indeed to Dr. C. C. Torrance who suggested this problem and took an interest in its progress. I am also indebted to the many FERA and NYA students who have helped with the numerical integration.

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[7] B. Edlén, Nova Acta Regiae Societatis Scientiarum Upsaliensis, [IV] **9**, No. 6 (1933); condensed in Zeits. f. Physik **84**, 746 (1933).

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

[9] J. H. Van Vleck, J. Chem. Phys. **2**, 297 (1934).

[10] N. F. Beardsley, Phys. Rev. **39**, 913 (1932).