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The Structure of the High Pressure Carbon Bands and the Swan System.

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Introduction.

The so-called high pressure "CO" bands—or high pressure carbon bands, as they are better called—were first found by Fowler* in 1910 in tubes containing carbon monoxide at relatively high pressures. The system was described as consisting of some six apparently double-headed bands degraded to the violet, their wave-lengths being approximately at—

$$\begin{array}{cccccc} 6441 \} & 5897 \} & 5431 \} & 5030 \} & 4679 \} & 4365 \} \\ 6420 \} & 5878 \} & 5413 \} & 5015 \} & 4663 \} & 4353 \} \end{array} \text{ \AA.U.}$$

In 1923 the conditions of production of this spectrum were further investigated by Merton and Johnson† who obtained the bands with considerable strength by condensed discharges in capillary tubes fitted with carbon electrodes, and containing CO at pressures of 5 mm. and more. It was found that while the high pressure bands and the Swan bands were mingled in the light from the capillary of the tube, the former bands were isolated in bluish jets where the two ends of the capillary merged into the wider parts of the tube. Further observations indicated that the introduction of a little CO₂ destroyed the bands, but that the system re-appeared after a few minutes, in which time presumably the carbon dioxide had been reduced to monoxide by the carbon electrodes. A reproduction of these bands photographed under low dispersion is given in the above-mentioned paper.

No further experimental work appears to have been done on this system, and it has not been correlated with any other band system or assigned any place in the system of electronic levels of the CO molecule. We have therefore made an attempt to photograph the system under high dispersion with a view to fine structure analysis and identification of the molecular emitter. For this purpose large discharge tubes having a bore of about 15 to 20 mm. and a length of 60 or 70 cm. were used. These had at least one of the electrodes

* 'M.N.R.A.S.,' vol. 70, p. 484 (1910).

† 'Roy. Soc. Proc.,' A, vol. 103, p. 386 (1923).

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made of carbon and were fitted with side bulbs containing caustic potash and phosphorus pentoxide and a palladium regulator. The tubes were filled with carbon monoxide to such a pressure (probably 20–40 mm.) that a condensed discharge could just be forced through by the $\frac{1}{4}$ kilowatt 15,000 volt transformer used. Some of the tubes had large side flasks attached to them, increasing thereby the volume of gas in the tube, and giving the tubes a life of 4 to 6 hours during which the high pressure bands were emitted strongly. After some such period the pressure fell below the optimum value, and deposits of carbon had accumulated on the walls of the tube. Impurities such as hydrogen, carbon dioxide, and water-vapour were found to inhibit formation of the high pressure bands, and the tube always attained its best condition after running for about an hour (removing meanwhile any little hydrogen present through the regulator). Under these conditions the wide bore is practically filled with light, and presents a remarkable appearance, as of dense pale blue puffs of smoke (showing the high pressure system), threaded by a narrow green ribbon (showing the Swan system). If side tubes having a fair capacity (*e.g.*, flasks) are attached to the discharge tube the high pressure glow is capable of diffusion into these. The appearance is suggestive of an afterglow emitter, but if this is its true nature it is of very short duration. Photographs of the H.P. bands were taken in times varying from 4 to 10 hours in the first order of a 21-foot grating. The green band in the neighbourhood of λ 5000 is exceedingly faint and was not attempted. Before considering the results obtained it will be an advantage to summarise our present knowledge of the Swan spectrum and its emitter, with which it will subsequently be shown that the high pressure carbon system is intimately related.

The Swan System.

The origin of this system has been the object of much controversy, although recently general agreement appears to have been reached that the emitter is a C_2 molecule. In 1926 an investigation of the system was made by one of the writers* who arrived at the conclusion that a HC–CH molecule was responsible. Since that time the definite recognition of band spectra from the molecule BeO^\dagger (which has the same number of electrons as C_2), and more especially the rapid theoretical developments due to the work of Mulliken‡ and others, have not only removed any intrinsic objection to a C_2 emitter but have given it

* 'Phil. Trans.,' A, vol. 226, p. 157 (1927).

† 'Roy. Soc. Proc.,' A, vol. 122, p. 211 (1929); 'Phys. Rev.,' vol. 33, p. 163 (1929).

‡ 'Phys. Rev.,' vol. 29, p. 637 (1927).

strong support. In addition, experimental work such as that of Pretty,* has shown that the Swan bands can be produced by a condensed discharge through CO, free as far as possible from hydrogen and water-vapour, and with an intensity apparently independent of the amount of hydrogen which may be introduced. Mention may also be made in passing of a paper by Shea,† who has published detail of a fine-structure analysis of five bands of the Swan system, in which a correction has been made to the author's previously assigned j -values. Shea has also derived accurate values of the molecular constants.

In the next section of this communication it will be shown that the Swan system and the H.P. carbon system have a common final state, and this furnishes entirely new and reliable evidence that the emitter responsible for both systems is certainly not a hydrocarbon and must indeed be a C_2 molecule. The inhibiting effect of hydrogen on the H.P. carbon system is definitely against a hydrocarbon emitter on the one hand, while on the other hand there is convincing evidence against an oxycarbon emitter for the Swan system (*vide* 'Phil. Trans.,' vol. 226, pp. 186-190). On the basis of a C_2 emitter much, if not all, of the experimental data described in that paper find a favourable explanation in the light of more recent developments. We take a few examples of this. The similarity between the Swan spectrum and the Second Positive Nitrogen spectrum—while a close one—is by no means as complete as was previously supposed. Both systems arise from $^3P \rightarrow ^3P$ transitions and the band structure in both cases exhibits σ -type rotational doubling. In the Swan molecule, however, rotational levels of one of the electronic states are *completely* suppressed (giving rise to the recorded staggering effect in the band structure), while in the Nitrogen molecule there is only a *partial* suppression. It may also be mentioned that while the two 3P states of the N_2 molecule are *normal* those of the Swan emitter are probably *inverted*. Such differences are intelligible if the emitters are C_2 and N_2 . Other experimental observations such as the association of the Swan bands with the CH bands λ 4315, etc., are to be expected under the experimental conditions described in the above-mentioned paper in which both carbon and hydrogen were present. Equally it is to be noted, Pretty's experiments produced the Swan bands in CO when no trace of the CH bands or $H\alpha$ was observed. These facts are consistent with a C_2 emitter and the present writers endorse this view.

* 'Phys. Soc. Proc.,' vol. 40, p. 71 (1928).

† 'Phys. Rev.,' vol. 30, p. 825 (1927).

High Pressure Carbon Bands and Swan System. 671*Correlation of the H.P. Carbon Bands and the Swan System.*

The six recorded H.P. bands belong to a single n'' progression ($n' = 0$). The proximity of the coefficient of n'' to that of the Swan system first suggested the possibility of a relationship between these systems. A careful search was subsequently made in the near ultra-violet and four comparatively faint bands were recorded. These therefore become the (0, 0), (0, 1), (0, 2), and (0, 3) bands of the system, and the correct n'' values of the six previously known bands are given by (0, 4) to (0, 9). By the use of neo-cyanine plates we have also identified two additional bands (0, 10) and (0, 11) in the near infra-red. These data are given in Table I and have been expressed by the formula :

$$\nu = 29212 - (1627n'' - 11.7n''^2) \quad (1)$$

Table I.—High Pressure Carbon Bands.

n'' ($n' = 0$).	Int.	λ (air) I.A.	$\nu_{vac.}$	$\Delta\nu$ O.-C.
0	1	3419	29241	+29
1	1	3619.5	27620	+23
2	1	(Conf.)	—	—
3	2	4093	24426	-10
4	7	4368.82	22883	- 8
5	15	4680.17	21361	- 8
6	1	(V. Faint)	—	—
7	5	5434.93	18394	- 2
8	10	5899.27	16946	+ 2
9	8	6442.27	15518	+ 1.
10	6	7083.2	14114	+ 2
11	4	7852.5	12731	0

The (Obs.—Calc.) values of column 5 are satisfactory when it is recalled that the bands (0, 0) to (0, 3) are particularly faint and settings were made on the apparent centre of the unresolved band-work. The other data refer to the band *heads*, all of which are degraded to the violet. The intensities of column 2 are approximate photographic intensities only, and are to be regarded as descriptive rather than quantitative. They illustrate, however, the main features of the peculiar intensity distribution, which has a notable minimum at about the (0, 6) band. The same oscillating intensity phenomenon is also found in the β bands of NO ($^2P \rightarrow ^2P$),* and as far as we know it has received no theoretical explanation. Equation (1) may be compared with the expression for the origins of the Swan system :

$$\nu = 19379.20 + (1773.42n' - 19.35n'^2) - (1629.88n'' - 11.67n''^2). \quad (2)$$

* 'Phil. Mag.,' vol. 2, p. 631 (1926).

It is at once apparent that the two-band systems have a common final electronic state, which is almost certainly the normal state of the C_2 molecule. The small difference between $f(n'')$ as deduced from the H.P. carbon system and the Swan system is accounted for by the fact that in the former case the wave-numbers relate to band heads, and in the latter case to band origins.

It may perhaps be mentioned at this point that the apparent doublet character of the H.P. bands as seen under low dispersion is due merely to condensations which constitute the P and R branches.

Fine-Structure of the H.P. Carbon Bands.

As previously mentioned, photographs of the H.P. carbon bands have been obtained in the first order of a 21-foot grating of the bands (0, 4), (0, 5), (0, 7), (0, 8) and (0, 9). Except in the case of the (0, 5) band these were not sufficiently strong to permit of satisfactory reproduction. The H.P. bands bear an exceptionally close resemblance in their fine-structure to the Swan bands as developed under low temperature conditions, and the Swan band $\lambda 4737$ of spectrum 3 ('Phil. Trans.,' vol. 226, opp. p. 230, 1927) may be taken as typical of the appearance of the H.P. carbon bands.

The H.P. bands consist of P and R branches only, and they undoubtedly represent a transition $^3P \rightarrow ^3P$. In the absence of fine-structure data Mulliken* had speculated that they might possibly arise from a $^1P \rightarrow ^1P$ transition of the molecule C_2 . This is now, however, seen to be impossible. We thus have knowledge at present of three levels of the C_2 molecule and these are all 3P levels. As in the case of the Swan bands, the first 16 to 18 members of the P branch (which goes to the head) either are not of sufficient strength or are insufficiently resolved to make identification possible. Under low temperature conditions, these constitute almost the whole of the P branch, and thus no analysis of the data by means of the combination principle has been possible. We have, however, been able to distinguish many of the triplets of the R branches of the bands, and to trace these, in part or whole, back to the band origins. The data for the (0, 7) yellow-green band proved somewhat fragmentary in this respect, and have therefore not been included in this paper. The data in the case of the violet (0, 4), blue (0, 5), yellow (0, 8) and red (0, 9) R branches are of sufficient reliability and interest to justify their inclusion. Tables II, III, IV and V contain these data. It was at first intended to make calculations of the moment of inertia of the molecule in several of the final vibrational states, by analysis of the data of the R branches only, but the

* 'Phys. Rev.,' vol. 32, p. 214 (1928).

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existence of perturbations led to the abandonment of this project. Nevertheless, the application of approximate graphical methods to the data, indicated for the moments of inertia of the vibrational states $n'' = 5, 8$ and 9 , values of the same order as those which are deducible from analysis of the Swan system.

Table II.—(ν_{vac}) R-branch Data of H.P. Band λ 4368.82.

j_1	R_2	Δ_{21}	R_1	Δ_{10}	R_0
$3\frac{1}{2}$			22936.4		
$4\frac{1}{2}$			38.3		
$5\frac{1}{2}$			40.0		
$6\frac{1}{2}$			42.8	(6.4)	22936.4
$7\frac{1}{2}$			45.2	(5.2)	40.0
$8\frac{1}{2}$			47.4 <i>d</i>	(4.6)	42.8
$9\frac{1}{2}$			50.3 <i>d</i>	(4.3)	46.0 <i>d</i>
$10\frac{1}{2}$			53.7 <i>d</i>	(3.4)	50.3 <i>d</i>
$11\frac{1}{2}$	22957.6 <i>d</i>	(0.4)	57.2 <i>d</i>	(2.5)	54.73 <i>d</i>
$12\frac{1}{2}$	61.7	(1.0)	60.7	(2.3)	58.4
$13\frac{1}{2}$	67.31	(1.57)	65.74	(1.33)	64.41
$14\frac{1}{2}$	72.60	(1.39)	71.21	(1.69)	69.52
$15\frac{1}{2}$	76.20	(1.13)	75.07	(1.05)	74.02
$16\frac{1}{2}$	80.65	(1.11)	79.54	(1.22)	78.32
$17\frac{1}{2}$	84.27	(0.94)	83.33	(0.81)	82.52
$18\frac{1}{2}$	89.22	(1.08)	88.14	(1.08)	87.06
$19\frac{1}{2}$	92.40	(0.54)	91.86	(0.66)	91.20
$20\frac{1}{2}$	98.02	(0.81)	97.21	—	—
$21\frac{1}{2}$	—	—	99.40	(0.39)	99.01

A → A. B → B.

Table III.—(ν_{vac}) R-branch Data of the H.P. Band λ 4680·17.

j_i	R_2	Δ_{21}	R_1	Δ_{10}	R_0
$1\frac{1}{2}$			21410·2	(12·4)	21397·8
$2\frac{1}{2}$			12·1	(10·1)	21402·0
$3\frac{1}{2}$			14·0	(8·7)	05·3
$4\frac{1}{2}$			15·74	(6·3)	09·4
$5\frac{1}{2}$			18·7 <i>d</i>	(5·7)	13·0
$6\frac{1}{2}$			21·1	(5·4)	15·7
$7\frac{1}{2}$			23·5	(4·8)	18·7 <i>d</i>
$8\frac{1}{2}$	21427·3	(0·7)	26·6	(4·5)	22·1
$9\frac{1}{2}$	31·3	(1·2)	30·1	(3·53)	26·57
$10\frac{1}{2}$	35·23	(1·5)	33·74	(3·61)	30·13
$11\frac{1}{2}$	38·97 <i>d</i>	(1·5)	37·48	(3·0)	34·50
$12\frac{1}{2}$	43·15	(1·61)	41·54	(2·8)	38·77 <i>d</i>
$13\frac{1}{2}$	46·99	(2·21)	44·78	(1·63)	43·15
$14\frac{1}{2}$	50·52	(1·45)	49·07	(1·53)	47·54
$15\frac{1}{2}$	54·49	(1·12)	53·37	(1·10)	52·27
$16\frac{1}{2}$	59·41	(1·13)	58·28	(1·18)	57·10
$17\frac{1}{2}$	63·40	(0·79)	62·61	(0·94)	61·67
$18\frac{1}{2}$	68·98	(1·07)	67·91	(1·12)	66·79
$19\frac{1}{2}$	72·55 <i>d</i>	(0·48)	72·07 <i>d</i>	(0·70)	71·37
			A \rightarrow A.		
				B \rightarrow B.	

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Table IV.—(ν_{vac}) R-branch Data of the H.P. band λ 5899.27.

j_1	R_2	Δ_{21}	R_1	Δ_{10}	R_0
$1\frac{1}{2}$			16976.4 <i>d</i>		
$2\frac{1}{2}$			78.3 <i>d</i>		
$3\frac{1}{2}$			80.3 <i>d</i>		
$4\frac{1}{2}$			82.4		
$5\frac{1}{2}$			85.55		
$6\frac{1}{2}$			87.8	(5.4)	16982.4
$7\frac{1}{2}$			90.76	(5.2)	85.55
$8\frac{1}{2}$	16995.45	(1.05)	94.4	(4.8)	89.6
$9\frac{1}{2}$	17000.11	(1.8)	98.33	(3.95)	94.38
$10\frac{1}{2}$	04.93	(2.1)	17002.81	(3.9)	98.92
$11\frac{1}{2}$	09.68	(2.42)	07.26	(3.11)	17004.15
$12\frac{1}{2}$	14.76	(2.4)	12.37	(3.17)	09.20
$13\frac{1}{2}$	18.59	(2.14)	16.45	(1.71)	14.74
$14\frac{1}{2}$	23.46	(1.62)	21.84	(1.52)	20.32
$15\frac{1}{2}$	28.44	(1.13)	27.31	(1.13)	26.18
$16\frac{1}{2}$	34.94	(1.36)	33.58	(1.29)	32.29
$17\frac{1}{2}$	40.18	(0.90)	39.28	(0.91)	38.37
$18\frac{1}{2}$	47.49	(1.22)	46.27	(1.22)	45.05
$19\frac{1}{2}$	52.53	(0.59)	51.94	(0.82)	51.12
$20\frac{1}{2}$	60.88 <i>d</i>	—	59.59	—	—
$21\frac{1}{2}$	—	—	—	—	—
$22\frac{1}{2}$	75.16	(0.74)	74.42	(1.05)	73.37
			A \rightarrow A.		
			B \rightarrow B.		

Table V.—(v_{vac}) R-branch Data of the H.P. Band λ 6442.27.

j_i	R_2	Δ_{21}	R_1	Δ_{10}	R_0
$1\frac{1}{2}$			15545.15		
$2\frac{1}{2}$			47.17		
$3\frac{1}{2}$			49.1 <i>d</i>		
$4\frac{1}{2}$			51.28		
$5\frac{1}{2}$			55.3		
$6\frac{1}{2}$			56.6		
$7\frac{1}{2}$			59.7		
$8\frac{1}{2}$	15564.8	(1.12)	63.68	(4.94)	15558.74
$9\frac{1}{2}$	69.65	(2.0)	67.68	(4.24)	63.44
$10\frac{1}{2}$	74.8	(2.5)	72.29	(3.76)	68.53
$11\frac{1}{2}$	79.78	(2.63)	77.15	(3.14)	74.01
$12\frac{1}{2}$	85.18	(2.84)	82.34	(3.10)	79.25
$13\frac{1}{2}$	89.10	(2.22)	86.92	(1.74)	85.18
$14\frac{1}{2}$	94.08	(1.52)	92.56	(1.53)	91.03
$15\frac{1}{2}$	99.77	(1.23)	98.54	(1.13)	97.41
$16\frac{1}{2}$	15606.30	(1.23)	15605.07	(1.24)	15603.83
$17\frac{1}{2}$	12.39	(0.94)	11.45	(0.93)	10.52
$18\frac{1}{2}$	19.76	(1.12)	18.64	(1.18)	17.46
$19\frac{1}{2}$	25.78	(0.67)	25.11	(0.73)	24.38
			A. A ↑		
			B. B ↑		

Perturbations.—The existence of perturbations in the R branches is exhibited by plotting the second differences (using the central component of each triplet) against j_i values. Instead of being constant, these exhibit a violent oscillation. In fig. 1 are plotted such data derived from Tables III, IV and V (the violet band includes a few somewhat uncertain identifications and is therefore not used). It is, of course, true, that if a line has been incorrectly identified, then an oscillation of the $\Delta^2 R(j_i) : j_i$ curve will result. It will be observed, however, that there is a very precise correspondence of the deviations in all three bands. It is certain that perturbations are largely responsible for the curves of fig. 1

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since otherwise (a) the close correspondence of the curves would require that a similar error (in both magnitude and direction) must have been made for

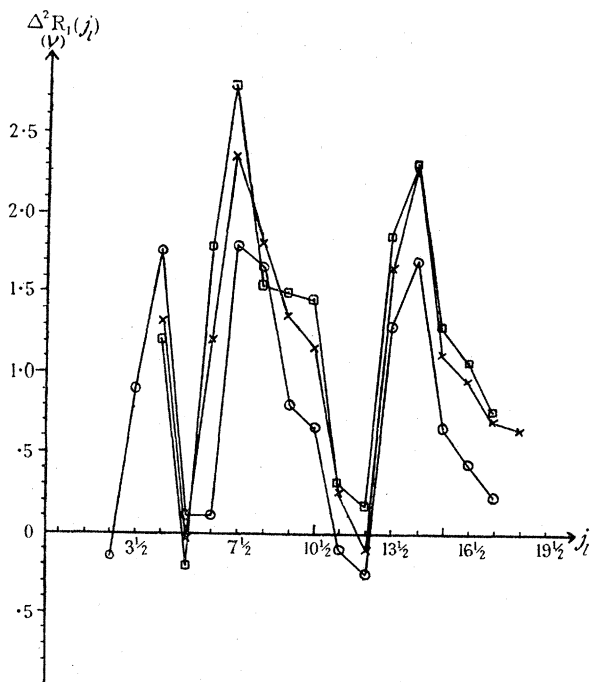


FIG. 1.—Perturbations in the R Branches of the H.P. Carbon Bands.

○ Blue Band. × Yellow Band. □ Red Band.

the corresponding member of each band, and (b) the fact that the second differences derived from the two alternate-missing-line series fall in the case of each band on to a fairly smooth oscillating curve will be unexplained. It is difficult with the present available data to say precisely which members are perturbed. There certainly appears to be a range of considerable disturbance between $R(12\frac{1}{2})$ and $R(7\frac{1}{2})$. It is clear that the perturbations are associated with the initial (excited) level of the H.P. bands since (a) they are common to all of the bands examined of the $n' = 0$ progression, and (b) there is no perturbation of the fine-structure of the Swan bands for these j_i values.

Attention may be drawn at this point to a feature which will be mentioned later, and which is shown in fig. 4. This is of the nature of a perturbation but appears to affect in this special way only the less refrangible components of the triplets. We refer to the discontinuity of about 1ν which occurs between $j_i = 12\frac{1}{2}$ and $13\frac{1}{2}$.

General Fine-Structure Interpretation.—From the close similarity of the Swan system and the high pressure carbon system, arising as they do in $^3P \rightarrow ^3P$ transitions in the C_2 molecule, it follows that within certain limitations to be discussed in the next section, the general interpretation of Swan structure given by Mulliken* is equally applicable to the H.P. bands. Fig. 2 illustrates

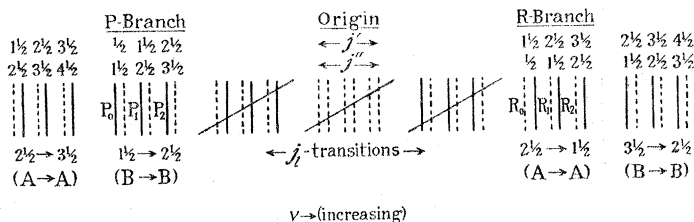


FIG. 2.—Fine-Structure near the Origin of typical H.P. and Swan Bands.

diagrammatically the structure of a typical Swan or H.P. band in the neighbourhood of the origin (except that to avoid confusion the rapid diminution in triplet width as we proceed outwards from the origin has not been indicated). Fig. 3

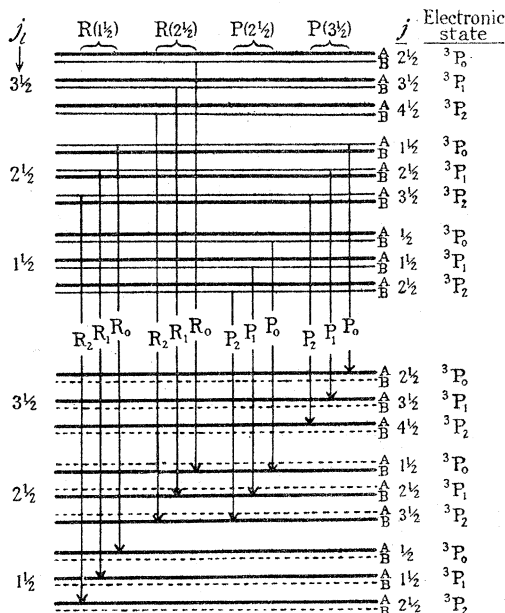


FIG. 3.—Rotational Transitions in a typical Swan Band.

has been constructed to show the precise transitions which are responsible for the band structure of fig. 2 in the case of the Swan bands. A slightly different

* 'Phys. Rev.,' vol. 29, p. 644 (1927).

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diagram appropriate to the H.P. bands is given later in fig. 5. In fig. 3 three rotational levels corresponding to values of $j_i^* = 1\frac{1}{2}, 2\frac{1}{2}, 3\frac{1}{2}, \dots$, have been drawn for each electronic state. Each rotational level is triple due to the presence of a resultant electronic spin momentum $s = 1$. Each component level is thus characterised by $j = j_i + s, j_i, j_i - s$, which is the vector sum of j_i and s . Each component of the triple levels is again double, the sub-states being denoted A and B (this is the so-called σ -type doubling). Transitions between sub-states $A \rightarrow A$ and $B \rightarrow B$ are permitted in the formation of P and R branches, and of the type $A \rightarrow B$ and $B \rightarrow A$ in the formation of Q branches. This particular hypothesis is at present accepted as a convention only, inasmuch as the reverse limitation may really be the true one.

The phenomenon of alternating intensities in band lines which occurs in all symmetrical molecules is manifest here in the case of C_2 . Analysis of the He_2 bands originally showed that the particular suppressed levels for the A and B sub-states were given by

$$\left. \begin{array}{l} j_i = \sigma_i + \frac{1}{2}, \quad \sigma_i + 2\frac{1}{2}, \quad \sigma_i + 4\frac{1}{2} \dots\dots \text{B type} \\ j_i = \sigma_i + 1\frac{1}{2}, \quad \sigma_i + 3\frac{1}{2}, \quad \sigma_i + 5\frac{1}{2} \dots\dots \text{A type} \end{array} \right\} \quad (3)$$

and in the absence of evidence to the contrary it may be assumed that this is generally true for homo-polar molecules. Here, as we are dealing with P states we have $\sigma_i = 1$. In He_2 we appear to have an extreme type of symmetry in which *complete* suppression takes place for *all* electronic levels in accordance with equation (3). It will therefore be clear from fig. 3 that in He_2 , transitions between like electronic states, *e.g.*, $^1S \rightarrow ^1S, ^3P \rightarrow ^3P$ will be impossible. In the Second Positive Nitrogen bands ($^3P \rightarrow ^3P$) there is but partial suppression of the sub-states given by equation (3) for the various electronic levels. This means of course merely a reduction of intensity. All the six components corresponding to a single rotational transition $\Delta j_i = \pm 1, 0$, are thus present. The Swan triplets indicate total suppression in one of the electronic states only, although in the absence of further information from other spectra of the C_2 molecule it would remain an open question whether this was in the initial or final state. The similar triplet structure of the H.P. carbon bands suggests—though it is not conclusive—that total suppression probably takes place in the common final state. It is not possible with the available experimental evidence to say whether partial suppression takes place in the initial electronic state as well, since, as fig. 3 will show, successive triplets would be reduced in

* j_i replaces the j_k of Mulliken's earlier papers, and σ_i replaces σ_k . For the latest notation *vide* 'Phys. Rev.', vol. 32, p. 186 (1928).

intensity to the same extent. The intensities of the initial levels in fig. 3 have been drawn to indicate how partial suppression would operate, on the assumption that it does so. It will be clear from the figure how the joint action of the two effects: σ -type doubling and suppression of alternate rotational levels, results in the so-called "staggering" in position of the triplets of fig. 2. This phenomenon occurs in both the Swan and the H.P. carbon bands.

In regard to the number of missing lines near the origin, the minimum value of j_i is limited by $j_i > \sigma_i$, and σ_i for both initial and final states is 1. As we are dealing with a molecule having an even number of electrons j_i takes half-integral values (using the old quantum theory), and its minimum value in both initial and final states is $1\frac{1}{2}$. The first observable triplets of the two branches R (j_i), P (j_i) are therefore R ($1\frac{1}{2}$) and P ($2\frac{1}{2}$).

There remains one further remark to make in explanation of the labelling of the three components of any triplet as R₂, R₁, R₀ or P₂, P₁, P₀. A somewhat different, and purely arbitrary numbering has been used by Mulliken* to distinguish the three components in the case of the Swan system. The designation employed in figs. 2 and 3 has the advantage of representing in the subscript a definite physical quantity σ , which on account of the selection principle $\Delta\sigma = 0$ is the same in the initial and final states.

The Triplet Intervals in the H.P. System.—The variation in triplet width from large values near the band origin to vanishingly small values for j_i large, is attributable to a change of the condition of the molecule from Hund's case (a) to Hund's case (b).† The facts briefly stated are these. In a diatomic molecule the total orbital angular momentum of the electrons, represented by the quantum number l (the group quantum number of atomic spectra), is in precession about the strong electric field along the inter-nuclear axis. The quantised component of l along this axis, viz., σ_l , is therefore responsible for a magnetic field in this direction, which, under the conditions of case (a) is the dominating magnetic field of the molecule. The resultant electronic spin momentum s (the algebraic sum of the several electronic spins $s_r = \pm \frac{1}{2}$) which is orientated by the internal magnetic field of the molecule is thus quantised with respect to the inter-nuclear axis, about which it precesses. Its quantised component σ_s along this axis may therefore take any one of the values lying between s and $-s$. In the case of a ³P molecular state we thus have $\sigma_l = 1$, $s = 1$, and hence $\sigma_s = 1, 0, -1$. This gives three values for

* 'Phys. Rev.', vol. 29, p. 644 (1927).

† 'Z. Physik,' vol. 36, p. 657 (1926).

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σ ($= \sigma_l + \sigma_s$), viz., 2, 1, and 0, which distinguish the three components of each rotational level. The vector sum of σ and m gives j the total angular momentum of the whole molecule. The rotational terms in Hund's case (a) are therefore given by

$$F(j) = f(\sigma) + B(j^2 - \sigma^2) \quad (4)$$

giving the triple structure when for σ its three values 0, 1 and 2 are substituted.

Case (b) arises when σ_l no longer gives rise to the dominating magnetic field in the molecule, and when as a result, it is no longer in exclusive control of the orientation of s . When, for example, rotation of the molecule takes place, there is a magnetic field along the m -axis, and s will then be quantised with respect to the resultant field, *i.e.*, along the j_l axis. This quantum number may appropriately be described as j_s , and may take values lying between s and $-s$, (precisely as did σ_s above). The resultant momentum of the whole molecule is here given by $j = j_l + j_s$. The structure of the rotational terms is then given by

$$F(j) = f(j, j_s) + B(j_l^2 - \sigma_l^2) \quad (5)$$

corresponding to triplets of constant separation when case (b) is fully attained. In practice between low and high values of j there is a transition stage in which we pass from conditions of approximately case (a) to case (b). This variable element in the triple separation is represented by the term $f(j, j_s)$ which for large j values will, of course, attain a constant value dependent on the particular value of j_s .

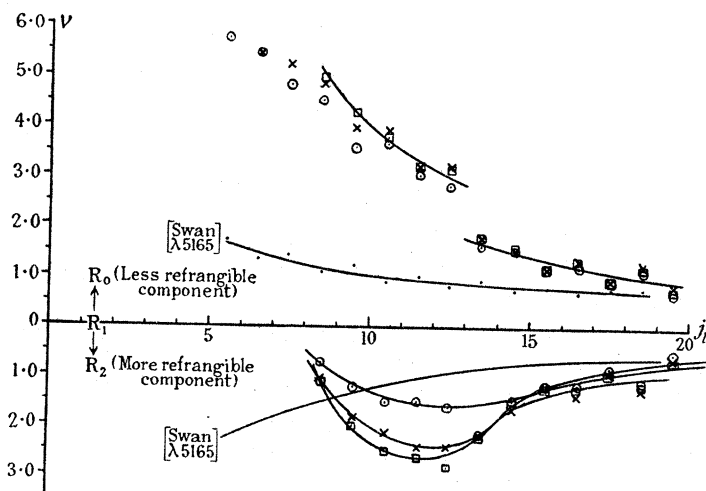


FIG. 4.—Triplet Intervals in the R Branches of the H.P. Carbon Bands.

○ Blue Band. × Yellow Band. ◻ Red Band.

We proceed now to consider the special case of the triplet intervals in the H.P. carbon bands. The data for the R branches of the red, yellow and blue bands have been plotted in fig. 4, and for comparison the triplet intervals of the Swan band λ 5165 have been plotted on the same diagram. The j_i axis represents the position of the central component R_1 , and the separations of the less refrangible and more refrangible components R_0 and R_2 respectively, are plotted above and below the line. There are several remarkable features.

(1) There is a notable discontinuity in the disposition of the R_0 branch at $j_i = 12\frac{1}{2} : 13\frac{1}{2}$. (To avoid undue complication of the R_0 branch below this point a smooth line has been drawn in the case of the red band only.) The effect is very remarkable and occurs in the case of all the bands at precisely this value of j_i .

(2) The R_2 branch presents an anomaly of a different character, which appears to begin at about the same value of j_i as the above and may be related to it. The R_1R_2 interval gradually ceases to increase as j_i diminishes, and ultimately a coalescence of the R_1R_2 components takes place at about $j_i = 7\frac{1}{2}$. The deflection of the R_2 component in fig. 4 appears the most marked in the case of the blue band, and it would be of considerable interest to have information of the magnitude of this effect in the bands of still lower final vibrational quantum number.

(3) As in the case of the Swan bands for high j values, there is a more rapid approach of R_2 to R_1 than of R_0 to R_1 , ultimately, we may presume, resulting in a coalescence of the two components. In the Swan band λ 5165 this takes place at about $j_i = 50$. We may perhaps summarise this anomaly and the preceding one described in (2) by remarking that there appears to be much less permanency about the component branch which has j_i in the same sense as j_i .

(4) The variation of triplet width with vibrational quantum number is comparatively small, especially for the higher j_i values (excepting of course, the anomalous region below $13\frac{1}{2}$ of the R_2 branch). The graph of triplet width for the (0, 0) Swan band in fig. 4 would thus be but little different for the (0, 1), (0, 2), etc., bands. It will be observed that the triplet width in the H.P. carbon bands is greater than that of the Swan bands. These observed triplet widths represent, as we see from fig. 3, the difference between the triplet separations of the initial and final electronic states. We should anticipate this feature as a consequence of the regular diminution in triplet width for the higher excited 3P levels. Now there is good reason to believe, as Mulliken* has

* 'Phys. Rev.', vol. 32, p. 186 (1928).

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indicated, that both the normal and the initial Swan states of the molecule are *inverted* 3P states. This is discussed fully in the concluding part of the present paper. It is not, however, possible to draw any conclusion from the previous observation of the relative triplet widths in the two band systems as to the character (normal or inverted) of the initial 3P level of the H.P. system. On either hypothesis plausible values of the triplet separations can be constructed for the three known electronic states. We mention here, however, that other considerations based on the construction of the C_2 molecule have led us to the conclusion that the initial H.P. level is a *normal* state, and contrasts in this respect with the other two. The rotational transitions giving rise to the H.P. bands are thus of the type shown in fig. 5.

(5) In fig. 4 in the unperturbed parts of the R branches (between about $j_i = 13\frac{1}{2}$ and $19\frac{1}{2}$) it is of interest to compare the magnitude of the stagger in *triplet width*, in the case of the H.P. bands and the Swan bands. Although this is not, as far as we can see, directly correlated with the positional staggering of the triplets, nevertheless its magnitude is probably an indirect indication of the magnitude of the σ -type doubling (*i.e.*, of the A-B sub-state separation) in the three electronic levels. The observed stagger represents

the difference of these two separations for the initial and final states of that particular system. As the magnitude of the effect is greater in the H.P. bands than in the Swan bands (*vide* fig. 4), it follows that the AB sub-state separation is considerably less for the initial state of the H.P. system than for the initial state of the Swan system. It is therefore probable that the latter is also smaller than the separation in the ground state.

The Structure of the C_2 Molecule.

In an important new series of papers by Mulliken* (based on the previous fundamental work of Hund†) we have laid for us the foundations of a detailed

* 'Phys. Rev.,' vol. 32, p. 186 (1928), and vol. 32, p. 761 (1928).

† 'Z. Physik,' vol. 36, p. 657 (1926); vol. 37, p. 742 (1927); vol. 42, p. 93 (1927), and vol. 43, p. 805 (1927).

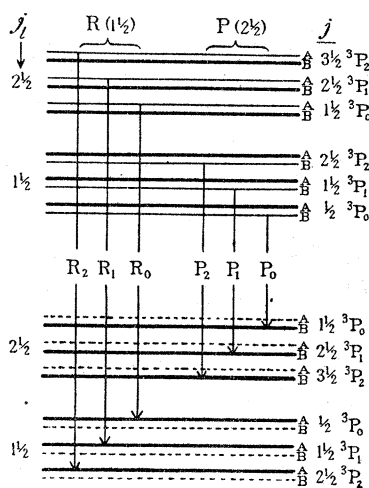


FIG. 5.—Rotational Transitions in a typical H.P. Carbon Band.

knowledge of the structure of diatomic molecules. By such detailed knowledge we mean the values of n_r , l_r , σ_r , and s_r ($= \frac{1}{2}$) for each electron of the molecule, together with the resultant l , σ , and s of the molecule as a whole. The methods which have been developed by Hund and Mulliken make use of band spectra data such as the evidence of fine-structure analysis, energy of dissociation, multiplet widths, and excitation potentials, and involve the important basic principles applied by Hund to line spectra, and an extended application of the Pauli principle to the "united atom." This work is difficult to summarise and reference should be made to the original papers. We proceed here to deal specifically with the C_2 molecule. We must derive three different electronic structures which all give 3P states and for which the two known transitions are possible and in accordance with the selection rule $\Delta l_r = \pm 1$. Our knowledge of adjacent molecules CN, N_2 , and CO, must lead us to anticipate that these particular transitions will be of the right energy order. It must be shown that the molecule can be synthesised from two carbon atoms in low-lying states, and conversely, the vibrational energy of dissociation of the molecule in these three electronic states must be consistent with the states of the two carbon atoms from which it can be built. Finally, we should be able to account for the peculiar experimental conditions (high pressure carbon monoxide) which seem to be necessary for the formation of one of the 3P states of the C_2 molecule.

Table VI.—States of the Carbon Atom.

(1) State without field.	(2) State with field.	(3) Detailed configuration with field.	(4) Component states in each configuration.	(5) Configura- tion summary.
3P	$\left\{ \begin{array}{l} {}^3SP \\ {}^3P_{r_n} \end{array} \right.$	$(1s^s)^2 (2s^s)^2 (2p^f)^2$	(3) $\sigma_l = 0, \sigma_s = 1, 0, -1$	s^4p^2
		$(1s^s)^2 (2s^s)^2 (2s^f)(2p^f)$	(6) $\sigma_l = \pm 1, \sigma_s = 1, 0, -1$	s^5p
1D	$\left\{ \begin{array}{l} {}^1SD \\ {}^1PD \\ {}^1DD \end{array} \right.$	$(1s^s)^2 (2s^s)^2 (2s^f)^2$	(1) $\sigma_l = 0, \sigma_s = 0$	s^6
		$(1s^s)^2 (2s^s)^2 (2s^f)(2p^f)$	(2) $\sigma_l = \pm 1, \sigma_s = 0$	s^5p
		$(1s^s)^2 (2s^s)^2 (2p^f)^2$	(2) $\sigma_l = \pm 2, \sigma_s = 0$	s^4p^2
1S	${}^1S^S$	$(1s^s)^2 (2s^s)^2 (2p^f)^2$	(1) $\sigma_l = 0, \sigma_s = 0$	s^4p^2

In Table VI are given some data of the carbon atom. The three lowest states of the atom are known to be 3P , 1D , and 1S , rising in the order given. These arise from the carbon atom $(1s)^2(2s)^2(2p)^2$. In column 2 are given the incipient states of the molecular type which are inherent in the atom when

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placed in an electric field. From these can be inferred the detailed electronic configurations which give rise to them, by using the data of Table I in Mulliken's paper. Details of these configurations are given in column 3. Column 4 gives the number of component states for each configuration class. In column 5 is Mulliken's brief and convenient summary of the configuration data of column 3. This latter description of the quasi-molecular state of the "atom in the field" is adequate for many purposes, inasmuch as when the molecule is formed by bringing close together two such atoms (the strong inter-nuclear field then replacing the artificial electric field) the molecular configuration class is simply obtained by addition of these data. This is the σ_r conservation rule. We cannot, however, deduce the *detailed* structure of the molecule by merely adding the two appropriate rows of column 3. The Pauli restriction principle limits the number of electrons in the molecule of any given type, and to form the molecule, "promotion" of some of the electrons is necessary. This convenient term is employed by Mulliken to indicate a forced increase of the principal quantum number of an electron (accompanied, of course, by an appropriate change $\Delta l_r = \pm 1$ in l).

Mulliken's view of the structure of the C_2 molecule in its ground state and in the initial Swan state is as follows:—

$$\left. \begin{array}{l} \text{Ground State : } (1s^s)^2 (2s^p)^2 (2s^s)^2 (3s^p)^2 (2p^p)^3 (3s^s) : {}^3P_i^P \\ \text{Initial Swan State : } (1s^s)^2 (2s^p)^2 (2s^s)^2 (3s^p) (2p^p)^3 (3s^s)^2 : {}^3P_i^D \end{array} \right\} \quad (6)$$

The electron types are given in the order which experimental evidence shows to be that of diminishing energy of binding. The characteristic $(2p^p)^3$ group, which requires one more electron to complete the shell, is responsible for the inverted character of the triplet level. The molecule is assumed to be of the s^9p^3 type since this would give inverted 3P levels, rather than, for example, of the s^7p^5 type which would have normal 3P levels. This is because in the adjacent molecule CN there is definite evidence that (in contrast to the united atom) the 2P levels *are* inverted, and therefore must contain the group $(2p^p)^3$. The C_2 molecule given above in (6) can be constructed from carbon atoms in several different states. We have selected from Table VI those pairs of atomic states which will give a s^9p^3 molecule in 3P molecule states, and have listed these in Table VII. (The molecular states are derived by compounding each pair of states of column 2.) Table VII is by no means a complete list of the pairs of atomic states which will provide a 3P molecular state. A considerable number of others can be derived from carbon atoms in excited states such as 3S , 1P , 3D , etc. The three states, ${}^3P_{0,1,2}$, 1D_2 and 1S

Table VII.—Synthesis of States of the C₂ Molecule.

Atom states without field.	Atom states with field.	Molecular states.
³ P + ³ P	³ P _g + ³ S ^P	¹ P, ³ P _g ⁱ , ^D , ⁵ P _g
³ P + ¹ D	³ S ^P + ¹ P ^D	³ P _g ⁱ , ^D , ^F
³ P + ¹ D	³ P _g + ¹ D ^D	³ P _g ⁱ , ^D , ^F , ³ F
³ P + ¹ S	³ P _g + ¹ S ^S	³ P _g ⁱ

are, however, the lowest states, and according to Fowler and Selwyn* their

term values (below the ionisation level) are $\left\{ \begin{array}{l} 91017.3 \\ 91002.5 \\ 90975.0 \end{array} \right\}$, 81312 and 69860 v.

All such pairs of atomic states from which the known ³P molecular states can be synthesised, are theoretically possible products of dissociation. The actual products can only be determined if the energy of dissociation (D) of the molecule is known for that particular state. The values of D are known for the ground state and the initial (Swan) state of the C₂ molecule. For the ground state D₀ = D = 7.02 volts, and as Mulliken suggests, it is reasonable to suppose that the products are two ³P atoms. For the initial (Swan) state the data are less reliable. D₀ has been given as 5.0 volts,† and from this D = 5.0 + 2.4 = 7.4 volts. Mulliken gives D₀ = 6.4 volts and from this D = 8.8 volts. It seems probable, however, as Mulliken suggests, that the dissociation products of the molecule in this state are a ³P and ¹D atom. From Fowler and Selwyn's data the ¹D state corresponds to an excitation of about v 9690 (= 1.2 volts) above the normal. In this case the best value of D for the initial (Swan) state is probably 7.0 + 1.2 = 8.2 volts, and hence D₀ should be 5.8 volts.

We shall now discuss the structure of the molecule in the initial H.P. state. We can theoretically derive an excited inverted ³P state of the C₂ molecule by displacing one of the (2sⁿ) electrons to the (3sⁿ) shell, but the energy to do this is probably far in excess of the excitation potential (3.61 volts) of the H.P. bands. Alternatively, we might imagine the outermost electron (3sⁿ) excited to (4sⁿ), but if so this type of transition is of the "optical" type rather than of the "X-ray" type (to which the Swan bands belong).

Incidentally, we may remark that most of the molecular electronic transitions

* 'Roy. Soc. Proc.,' A, vol. 118, p. 34 (1928).

† 'Phil. Trans.,' A, vol. 226, p. 181 (1927).

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discussed by Mulliken are described by him as of this "X-ray" type. This valuable conception seems to us to throw light on a puzzling feature associated with the terms of many molecules. If the ionisation potential v_i of the molecule is available, it is well known that the effective principal quantum numbers of the various terms can be deduced from $\sqrt{R/(v_i - v)}$. Now for molecular terms of the same type these quantum numbers are seldom found to differ by unity—as they should do if, as in atoms, the electronic terms are expressible by a Rydberg formula. We can thus say that if the effective principal quantum numbers of molecular terms increase by unity (as in He_2 , for example), this is evidence that the electronic transitions are of the atomic or "optical" type. But if, as is frequently the case, there is no simple relationship between the effective quantum numbers, it is evidence of the "X-ray" type of transition. There is, in fact, no simple meaning to be attached to the effective principal quantum number of the molecular term in these cases. The electronic transition giving the Swan bands, for example, is $(3s^s) \rightarrow (3s^p)$ involving a change in l_r only.

We are of the opinion that the structure of the C_2 molecule in the initial (H.P.) state is :

$$(1s^s)^2 (2s^p)^2 (2s^s)^2 (3s^p)^2 (2p^p)^2 (3s^s) (3p^d) : {}^3P_n^D. \quad (7)$$

This produces a *normal* 3P state, and the electronic transition giving the H.P. bands is $(3p^d) \rightarrow (2p^p)$. Details of the typical rotational transitions have already been given in fig. 5. Unfortunately the H.P. bands consist of one ($n' = 0$) progression only, and the vibrational energy of dissociation of the molecule in this state is not known. We suggest, however, that the dissociation products are possibly a 3P and a 1S atom, in which case we predict $D = 9.63$ volts, and hence $D_0 = 9.63 - 3.61 = 6.02$ volts.

The experimental conditions under which the H.P. bands are produced call for some discussion. We should be disposed at first sight to imagine that a C_2 molecule loaded with 3.61 volts energy could be produced in such gases as CO_2 , C_2N_2 , C_2H_2 , etc., as well as in CO . We incline to the opinion that the difference is found in the comparatively low resonance potentials of these gases. That of CH is 2.86 volts; that of CN is 3.18 volts. C_2 molecules of 3.61 volts energy would be unlikely in the presence of a large excess of such molecules as these which have lower excitation potentials. The inhibiting effect of traces of hydrogen, water-vapour, carbon dioxide, etc., in CO is explicable along these lines also. On the other hand the resonance potential of CO is 5.98 volts,* and C_2 molecules of 3.61 volts energy will be capable of

* Corresponding to the excitation of the Cameron bands.

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existence among these, inasmuch as collisions will be possible without loss of energy. The rôle of pressure in the production of the spectrum is more obscure.

The absence of a combination system between the initial H.P. level and the initial Swan level is in harmony with Hund's selection principle $\Delta l_r = \pm 1$ for symmetrical molecules. On this basis the ground state and two excited states have been classed as ${}^3P_i^P$, ${}^3P_i^D$, and ${}^3P_n^D$.

It is scarcely necessary to add in conclusion that there remain a vast number of problems to which theory at present gives no answer. It is, for example, remarkable that of the theoretically possible C_2 molecules which may be constructed from the data of Table VI: s^8p^4 , s^9p^3 , $s^{10}p^2$, etc., we should only have spectroscopic evidence of one of these, and that in this molecule (s^9p^3) only the 3P state is found out of the possibilities 3P , 3S , 3F , 1P , 1F , 5P . Such problems as these will require a fuller understanding of molecular structure.

Summary.

(1) The conditions of production of the high pressure carbon system and the Swan system are discussed. Both these systems are due to a C_2 molecule.

(2) Four new H.P. bands have been found in the near ultra-violet, and two more in the near infra-red. These, with the known bands, form a single vibrational progression ($n' = 0$), and the H.P. system and the Swan system are found both to represent transitions to a common final state.

(3) The fine-structure of the H.P. bands (0, 4), (0, 5), (0, 8) and (0, 9) has been investigated. The bands consist of P and R branches only, and the electronic transition involved is ${}^3P_n^D \rightarrow {}^3P_i^P$.

(4) Detailed examination of the structure of the R branches of these bands has revealed several anomalies and perturbations of an unusual type.

(5) The methods employed by Hund and Mulliken for the elucidation of molecular structure are summarised, and Mulliken's application to the C_2 molecule has been extended to cover the initial state of the H.P. system. This is believed to be a *normal* 3P level and different in this respect from the two lower 3P levels which are believed to be inverted.
