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A New Band System of Carbon Monoxide ($3\,{}^1S \rightarrow 2\,{}^1P$), with remarks on the Ångström Band System.

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Introduction.

A large number of band spectra have now been discovered and correlated, which are definitely attributable to the CO molecule. It is not proposed to enter in this communication into a general discussion of these, but a summary of the recognised energy levels is given in Table I. Column (1) gives a purely arbitrary designation employed by Birge in referring to them in his papers. Column (3) gives the nature of the electronic levels as at present accepted.

Table I.

Name.	Energy (ν).	Nature.	Name.	Energy (ν).	Nature.
X	0	$1\,{}^1S$	B*	86929	$2\,{}^1S$
	⎧ 48438		C*	91923	$3\,{}^1S$
a*	⎨ to	$2\,{}^5P$?	c	92093	
	⎩ 48534		E*	92923	
a'	58927		F	99730	
A*	64765	$2\,{}^1P$	G	105266	
b*	83825	$2\,{}^5S$?	X'	114966	Ionisation

The following band systems arising from these levels are well known :—

$a \rightarrow X$ Cameron bands.

$A \rightarrow X$ 4th positive carbon bands.

$b \rightarrow a$ 3rd positive carbon bands.

$B \rightarrow A$ Ångström bands.

$c \rightarrow a$ " 3A " bands of Duffendack and Fox.

In point of fact, all the levels which are starred (*) give rise to emission spectra by transitions down to the normal level X, and these have been observed by Hopfield and Birge.† Excepting the Cameron bands they are all, however,

† ' Phys. Rev.,' vol. 29, p. 922 (1927).

in the Schumann region, and being less familiar have not been given special names. The four levels a', E, F, and G, were found first in absorption by Birge and Hopfield and they have only been announced comparatively recently. The level C has been located hitherto as the initial level of a system $C \rightleftarrows X$ found in both emission and absorption in the Schumann region, and its nature has not been known with any certainty. The purpose of the present communication is to give details of a new band system* from this initial level C to the final level A. This has its final state in common with the Ångström system. Four bands have been observed, (0, 0), (0, 1), (0, 2) and (0, 3), and a fine structure analysis has been made of three of these. From this it is clear that the nature of the initial level is $3\,^1S$, and it has been labelled as such in Table I.

Vibrational Quantum Analysis and Correlation with the Ångström System.

The Ångström bands are due to an electronic transition $2\,^1S \rightarrow 2\,^1P$, and consist of two n'' progressions ($n' = 0$ and 1). Some doubtful bands which have been supposed to constitute a third progression $n' = 2$ are probably part of a different system. The vibrational quantum analysis of the Ångström system is recorded in Table II in the case of those bands for which accurate data are available. Higher members of the two progressions are known but have not been accurately measured under high dispersion. The bands (0, 1), (0, 2), (0, 3) and (1, 1) have been analysed in detail by Hulthén† in work which furnished one of the earliest verifications of the combination principle. The correct assignment of j-values (and here $j = m$), to these bands, is obtained by reducing Hulthén's m-values by half on the old quantum theory, or by 1 on the new quantum theory. The constants of Table II have been re-evaluated by us from Hulthén's data. The fine structure of the (0, 0) and (1, 0) bands was first given by Jassé,‡ but as the data on these bands appeared to be much less extensive than Hulthén's, and as moreover these bands have been alleged to have an abnormal structure, we have obtained new plates in the first order of a 21-foot grating, and the constants of Table II have been evaluated from these. The data for the (0, 4) and (0, 5) bands have also been obtained from a fine structure analysis which we have made from our own plates.

We have obtained four bands of the new CO system, the data of which are given in Table III. Only approximate measurements of the (0, 0) band were

* Asundi, 'Nature,' vol. 123, p. 47 (1929).

† 'Ann. Physik,' vol. 71, p. 41 (1923).

‡ 'C. R.,' vol. 182, p. 692 (1926).

Table II.—Ångström Bands. $(2\,^1S \rightarrow 2\,^1P.)$ $[\nu_0 \text{ (vac.)}\quad \nu_H \text{ (vac.)}\quad \lambda_H \text{ (air).}]$

n' \ n''	0.	1.	2.	3.	4.	5.
0	22171·2 (1489·1) 22162·3 (1487·0) 4510·90	20682·1 (1441·8) 20675·3 (1443·3) 4835·34	19240·3 (1413·1) 19232·0 (1412·1) 5198·22	17827·2 (1377·4) 17819·9 (1376·9) 5610·15	16449·8 (1342·6) 16443·0 (1342·0) 6079·94	15107·2 15100·8 6620·34
1	24253·7 (1489·8) 24243·8 (1487·4) 4123·61	22763·9 22756·4 4393·14				

Table III.—New System. $(3\,^1S \rightarrow 2\,^1P.)$ $[\nu_0 \text{ (vac.)}\quad \nu_{II} \text{ (vac.)}\quad \lambda_H \text{ (air).}]$

n' \ n''	0.	1.	2.	3.
0	⎡27174·7⎤ ⎢27165·8⎥ ⎣3680·05⎦	25686·1 (1442·9) 25678·6 (1443·1) 3893·19	24243·2 (1412·7) 24235·5 (1411·8) 4125·02	22830·5 22823·7 4380·18

possible owing to confusion with one of the so-called spurious bands associated with the third positive carbon system. The constants of the (0, 0) band are therefore values calculated from the (0, 0) Ångström band by addition of $\nu\,5003\cdot5$, which is the interval between the $3\,^1S$ and $2\,^1S$ levels as deduced from the other bands. The fine structure analysis of the (0, 1), (0, 2) and (0, 3) bands has been effected, and details are presented later. It will be found that the combination data obtained from this analysis fully support the evidence of Tables II and III that this new system and the Ångström system have a common final state $2\,^1P$. The fact that the new system has only one progression corresponding to $n' = 0$ is to be expected ; it is similar in this respect to the third positive carbon bands, the 3A bands, etc., and this feature appears to be generally true for the higher electronic levels of molecules.

Three of the bands recorded in Table III were observed by Duffendack and Fox* when investigating the excitation of the spectra of CO by electronic impacts. Their wave-lengths (under low dispersion) were $\lambda\lambda\,3679\cdot5$, $3894\cdot8$ and $4380\cdot1$. On the basis of their general similarity in appearance and behaviour to the Ångström system, these writers criticise the validity of the vibrational quantum analysis of the latter system, which they considered should be

* ' Phys. Rev.,' vol. 65, p. 220 (1927).

modified in some way to include these new bands. There is, however, no doubt of the correctness of the present vibrational analysis of the Ångström system (due originally to Birge).* The above three bands are seen to be the (0, 0), (0, 1) and (0, 3) bands of a distinct system arising from an electronic level $5003 \cdot 5 \nu$ ($= 0 \cdot 62$ volts) above the initial level of the Ångström bands. Fine structure analysis shows this level to be $3\,^1S$. Deslandres' band at $\lambda\,3893$ which Wolter† could not obtain, is undoubtedly the (0, 1) band of this system.

Fine Structure Analysis.

Fine structure data for the (0, 1), (0, 2) and (0, 3) bands have been obtained from two independent sets of plates taken in the first order of a 21-foot grating. These are analysed and recorded in Tables IV, V and VI. The wave-length data are believed to be accurate to within $0 \cdot 01$ A.U. for the stronger lines.

Table IV.—Fine Structure of (0, 1) Band.

Old Q.T. j.	New Q.T. j.	P branch.			Q branch.		R branch.		
		λ_{air}.		ν_{vac}.	λ_{air}.	ν_{vac}.	λ_{air}.		ν_{vac}.
$1\frac{1}{2}$	1	$3892 \cdot 495$	c	$25683 \cdot 2$	—	—	—		—
$2\frac{1}{2}$	2	$92 \cdot 843$	b	$680 \cdot 9$	—	—	$3890 \cdot 10$		$25699 \cdot 0$
$3\frac{1}{2}$	3	$93 \cdot 083$	a	$679 \cdot 3$	$3891 \cdot 34$	$25690 \cdot 8$	$88 \cdot 96$		$706 \cdot 5$
$4\frac{1}{2}$	4	$93 \cdot 186$		$678 \cdot 7$	$90 \cdot 85$	$694 \cdot 1$	—		$(713 \cdot 2)$
$5\frac{1}{2}$	5	$93 \cdot 083$	a	$679 \cdot 3$	$90 \cdot 25$	$698 \cdot 1$	$86 \cdot 748$	d	$721 \cdot 2$
$6\frac{1}{2}$	6	$92 \cdot 843$	b	$680 \cdot 9$	$89 \cdot 52$	$702 \cdot 8$	$85 \cdot 431$		$729 \cdot 9$
$7\frac{1}{2}$	7	$92 \cdot 495$	c	$683 \cdot 2$	$88 \cdot 717$	$708 \cdot 2$	$84 \cdot 013$		$739 \cdot 3$
$8\frac{1}{2}$	8	$92 \cdot 084$		$685 \cdot 9$	$87 \cdot 806$	$714 \cdot 2$	$82 \cdot 514$		$749 \cdot 3$
$9\frac{1}{2}$	9	$91 \cdot 503$		$689 \cdot 8$	$86 \cdot 748$	d $721 \cdot 2$	$80 \cdot 91$		$759 \cdot 9$
$10\frac{1}{2}$	10	—		—	$85 \cdot 63$	$728 \cdot 6$	$79 \cdot 19$		$771 \cdot 3$
$11\frac{1}{2}$	11	—		—	$84 \cdot 394$	$736 \cdot 7$	$77 \cdot 377$		$783 \cdot 4$
$12\frac{1}{2}$	12	$89 \cdot 252$		$704 \cdot 6$	$83 \cdot 06$	$745 \cdot 6$	$75 \cdot 46$		$796 \cdot 1$
$13\frac{1}{2}$	13	$88 \cdot 264$		$711 \cdot 2$	$81 \cdot 605$	$755 \cdot 3$	$73 \cdot 30$		$810 \cdot 5$
$14\frac{1}{2}$	14	$87 \cdot 190$		$718 \cdot 3$	$80 \cdot 058$	$765 \cdot 5$	$71 \cdot 33$		$823 \cdot 6$
$15\frac{1}{2}$	15	$86 \cdot 007$		$726 \cdot 1$	$78 \cdot 413$	$776 \cdot 5$	$69 \cdot 096$		$838 \cdot 5$
$16\frac{1}{2}$	16	$84 \cdot 730$		$734 \cdot 6$	$76 \cdot 648$	$788 \cdot 2$	—		—
$17\frac{1}{2}$	17	$83 \cdot 28$		$744 \cdot 1$	$74 \cdot 78$	$800 \cdot 7$	—		—
$18\frac{1}{2}$	18	—		—	$72 \cdot 819$	$813 \cdot 7$	—		—
$19\frac{1}{2}$	19	—		—	$70 \cdot 736$	$827 \cdot 6$	—		—
$20\frac{1}{2}$	20	—		—	$68 \cdot 59$	$841 \cdot 9$	—		—

a, b, c, d, are blends of 2 lines.

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Table V.—Fine Structure of (0, 2) Band.

Old Q.T. j.	New Q.T. j.	P branch.		Q branch.		R branch.	
		λ_{air}.	ν_{vac}.	λ_{air}.	ν_{vac}.	λ_{air}.	ν_{vac}.
1½	1	4124·30	a 24240·1	4123·44	*24244·8	4122·11	*24252·6
2½	2	24·61	b 237·9	23·25	* 246·5	21·29	*f 257·4
3½	3	24·885	c 236·3	22·87	* 248·1	20·26	* 263·5
4½	4	24·997	d 235·6	22·33	e 251·3	19·09	270·4
5½	5	24·997	d 235·6	21·69	255·1	17·75	278·3
6½	6	24·885	c 236·3	20·89	259·8	16·33	* 286·6
7½	7	24·61	b 237·9	19·94	265·3	14·75	296·0
8½	8	24·30	a 240·1	18·983	271·0	13·04	306·1
9½	9	23·695	243·3	17·75	278·3	11·19	317·0
10½	10	23·059	247·0	16·45	285·9	09·26	328·4
11½	11	22·33	e 251·4	15·04	* 294·2	07·17	340·8
12½	12	21·29	f* 257·4	13·46	* 303·6	04·95	354·0
13½	13	20·26	* 263·5	11·78	313·5	02·61	367·9
14½	14	19·09	270·4	09·93	324·4	—	—
15½	15	17·82	277·9	07·97	336·1	—	—
16½	16	16·33	* 286·6	05·896	348·4	—	—
17½	17	14·77	295·9	03·66	361·6	—	—

* Confused with fine structure lines of Ångström band λ 4123.
a, b, c, d, e, f, are blends of 2 lines.

Table VI.—Fine Structure of (0, 3) Band.

Old Q.T. j.	New Q.T. j.	P branch.		Q branch.		R branch.	
		λ_{air}.	ν_{vac}.	λ_{air}.	ν_{vac}.	λ_{air}.	ν_{vac}.
1½	1	4379·42	22827·7	4378·71	22831·3	4377·273	c 22838·8
2½	2	79·84	825·3	78·44	832·8	76·19	844·5
3½	3	80·08	a 824·3	77·925	* 835·5	75·02	850·6
4½	4	80·25	b 823·4	77·273	c 838·8	73·59	858·1
5½	5	80·25	b 823·4	76·54	842·6	72·06	866·1
6½	6	80·08	a 824·3	75·57	847·8	70·23	d 875·7
7½	7	79·68	* 826·3	74·485	853·4	68·534	e 884·6
8½	8	79·19	828·9	73·22	860·0	66·60	f 894·7
9½	9	78·50	832·5	71·82	867·6	—	—
10½	10	77·68	836·8	70·23	d 875·7	—	—
11½	11	76·69	841·9	68·534	e 884·6	—	—
12½	12	75·57	847·8	66·60	f 894·7	—	—
13½	13	74·29	854·5	64·61	905·1	—	—
14½	14	72·86	861·9	—	—	—	—

* Confused with lines of the Ångström band λ 4393.
a, b, c, d, e, f, denote blends of 2 lines.

The bands each have three branches of the P, Q and R type, and are precisely similar to the Ångström bands in structure. The lines R $(\frac{1}{2})$ and Q $(\frac{1}{2})$ were not observed, and this is consistent with a $^1S \rightarrow {}^1P$ transition for which $\sigma'' = 1$

and hence for which $j''_{min.} = 1\frac{1}{2}$. (Using the numbering of the new quantum theory R (0) and Q (0) would be the missing lines. Unless otherwise stated we shall employ the numbering of the old quantum theory in the present paper.)

The three branches which theory predicts for a transition of this type are :—

$$
\left.
\begin{aligned}
R\,(j) &= F_B{}'\,(j+1) - F_B{}''\,(j) \\
Q\,(j) &= F_B{}'\,(j) - F_A{}''\,(j) \\
P\,(j) &= F_B{}'\,(j-1) - F_B{}''\,(j)
\end{aligned}
\right\}
\qquad (1)
$$

and the combination principle provides the following relationships :—

$$
\left.
\begin{aligned}
&(a) \quad R\,(j) - Q\,(j) = \Delta_1 F_B{}'\,(j) + [F_A{}''\,(j) - F_B{}''\,(j)] \\
&(b) \quad Q\,(j+1) - P\,(j+1) = \Delta_1 F_B{}'\,(j) - [F_A{}''\,(j+1) - F_B{}''\,(j+1)] \\
&(c) \quad R\,(j) - P\,(j) = \Delta_2 F_B{}'\,(j) \\
&(d) \quad R\,(j) - Q\,(j+1) = F_A{}''\,(j+1) - F_B{}''\,(j) \\
&(e) \quad Q\,(j) - P\,(j+1) = F_B{}''\,(j+1) - F_A{}''\,(j) \\
&(f) \quad R\,(j-1) - P\,(j+1) = \Delta_2 F_B{}''\,(j) \\
&(g) \quad R\,(j) - Q\,(j+1) + Q\,(j-1) - P\,(j) = \Delta_2 F_A{}''\,(j)
\end{aligned}
\right\}
\quad (2)
$$

In general, the quantities (a) and (b) will not be exactly equal, but will exhibit so-called combination defects. The same is true of (d) and (e). In Table VII

Table VII.—Combination Data for the State $3\,^1S$ ($n = 0$).

Old Q.T. j.	$\lambda\,3893\cdot19$ (0, 1).		$\lambda\,4125\cdot02$ (0, 2).		$\lambda\,4380\cdot18$ (0, 3).		Weighted mean value.
	$R(j)$ $-Q(j)$.	$Q(j+1)$ $-P(j+1)$.	$R(j)$ $-Q(j)$.	$Q(j+1)$ $-P(j+1)$.	$R(j)$ $-Q(j)$.	$Q(j+1)$ $-P(j+1)$.	
$\frac{1}{2}$	—	—	—	4·7*	—	3·6	3·6
$1\frac{1}{2}$	—	—	7·8*	8·7*	7·5	7·5	7·5
$2\frac{1}{2}$	—	11·5	10·9*	11·8*	11·7	11·2*	11·6
$3\frac{1}{2}$	15·7	15·4	15·4*	15·7	15·1	15·4	15·5
$4\frac{1}{2}$	19·1	19·4	19·1	19·5	19·3	19·2	19·3
$5\frac{1}{2}$	23·1	23·5	23·2	23·5	23·5	23·5	23·5
$6\frac{1}{2}$	27·1	27·3	26·8	27·4	27·9*	27·1	27·2
$7\frac{1}{2}$	31·1	31·0	30·7	30·9	31·2	31·1	31·1
$8\frac{1}{2}$	35·1	35·3	35·1	35·0	34·7*	35·1	35·1
$9\frac{1}{2}$	38·7	38·8	38·7	38·9	—	38·9	38·8
$10\frac{1}{2}$	42·7	—	42·5	42·8	—	42·7	42·7
$11\frac{1}{2}$	46·7	—	46·6	46·2*	—	46·9	46·7
$12\frac{1}{2}$	50·5	50·7	50·4	50·0*	—	50·6	50·6
$13\frac{1}{2}$	(55·2)*	54·3	54·4	54·0	—	—	54·3
$14\frac{1}{2}$	58·1	58·2	—	58·2	—	—	58·2
$15\frac{1}{2}$	62·0	62·1	—	61·8*	—	—	62·1
$16\frac{1}{2}$	—	66·1	—	65·7	—	—	65·9
$17\frac{1}{2}$	—	69·6	—	—	—	—	69·6

* Unreliable ; arising from lines which are blends.

are given the values of (a) and (b) the combination data for the initial state of the system. It will be noted that no appreciable combination defect appears up to the limit of observations $(j = 17\frac{1}{2})$. This is a feature characteristic of the highly stable CO molecule ; the A and B sub-states of the P levels do not become appreciably separate till quite high values of the rotational quantum number are attained. While this statement is true for the vibrational levels $n = 1, 2, 3, 4$ and 5 of the 2P state, it would appear to need qualification for the state $n = 0$, for which combination defects seem to arise from almost the lowest j-values. This curious result is evident from the data of the (0, 0) Ångström band, as we shall see later.

The procedure adopted to evaluate the molecular constants of the electronic levels from combination data has been as follows. The combination data were expressed by a cubic formula thus :—

$$\Delta_1 F (j) = \alpha + \beta j + \gamma j^2 + \delta j^3, \tag{3}$$

the coefficients α, β, γ, and δ being evaluated by the method of least squares. From this the value of $F (j)$ can at once be written down :—

$$F (j) = \text{constant} + \left(\alpha - \frac{\beta}{2} + \frac{\gamma}{6}\right)j + \frac{1}{2}\left(\beta - \gamma + \frac{\delta}{2}\right)j^2 + \frac{1}{3}\left(\gamma - \frac{3}{2}\delta\right)j^3 + \delta j^4. \tag{4}$$

In the case of the initial state (of a ^{1}S type) we know $F (j)$ should have the form

$$F' (j) = B' (j - \rho)^2 + D' (j - \rho)^4$$
$$= \text{const.} - 2\rho (B' + 2\rho^2 D')j + (B' + 6\rho^2 D')j^2 - 4\rho D' j^3 + D' j^4, \tag{5}$$

where ρ is a " secondary ρ " representing a very small departure from exact half-integral j-values. Comparison of the coefficients of j, j^2 and j^3, in equations (4) and (5), gives the molecular constants B', ρ and D'. The value of D' obtained thus is not usually in agreement with the coefficient of j^4 in (4), but the former value is considered more reliable as being less subject to errors arising from the existence of still higher terms in j. Subsequent to the evaluation of the constants on this basis, a linear form for $\Delta_1 F$ was found to express the combination data to an accuracy well within the limits of error. The constants B' and ρ derived in this way differed slightly from those already obtained on the basis of a cubic equation for $\Delta_1 F$. A linear form was also found to be quite adequate to express the combination data of the initial Ångström level (2 ^{1}S, $n' = 0$) and also that of the four common final levels (2P, $n'' = 0, 1, 2, 3$). The constants B and ρ as deduced on these alternative bases are given in Table X. It will be observed that the values of D obtained

on the assumption of a cubic form for $\Delta_1 F$ are positive in all but one case, an indication that no physical value can be attached to this coefficient. We consider that the values of B and ρ obtained by use of a linear form for $\Delta_1 F$ are the more reliable. On this basis the probable errors of representation of the data are about $0 \cdot 05 \, \nu$ for the $2\,^1P$ state and $0 \cdot 1 \, \nu$ for the ^1S states. The linear representation of the data of Table VII is

$$\Delta_1 F'(j) = 1 \cdot 8837 + 3 \cdot 88638 j$$

giving for the rotational function of the state $(3\,^1S, \; n' = 0)$

$$1 \cdot 94319 \, (j - 0 \cdot 01530)^2, \qquad j = \tfrac{1}{2}, \, 1\tfrac{1}{2}, \, 2\tfrac{1}{2}, \, \ldots .$$

It is interesting to compare these constants with those of the initial state of the Ångström bands $(2\,^1S, \; n = 0)$. For the constant B_0' Hulthén gives $1 \cdot 943$. The slight departure from exact half-integral quantum numbers is, however, not discussed by Hulthén and we have therefore re-evaluated B_0' (and ρ) using his data for the Ångström bands $(0, 1)$, $(0, 2)$ and $(0, 3)$. Here again the combination defect is not apparent up to the limit of observations (near $j = 25\tfrac{1}{2}$), so that $\Delta_1 F'(j) = R(j) - Q(j) = Q(j + 1) - P(j + 1)$. The mean of the six values of $\Delta_1 F'(j)$ thus obtained for each value of j are given in Table VIII. These are expressed by :—

$$\cdot \Delta_1 F'(j) = 2 \cdot 0388 + 3 \cdot 88083 j,$$

giving for the rotational function

$$1 \cdot 94041 \, (j + 0 \cdot 02535)^2.$$

Table VIII.—$\Delta_1 F'(j)$ Values for State $2\,^1S$, $(n = 0)$.

$j.$	$\Delta_1 F'(j).$	$j.$	$\Delta_1 F'(j).$	$j.$	$\Delta_1 F'(j).$	$j.$	$\Delta_1 F'(j).$
$\tfrac{1}{2}$	$3 \cdot 80$	$7\tfrac{1}{2}$	$31 \cdot 10$	$14\tfrac{1}{2}$	$58 \cdot 40$	$20\tfrac{1}{2}$	$81 \cdot 60$
$1\tfrac{1}{2}$	$7 \cdot 80$	$8\tfrac{1}{2}$	$35 \cdot 05$	$15\tfrac{1}{2}$	$62 \cdot 23$	$21\tfrac{1}{2}$	$85 \cdot 40$
$2\tfrac{1}{2}$	$11 \cdot 65$	$9\tfrac{1}{2}$	$38 \cdot 90$	$16\tfrac{1}{2}$	$66 \cdot 13$	$22\tfrac{1}{2}$	$89 \cdot 30$
$3\tfrac{1}{2}$	$15 \cdot 60$	$10\tfrac{1}{2}$	$42 \cdot 80$	$17\tfrac{1}{2}$	$70 \cdot 00$	$23\tfrac{1}{2}$	$93 \cdot 15$
$4\tfrac{1}{2}$	$19 \cdot 54$	$11\tfrac{1}{2}$	$46 \cdot 75$	$18\tfrac{1}{2}$	$73 \cdot 85$	$24\tfrac{1}{2}$	$97 \cdot 05$
$5\tfrac{1}{2}$	$23 \cdot 43$	$12\tfrac{1}{2}$	$50 \cdot 65$	$19\tfrac{1}{2}$	$77 \cdot 80$	$25\tfrac{1}{2}$	$100 \cdot 90$
$6\tfrac{1}{2}$	$27 \cdot 35$	$13\tfrac{1}{2}$	$54 \cdot 50$				

One would have expected the value of B_0 for the $2\,^1S$ state to be somewhat greater than for $3\,^1S$, arising out of a smaller moment of inertia which is consequent upon a closer binding for the former electron. The slight change the other way clearly arises from the change of sign of the small secondary ρ involved in the two cases. The closeness of the values of B_0, and hence of I_0,

for the two ^{1}S states is remarkable—and is indicative of the high stability of the CO molecule. This stability shows itself in several ways, *e.g.*, in the high value of the heat of dissociation, in the large number of vibration quanta which may be associated with the molecule in its normal ($1\,^1$S) state, and in the existence of several band spectra of the ionised molecule. We turn now to the common final electronic state ($2\,^1$P) of both these band systems. The combination data are furnished by Table IX. The two columns for each band give respectively $R(j) - Q(j + 1)$ and $Q(j) - P(j + 1)$. Excepting the state $n = 0$ it will be observed here also that

$$R(j) - Q(j + 1) = Q(j) - P(j + 1)$$

up to about $j = 22\frac{1}{2}$, say. Beyond this point slight combination defects appear giving $Q(j) - P(j + 1) < R(j) - Q(j + 1)$. (See (*d*) and (*e*) of equation (2).) In the case of the (0, 0) and (1, 0) bands such defects appear with the lowest *j*-values, and for purposes of evaluating $\Delta_1 F''(j)$, and hence the constants of the level $n = 0$, the arithmetic mean has been used. The

Table IX.—Combination Data for the $2\,^1$P State.

$(Q(j) - P(j + 1))\quad (R(j) - Q(j + 1))$.

j.	n''= 0.				n''= 1.						n''= 2.				n''= 3.			
	λ4511.		λ4123.		λ3893*.		λ4835.		λ4393.		λ4125*.		λ5198.		λ4380.*		λ5610.	
1½	6·25	6·36	6·12	—	5·0	5·6	5·8	—	6·1	—	6·9	6·1	6·2	6·5	6·0	6·0	6·0	6·2
2½	9·48	9·57	9·57	9·86	9·2	8·2	9·0	9·1	9·2	9·2	10·2	9·3	9·3	9·6	8·5	9·0	9·2	9·2
3½	12·75	12·91	12·93	13·24	12·1	12·4	11·9	12·2	12·3	12·1	12·5	12·2	12·4	12·6	12·1	11·8	12·2	12·3
4½	—	16·0	(15·3)	15·96	15·4	15·1	15·7	15·5	15·4	15·3	15·7	15·3	15·6	15·7	15·4	15·5	15·3	15·4
5½	19·09	19·3	—	19·4	18·8	18·4	18·5	18·6	18·5	19·0	18·8	18·5	18·7	18·8	18·3	18·3	18·4	18·4
6½	21·5	22·5	—	22·2	21·9	21·7	21·9	21·7	21·8	21·7	21·9	21·3	21·8	21·6	21·5	—	21·5	21·5
7½	24·85	25·89	26·0	25·7	25·0	25·1	25·1	24·9	25·1	24·9	25·2	25·0	25·1	25·0	24·5	—	24·5	24·6
8½	28·9	29·6	29·56	29·64	28·3	28·1	28·2	28·2	28·1	28·0	27·7	27·8	28·0	28·0	27·5	—	27·5	27·6
9½	—	31·8	32·4	32·1	31·4	31·3	31·3	31·3	31·4	31·3	31·3	31·1	31·1	31·1	30·8	—	30·7	30·7
10½	—	34·6	—	34·6	—	34·9	34·5	34·5	34·5	34·6	34·5	34·2	34·2	34·2	33·8	—	33·7	33·6
11½	—	—	—	—	—	37·8	37·7	37·7	37·6	37·8	36·8	37·2	37·4	37·3	36·8	—	36·8	36·8
12½	—	—	—	—	41·0	40·8	40·9	40·9	40·8	40·7	40·1	40·5	40·6	40·4	40·2	—	39·9	39·9
13½	—	—	—	—	44·1	—	44·0	44·1	44·5	44·2	43·1	43·5	43·6	43·5	34·2	—	42·9	43·0
14½	—	—	—	—	47·2	47·1	47·2	47·3	47·3	47·2	46·5	—	46·7	46·7	—	—	45·9	46·0
15½	—	—	—	—	50·4	50·3	50·4	50·5	—	50·6	49·5	—	49·7	49·9	—	—	49·0	49·0
16½	—	—	—	—	53·6	—	53·5	53·6	—	53·7	52·5	—	52·6	52·9	—	—	52·0	52·1
17½	—	—	—	—	56·6	—	56·7	56·7	—	—	—	—	55·8	55·9	—	—	55·1	55·1
18½	—	—	—	—	—	—	59·9	59·8	—	—	—	—	59·0	59·5	—	—	58·1	58·2
19½	—	—	—	—	—	—	63·0	62·9	—	—	—	—	61·8	62·1	—	—	61·1	61·2
20½	—	—	—	—	—	—	66·1	66·0	—	—	—	—	65·1	65·0	—	—	64·1	64·3
21½	—	—	—	—	—	—	69·2	69·0	—	—	—	—	68·2	68·3	—	—	67·2	67·3
22½	—	—	—	—	—	—	—	—	—	—	—	—	71·0	71·5	—	—	70·2	70·4
23½	—	—	—	—	—	—	—	—	—	—	—	—	73·9	74·5	—	—	73·1	73·5
24½	—	—	—	—	—	—	—	—	—	—	—	—	—	77·9	—	—	76·2	76·5
25½	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	79·1	79·6

combination data relating to the Ångström bands (0, 1), (1, 1), (0, 2) and (0, 3) are taken from Hulthén's paper. The data for the (0, 0) and (1, 0) bands have been taken from our own plates. We have used these data in preference to those of Jassé for reasons previously given—and incidentally, Jassé's assignment of quantum numbers has been found to be subject to a slight error. Details of this are presented later. Data of the $n'' = 0$ state are not available from the (0, 0) band of the new $3\,^1S \to 2\,^1P$ system, this band being confused with other fine structure work and at present impossible of analysis. The best values of the $\Delta_1 F'' (j)$ data have been taken for each of the four vibrational levels $n'' = 0, 1, 2$ and 3, and these have been subject to the procedure already outlined in the case of data of the $(3\,^1S, n = 0)$ and $(2\,^1S, n = 0)$ levels. Equation (5) is, however, replaced in the case of the $2\,^1P$ level by

$$F'' (j) = B\,[(j - \rho)^2 - 1 + \rho/j]^2 + D\,[(j - \rho)^2 - 1 + \rho/j]^4$$
$$= Dj^4 - 4\rho Dj^3 + (B - 2D + 6\rho^2 D)j^2 - 2\rho\,(B - 3D + 2\rho^2 D)j$$
$$+ \text{constant} + \text{small terms in negative powers of } j,$$

and by comparison of terms in j, j^2 and j^3, the values of B, ρ and D can be evaluated. The data thus obtained are collected in Table X. As in the case of the other levels, the assumption of a linear form for $\Delta_1 F'' (j)$, corresponding to the simpler rotational function $B'' (j - \rho)^2$ was found to express the data adequately. For the four vibrational levels of the $2\,^1P$ state the equations obtained were :—

$$\Delta_1 F'' (j) = 1\cdot6918 + 3\cdot18970j \quad (n'' = 0)$$
$$\Delta_1 F'' (j) = 1\cdot2191 + 3\cdot16778j \quad (n'' = 1)$$
$$\Delta_1 F'' (j) = 1\cdot7481 + 3\cdot09076j \quad (n'' = 2)$$
$$\Delta_1 F'' (j) = 1\cdot6239 + 3\cdot05319j \quad (n'' = 3)$$

and these represent the data in each case with a probable error of about $0\cdot05$ ν.

Table X.—Molecular Constants.

Electron level.	Vibra-tional level. (n.)	(Cubic form for $\Delta_1 F$.)			(Linear form for $\Delta_1 F$.)		$I \times 10^{40}$ gm. cm².	r (A.U.).
		D.	B.	ρ.	B.	ρ.		
$2\,^1P$	0	—	—	—	$1\cdot59485$	$-0\cdot03040$	$17\cdot343$	$1\cdot2384$
	1	$+0\cdot000278$	$1\cdot60410$	$+0\cdot18536$	$1\cdot58389$	$+0\cdot11515$	$17\cdot463$	$1\cdot2427$
	2	$+0\cdot003253$	$1\cdot55883$	$-0\cdot02480$	$1\cdot54538$	$-0\cdot06559$	$17\cdot898$	$1\cdot2589$
	3	$+0\cdot005035$	$1\cdot54892$	$+0\cdot01821$	$1\cdot52660$	$-0\cdot03187$	$18\cdot119$	$1\cdot2658$
	4	—	—	—	$1\cdot51060$	$+0\cdot01940$	$18\cdot310$	$1\cdot2724$
	5	—	—	—	$1\cdot48592$	$-0\cdot00433$	$18\cdot615$	$1\cdot2832$
$2\,^1S$	0	$+0\cdot008532$	$1\cdot95978$	$+0\cdot01737$	$1\cdot94041$	$-0\cdot02536$	$14\cdot2547$	$1\cdot1228$
$3\,^1S$	0	$-0\cdot004583$	$1\cdot94214$	$+0\cdot01820$	$1\cdot94319$	$+0\cdot01530$	$14\cdot234$	$1\cdot1220$

The values of B″ and ρ thus derived are believed to be the more accurate and from these the corresponding values of $I_n″$ and $r_n″$ have been calculated.

The constants of the $n″ = 0$ state call for several detailed remarks. The first of the above equations was obtained from the values which we summarise below :—

j	$1\frac{1}{2}$	$2\frac{1}{2}$	$3\frac{1}{2}$	$4\frac{1}{2}$	$5\frac{1}{2}$	$6\frac{1}{2}$	$7\frac{1}{2}$	$8\frac{1}{2}$	$9\frac{1}{2}$	$10\frac{1}{2}$
$\Delta_1 F″(j)$	6·36	9·6	12·9	15·98	19·2	22·36	25·8	29·62	31·9	34·58

From the data of the λ 4511 and λ 4123 bands of Table IX it will be observed that combination defects are present. The $Q(j) - P(j + 1)$ data are, however, less reliable than those of $R(j) - Q(j + 1)$ owing to the somewhat imperfect resolution of P branch lines round the head. For the latter reason the combination relations $(2f)$ and $(2g)$ have not been used. The actual data used and recorded above are the weighted means of the $R(j) - Q(j + 1)$ values obtained from the bands λλ 4511 and 4123 in Table IX. An analysis of Jassé's data using equations $(2f)$ and $(2g)$ gave B″ $= 1·5661$, ρ $= -0·0587$. The constants for the levels $n = 4$ and 5 have been deduced from a fine structure analysis which we have made, for the first time, of the (0, 4) and (0, 5) Ångström bands at λλ 6080 and 6620. These are preliminary values only, and it is not proposed to enter into fuller details of these in the present paper. Before discussing the molecular constants of Table X it will be convenient to present the new experimental data, and corrected analysis of the (0, 0) and (1, 0) Ångström bands.

The Ångström Bands λλ 4511 and 4123.

New measurements of these bands have been made with the aid of a 21-foot grating, and the data are recorded and analysed in Table XI. The line P $(\frac{1}{2})$ is, of course, the null line, while Q $(\frac{1}{2})$ and R $(\frac{1}{2})$ should be absent by reason of the ¹P character of the final state. This we have verified. Referring to Jassé's analysis of the λ 4511 band, the line ν 22172·3 is believed to be extraneous to the band, and ν 22171·8 should be labelled Q $(1\frac{1}{2})$. In addition ν 22175·7 is considered to be extraneous in origin. It has also been alleged that these bands λλ 4511, 4123 differed in their structure from the remaining bands of the Ångström system, each having an additional P′ and R′ branch. Three or four lines purporting to belong to each of such branches are given by Jassé, and from these Birge* has calculated a moment of inertia of about $\frac{3}{4}$ the normal value. We incline to the opinion, from a study of our experimental data, that these "branches" are spurious. There is a considerable amount of fine

* ' Phys. Rev.,' vol. 28, p. 1170 (1926).

Table XI.—Fine Structure of the Ångström Bands λλ 4511, 4123.

Old Q.T. j.	P branch.		Q branch.		R branch.	
	$\lambda_{air.}$	$\nu_{vac.}$	$\lambda_{air.}$	$\nu_{vac.}$	$\lambda_{air.}$	$\nu_{vac.}$
$1\frac{1}{2}$	4509·714	*a* 22168·16	4508·96	22171·87	4507·35	22179·78
$2\frac{1}{2}$	10·236	165·62	08·64	173·42	06·246	185·12
$3\frac{1}{2}$	10·576	163·94	08·21	175·55	05·03	*c* 191·22
$4\frac{1}{2}$	10·80	*b* 162·8	07·65	178·31	03·67	197·89
$5\frac{1}{2}$	(10·90)	(162·3)	06·92	181·89	02·13	205·5
$6\frac{1}{2}$	10·80	*b* 162·8	06·046	186·20	00·455	213·76
$7\frac{1}{2}$	10·43	164·66	05·03	*c* 191·22	4498·59	222·95
$8\frac{1}{2}$	10·079	166·37	03·84	197·06	96·48	233·40
$9\frac{1}{2}$	09·714	*a* 168·16	02·476	203·80	94·46	243·29
$10\frac{1}{2}$	—	—	00·91	211·52	92·06	255·13
$11\frac{1}{2}$	—	—	4499·08	220·56	—	—
$12\frac{1}{2}$	—	—	96·795	231·84	—	—
$13\frac{1}{2}$	—	—	93·926	246·03	—	—
$14\frac{1}{2}$	—	—	90·427	263·37	—	—
$1\frac{1}{2}$	4122·35	*a* 24251·20	4121·85	24254·13	—	—
$2\frac{1}{2}$	22·89	*b* 248·01	21·607	255·56	4119·596	*e* 24267·40
$3\frac{1}{2}$	23·235	*c* 245·99	21·27	257·54	18·62	273·15
$4\frac{1}{2}$			20·868	259·91	17·564	279·38
$5\frac{1}{2}$	23·47	*d* 244·61	20·272	263·42	16·35	286·54
$6\frac{1}{2}$			19·596	*e* 267·40	15·05	294·21
$7\frac{1}{2}$			18·81	272·03	13·52	303·25
$8\frac{1}{2}$	23·235	*c* 245·99	17·87	277·57	11·82	313·29
$9\frac{1}{2}$	22·89	*b* 248·01	16·84	283·65	10·18	323·00
$10\frac{1}{2}$	22·35	*a* 251·20	15·62	290·85	08·34	333·89
$11\frac{1}{2}$	—	—	14·19	299·29	—	—
$12\frac{1}{2}$	—	—	12·40	309·86	—	—

a, b, c, d, e, indicate blends of 2 lines.

structure work in these regions arising from the triplet system[*] of carbon, and possibly from another system at present unrecorded. This, we consider, may account for the above additional " branches."

The Vibrational Levels of the $2\,^1P$ State.

With regard to the molecular constants of the ^1S states of the CO molecule (see Table X), we have already remarked on their exceptionally small variation. The constants of the various vibrational levels of the $2\,^1P$ state require further examination. The value of B_n falls with increasing vibrational quantum number roughly according to the expected relation $B_n = B_0 - \alpha n$ where α is approximately $0 \cdot 022$. The value of B_1 appears to be somewhat high however (this was very pronounced when the cubic form was used). In addition, the unusually large positive value of ρ at once marks out the state $n = 1$ as

[*] ' Roy. Soc. Proc.,' A, vol. 103, p. 383 (1923).

unusual. The constants for the $n = 0$ state appear to be normal. Numerous calculations were made on the data of the $n = 1$ state, and all confirmed its exceptional nature. For example, the intervals between head and origin for the (0, 0), (0, 1), (0, 2), (0, 3), (0, 4) and (0, 5) bands are respectively $8 \cdot 9$, $6 \cdot 8$, $8 \cdot 3$, $7 \cdot 3$, $6 \cdot 8$ and $6 \cdot 4$ ν. If such unusual features had occurred in B_0 and ρ_0 they would have occasioned less surprise in view of the fact that the $n = 0$ level has hitherto been regarded as subject to a perturbation of some 6 ν from the expected position. This was announced and discussed by Birge (*loc. cit.*). We have therefore been led to make a re-examination of the vibrational data of the Ångström system with a view to determining the reality of this supposed perturbation of the $n'' = 0$ level, and if possible to find a clue to the unusual nature of the $n'' = 1$ level. The data for this purpose are given in Table II. The band heads of the two progressions ($n' = 0$ and 1) of the Ångström system are according to Birge given by

$$\nu = \left\{ \begin{array}{c} 22156 \cdot 6 \\ 24238 \cdot 0 \end{array} \right\} - (1497 \cdot 28 n'' - 17 \cdot 2 n''^2).$$

This expresses the Ångström heads with the following residual errors $(o - c)$ ν :

n'' $\backslash$ n'	0	1	2	3	4	5
0	$+5 \cdot 7$	$-1 \cdot 3$	$+1 \cdot 1$	0	$+0 \cdot 3$	$+0 \cdot 6$
1	$+5 \cdot 8$	$-1 \cdot 5$				

It has been found, however, that if the following expression is used, the residuals are, on the whole, smaller, and *the perturbed level is $n'' = 1$ and not $n'' = 0$ (as given by Birge).*

$$\nu_H = \left\{ \begin{array}{c} 22162 \cdot 3 \\ 24243 \cdot 8 \end{array} \right\} - (1500 \cdot 52 n'' - 17 \cdot 68 n''^2).$$

The corresponding residuals are :—

n'' $\backslash$ n'	0	1	2	3	4	5
0	0	$-4 \cdot 2$	0	0	$-0 \cdot 1$	$-0 \cdot 9$
1	0	$-4 \cdot 6$				

The level $n'' = 1$ appears to be perturbed by about $4 \cdot 2$ ν (probably the more reliable figure). The final state of the Ångström system being identical with

the initial state of the 4th positive carbon system, we have tested the above vibrational function $(1500 \cdot 52n' - 17 \cdot 68n'^2)$ on a number of n' progressions of the latter system, using the data available (see Birge's paper, p. 1164). The available data are admittedly so poor (most of the bands are in the Schumann region) that it is impossible to verify a displacement of the $n = 1$ level. The above vibrational function appears however to give at least as good a representation of the available data as that proposed by Birge. More accurate data are very desirable, and in the light of such data a slight readjustment of the above vibrational function may be necessary, but of the perturbation of the $n = 1$ level we think that little doubt can be entertained. If the data for ν_0 (see Table II) are used, the $n' = 0$ progression can be expressed by

$$\nu_0 = 22172 \cdot 7 - (1501 \cdot 6n'' - 17 \cdot 7n''^2)$$

with residuals

n' \ n''	0	1	2	3	4	5
0	$-1 \cdot 5$	$-6 \cdot 7$	0	0	$+0 \cdot 3$	0

We have been unable to satisfy ourselves how far $-1 \cdot 5 \, \nu$ represents a small but genuine perturbation of the $n'' = 0$ level. It would appear to be an amount well outside the limits of experimental error. Such a small perturbation of a level adjacent to a strongly disturbed one is by no means unprecedented in band spectra. We hope to make a fuller critical survey of this and other matters with still better data.*

We have examined our grating plates on which the $3\,^1S \rightarrow 2\,^1P$ system was photographed, for a possible system arising from the $E \rightarrow A$ transition (see Table I). The first four members of the $n' = 0$ progression should be at about $\lambda\lambda\ 3550 \cdot 4, 3747 \cdot 2, 3961 \cdot 6$ and $4196 \cdot 4$. There is some evidence of the presence of these bands, although they are faint, and much confused with " spurious " third positive, and other band structure.*

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* *Note added in Proof.*—A paper has just appeared by G. Herzberg ('Z. Physik,' vol. 52, p. 815 (1929)), in which eight bands of the new CO system are recorded. The initial state is there described as D^1. There can however be no doubt, in the author's opinion, that the initial state is $3\,^1S$.

Summary.

(1) Details are given of a new band system of CO corresponding to the electronic transition $3\,^1S \rightarrow 2\,^1P$. Four bands of the $n' = 0$ progression have been observed, the heads of which are at $\lambda\lambda\ 3680\cdot05$, $3893\cdot15$, $4125\cdot02$ and $4380\cdot18$.

(2) Fine structure analysis of the (0, 1), (0, 2) and (0, 3) bands has been made. The missing lines $R\,(\tfrac{1}{2})$ and $Q\,(\tfrac{1}{2})$ confirm the nature of the electronic transition. The structure of these bands is in every respect similar to the Ångström system with which they share the final state in common. Combination defects are not apparent until high j-values are attained.

(3) The correct assignment of (half-integral) j-values has been applied to the Ångström system. New experimental data are provided in the case of the (0, 0), (1, 0), (0, 4) and (0, 5) bands, and the combination data derived from these, and from the new system, along with Hulthén's data, have been used to evaluate the constants of the $3\,^1S$, $2\,^1S$ and $2\,^1P$ levels of the CO molecule.

(4) Minor corrections have been made to Jassé's analysis of the (0, 0) Ångström band. This, with the (1, 0) band, is believed to be normal in type, differing from the other bands only in the earlier onset of combination defects

(5) The state $n = 1$ of the $2\,^1P$ level is believed to suffer a vibrational perturbation. The level $n = 0$, which has been hitherto regarded as perturbed, is believed to be normal, or, alternately, to suffer from perturbation of a secondary character.