The Third Positive Carbon and Associated Bands

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In conclusion, the writer would like to express her gratitude to Prof. Richardson for suggesting this problem and for interest and advice during the experiments.

Summary.

The effect of oxidation on the total soft X-ray emission from the following elements has been studied : Silicon, manganese, iron, cobalt, nickel, copper, molybdenum, palladium and tungsten. The efficiencies are levelled up after oxidation, and this suggests that the efficiency of the oxide is the average efficiency of the oxygen and element present. On this assumption, the efficiency for oxygen is calculated and its mean value is at 600 volts, $3 \cdot 61 \times 10^{-6}$ at 500 volts, $3 \cdot 15 \times 10^{-6}$, at 400 volts, $2 \cdot 82 \times 10^{-6}$, at 300 volts, $2 \cdot 06 \times 10^{-6}$.

The Third Positive Carbon and Associated Bands.

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[PLATE 3.]

Introduction.

The band spectra associated with carbon are numerous and many of then were known to the earliest workers in spectroscopy.* They divided the bands into two main divisions, the positive and the negative bands. Thus they recognised the first positive carbon bands which are now called the Swan bands, the second positive bands which we now call the Ångström bands, the third positive and the fourth positive carbon bands. Among the negative bands known to them were the first negative or Deslandres' bands which are now known to be due to the ionised CO (CO^+) molecule. With the exception of the first positive bands or Swan bands, all the positive bands are now attributed to the neutral CO molecule. In recent years several new band systems have been added to the positive list,† and two, the comet-tail bands or low pressure

* Kayser, ' Handbuch der Spectroscopie,' vol. 5, pp. 226–234.

† Cameron, ' Phil. Mag.,' vol. 1, p. 405 (1926) ; Hopfield and Birge, ' Phys. Rev.,' vol. 29, p. 922 (1927) ; Asundi, ' Nature,' vol. 123, p. 47 (1929) ; Johnson and Asundi, ' Roy. Soc. Proc.,' A, vol. 123, p. 560 (1929) ; Herzberg, ' Z. Physik,' vol. 52, p. 825 (1929).

carbon bands,* and the Baldet-Johnson combination bands,† to the negative band systems. The history of the correlation of all these band systems is an interesting one and is adequate proof of the extraordinary usefulness of the quantum theory in the interpretation of molecular spectra. In this paper we are mainly concerned with the third positive carbon bands and such other bands as are usually associated with them.

These bands‡ were originally measured by Deslandres. Wolter could not obtain some of them which therefore were considered as spurious. Johnson and Birge gave the quantum interpretation of these bands, which fell into three n'' progressions, viz., $n' = 0$, 1 and 4, the last two being spurious according to Wolter. Duffendack and Fox proved that the bands forming the $n' = 4$ progression belong to a new system of bands which they called 3A, with an initial electronic level higher than that of the third positive bands. All these bands have been obtained on all the plates taken in the first order of a 21-foot Rowland grating, by the present writer. The superficial structure of all the bands forming the same n'' progression is the same but differs from the structure of the rest of the bands. It is therefore suggested that the bands forming the $n'' = 1$ progression also arise from an initial electronic level different from that of the third positive bands. These may be called the 5 B bands. It is scarcely necessary to say that all these band systems have the same final electronic level.

By the discovery due to Cameron (*loc. cit.*) in 1926 of some new bands in the ultra-violet, in a tube containing CO in high pressure neon, and their quantum interpretation by Johnson (*loc. cit.*), who showed that the initial and the final electronic levels of these bands were respectively identical with the final of the third positive and the final of the fourth positive carbon bands, the emitter of all these bands has been conclusively proved to be the CO molecule. Related to these bands has been discovered a new band system described later in this paper, which has the same final state as all these bands and an initial state which is identical with the new level at $\nu = 58927$, found by Hopfield and Birge (*loc. cit.*).

The final electronic level which is common to all these band-systems of the CO molecule is generally believed to be a ^3P level. The Cameron bands are

* Pluvinet and Baldet, ' Astrophys. J.,' vol. 34, p. 89 (1911) ; Fowler, ' Monthly Notices, R.A.S.,' vol. 70, p. 484 (1910) ; Johnson, ' Roy. Soc. Proc.,' A, vol. 108, p. 343 (1925).

† Johnson, *loc. cit.* ; Baldet, ' C. R.,' vol. 178, p. 1525 (1924).

‡ Deslandres, ' C. R.,' vol. 106, p. 842 (1888) ; Wolter, ' Z. Wiss. Phot.,' vol. 9, p. 361 (1911) ; Johnson, ' Nature,' vol. 117, p. 376 (1926) ; Birge, ' Phys. Rev.,' vol. 28, p. 1175 (1926) ; Duffendack and Fox, ' Nature,' vol. 118, p. 12 (1926).

five-headed and Johnson (*loc. cit.*) found that the electronic separations between successive heads are almost the same as the separations between corresponding heads of the third positive bands, if the second head of the latter bands is disregarded. This indicated that the level in question might be a quintet level. Birge (*loc. cit.*), however, took exception to this view. He believed that the level was a triple level; that the six heads of the third positive bands were due to three P and three Q branches; that in the Cameron bands the first Q head was missing; and that the equality of electronic separations indicated by Johnson was fortuitous. On Birge's assumption that the second, fourth and sixth heads of the third positive bands are Q heads, it is necessary that the electronic separation between the fourth and second heads should be the same for all bands of the third positive carbon and Cameron systems, as also the separation between the sixth and the fourth heads. These separations are tabulated below :—

Band.	Third positive.				Cameron.
	4–2.		6–4.		6–4.
	Wolter.	Asundi.	Wolter.	Asundi.	
0–0	43·7	42·5	48·4	48·5	—
0–1	40·2	39·7	49·2	48·3	—
0–2	37·8	37·6	47·1	46·8	—
0–3	34·2	34·8	46·6	45·9	48·1*
0–4	32·8	32·7	47·0	45·2	48·1*

* Mean value from five bands of the same sequence.

The table shows that whereas the difference 6–4 is fairly constant throughout all the bands, the maximum difference between two values being 3·3 v, the difference 4–2 is far from being constant, changing as it does by about 10 v. Moreover, the distance of each band head from its origin should ordinarily be roughly constant in all the bands of the same system. This will hardly be the case on this interpretation. Birge has entered into a detailed consideration of this point (*loc. cit.*) and concludes that this need not be taken as a serious objection since a similar discrepancy is said to be observed in the case of red CN bands by Mulliken. The fine structure analysis of the third positive bands given in this paper, however, points to the level being a quintet one, so that the five heads of the Cameron bands are all R heads, and the rough equality of the electronic separations observed by Johnson is what one would expect on this

view, if the distance of heads from origins is fairly constant. The following table gives the unweighted mean values from all bands, of the electronic separations between successive heads on this basis, and the mean value of the true electronic separations between successive origins of the quintet level, as determined from the analysis of the 0–0 and 0–1 third positive bands.

| Heads. | Cameron. | Third positive. | | True mean value from origins. |
		Wolter.	Asundi.	
1–2	37·3*	29·6	30·6	29·5
2–3	18·9	20·0	20·0	19·9
3–4	18·0	19·9	18·8	20·8
4–5	29·2	27·7	28·4	29·8

* This value is likely to be much in error since the first two heads of these bands are very faint.

This table shows the rough equality of intervals in the Cameron and third positive bands. It also shows that the distance of each band head from its origin is roughly constant. As a matter of fact, if the second and third heads in the 0–0 and 0–1 bands, where, as the fine structure analysis also indicates, there is much crowding together of unresolved lines, are not taken into consideration, this distance is about $8 \cdot 6$ ν, comparable with the value $7 \cdot 7$ ν from Ångström* or the new bands† $(3\,^1S \rightarrow 2\,^1P)$. In the third positive bands, therefore, only the second head is a Q head all the rest being P heads. It is just a matter of chance that this Q branch alone out of the five Q branches forms a head; for it is a surprising fact that in the spectra of the neutral CO molecule no other Q branch forms a head. The Ångström bands, the new $3\,^1S \rightarrow 2\,^1P$ bands, the fourth positive bands, all contain strong Q branches but in none of them do they form heads.

Production of the Bands.

The production of these bands is exceedingly simple. Any ordinary discharge tube containing CO or CO_2, when excited by an uncondensed discharge will show these bands. In these experiments a H type tube having a small capillary was used. It has carbon electrodes, a mirror on one end and a quartz window at the other. A small bulb containing magnesite was attached to the tube and this was gently heated to give the necessary CO_2 in the tube whenever required. The tube was arranged in an end-on position and the light was

* Huithen, 'Ann. Physik,' vol. 71, p. 41 (1923).
† Johnson and Asundi, *loc. cit.*

focussed by a quartz lens on to the slit of the instrument. The third positive and the associated bands were photographed in the first order of a 21-foot Rowland grating. This grating has a dispersion of 2·6 Å. per millimetre in the first order. Wolter has photographed the 0–1 band in the second order of a similar grating. On comparing the present measurements of this band taken in the first order, with those recorded by him, it was found that there is very good agreement among them and that no line measured by him up to about 35 Å. from the first head has been missed in these plates. Measurements were made on two independent plates and they agreed to 0·02 Å. The exposures necessary were about 7 hours for all except some 3 A bands. The temperature of the sub-basement room in which the grating is mounted in a suitable case, did not alter by more than 0·1° C. during the exposure. For comparison the international standards of the iron arc spectrum were used. The new bands previously mentioned lie in the near infra-red and the visible region. These were photographed on a glass c.d. instrument having a dispersion of about 150 Å. per millimetre in the region 7000–9000 $\lambda\lambda$, and of about 60 Å. between 5000–7000 $\lambda\lambda$. Neocyanine and kryptocyanine plates hypersensitised by ammonia before use were employed.

Third Positive Carbon Bands.

These bands extend from λ 2825 to λ 3493 and consist of only one n'' progression. The bands are apparently six-headed the overall multiplet width being 102·5 ν for the 0–0 band with a marked tendency to decrease with higher vibrational states, so that for the 0–4 band this value is 91 ν. The bands are very intense and apart from the complexity of structure due to the many heads, are just as simple to resolve as the Ångström bands. Wolter's observation that there is a repeated alternation of intensity in the structure of the bands is not exactly correct. A repeated rise and fall of intensity is no doubt observable in the reproduction of the 0–1 band given by Wolter. It is due to the fact that just where the structure lines of this band fade away, the 5 B band beginning at λ 2930 starts and the three or four heads of this band give an impression of such intensity distribution. The 5 B band at λ 2930 is comparatively weak but its heads are stronger than the fading structure lines of the third positive band. Such sort of repeated rise and fall of intensity due to proximity of complicated bands is more striking when one tries to photograph the new bands described in this paper on a high dispersion instrument like the grating used in these experiments. There is, however, one peculiarity associated with the third positive bands which does not seem to have been

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observed by previous workers.   These bands as is well known are degraded to
the violet, but outside the first head there are a number of structure lines which
decrease in spacing towards the higher wave-lengths forming ultimately a faint
diffuse head, after which they continue further with gradual increase in spacing.
These are very faint but they seem to accompany all the third positive bands.
We cannot at present say whether they form part of these bands.   No attempt
has been made in the present paper to explain them.   The fine structure
analysis of only the 0–0 and 0–1 bands has been done, and therefore it has not
been possible to give a vibrational equation representing the origins.   The
following equation is based on the values of the heads, ω_0 and $\omega_0 x$ being
deduced from the mean values of the five intervals from band to band :—

$$\nu = \left.\begin{array}{c} 35287\cdot0 \\ 323\cdot4 \\ 341\cdot4 \\ 359\cdot2 \\ 389\cdot5 \end{array}\right\} - (1726\cdot5\,n'' - 14\cdot4\,n''^2).$$

The following table gives the heads arranged according to vibrational
analysis :—

n'' n'	0.		1.	
	λ (air).	ν (vac.).	λ (air).	ν (vac.).
0	2833·08 (7)	35287·0	2977·38 (7)	33576·8
	30·15 (10)	323·4	74·49 (10)	609·5
	28·73 (9)	341·4	72·86 (9)	628·1
	27·28 (8)	359·2	71·16 (5)	647·1
	24·86 (8)	389·5	68·57 (7)	676·5
	2.		3.	
0	3134·35 (7)	31895·3	3305·66 (7)	30242·5
	31·47 (10)	924·6	02·76 (8)	269·7
	29·51 (9)	944·6	00·51 (6)	289·7
	27·68 (5)	963·3	3298·43 (5)	308·7
	24·94 (5)	991·4	95·52 (5)	335·6
	4.			
0	3493·31 (5)	28618·0		
	90·44 (4)	641·6		
	87·73 (9)	663·8		
	85·36 (3)	683·2		
	82·23 (5)	709·0		

The figures in brackets indicate estimated intensity.

3 A *Bands.*

These bands are five-headed. But they are very faint and could be photographed only after long exposures. Moreover, the absorption of rays by air becomes pronounced in these bands so that the 0–0 band could only be photographed with an exposure of 30 hours on the grating. The fifth head is the strongest with estimated intensity 5 and the first head has an intensity 2. Therefore under low dispersion they appear to be double-headed.* The electronic separation between the two extreme heads is 70 ν for the 0–0 band with a tendency, as in the third positive bands, to decrease with higher vibration states, the 0–4 band having a value 65 ν. The quantum analysis of the gross structure of these bands is tabulated below :—

n'' / n'	0.		1.	
	λ (air).	ν (vac.).	λ (air).	ν (vac.).
0	2295·9 (0)	43542·5	2389·75 (2)	41832·6
	—	—	88·95 (1)	846·7
	—	—	88·51 (1)	854·3
	—	—	86·95 (2)	881·7
	2292·22 (3)	43612·4	85·89 (5)	900·3

	2.		3.	
0	2489·94 (2)	40149·6	2596·93 (2)	38495·5
	89·07 (0)	163·7	95·94 (1)	510·2
	88·69 (0)	169·7	—	—
	87·11 (1)	195·1	93·84 (0)	541·4
	85·81 (5)	216·2	92·56 (5)	560·4

	4.			
0	2711·40 (2)	36871·0		
	10·25 (2)	886·0		
	—	—		
	2708·09 (0)	36915·0		
	06·59 (5)	935·9		

The equation representing the heads is :—

$$\nu = \left.\begin{array}{c} 43542\cdot5 \\ \overline{} \\ \overline{} \\ \overline{} \\ 43612\cdot4 \end{array}\right\} - (1726\cdot5\, n'' - 14\cdot4\, n''^{2}).$$

* Duffendack and Fox, 'Astrophys. Journ.,' vol. 65, p. 220 (1927).

The final state is thus identical with that of the third positive bands. The overall electronic separation for the 0–0 band is 69·9 ν, while the corresponding separation in the third positive band is 102·5 ν. There is thus a shrinkage of 32·6 ν, which can be explained on the assumption that the transition involved is $^5P \rightarrow {}^5P$. On this basis the overall $\Delta\nu$ for the higher ^5P level will be 32·6. Just as in the case of $^2P \rightarrow {}^2P$ or $^3P \rightarrow {}^3P$ transitions the Hund selection rule $\Delta\sigma s = 0$ is obeyed here also, as a result of which there are only five heads.

5 B *Bands*.

These bands also degrade towards the violet and are more intense than the 3 A bands. They are also undoubtedly five-headed but in each of the bands one or other of the heads is missing, probably being confused with other lines and therefore not prominently observed. Outside the third head, which is the first observed of the 0–0 band, there is a double-headed band, probably due to CO_2, degraded towards the red and it is likely that the first two heads of the 5 B band are masked by the structure work of this extraneous band. The following table gives the vibrational analysis of these bands :—

n'' \ n'	0.		1.	
	λ (air).	ν (vac.).	λ (air).	ν (vac.).
0	—	—	2793·07 (6)	35792·9
	—	—	—	—
	2661·87 (8)	37556·4	2789·11 (6)	843·3
	60·42 (8)	577·0	87·37 (8)	865·5
	58·80 (6)	599·8	85·80 (6)	885·8
	2		**3.**	
0	2930·76 (3)	34110·9	3079·90 (8)	32459·2
	29·25 (3)	128·5	78·40 (2)	475·0
	—	—	75·73 (4)	503·2
	24·86 (2)	179·7	73·49 (6)	526·9
	—	—	—	—
	4.		**5.**	
0	3242·14 (8)	30835·0	3419·17 (6)	29238·5
	40·69 (6)	848·8	17·49 (6)	252·9
	37·74 (6)	876·9	14·65 (4)	277·2
	35·18 (8)	901·3	11·52 (3)	304·1
	—	—	—	—

Figures in brackets indicate estimated intensity.

The following equation represents the heads satisfactorily :—

$$\nu = \left. \begin{array}{r} \text{—} \\ \text{—} \\ 37556\cdot4 \\ 577\cdot0 \\ 599\cdot8 \end{array} \right\} - (1726\cdot5 \; n'' - 14\cdot4 \; n''^2).$$

The electronic separation between the first and fourth heads is about 67 ν very nearly the same as in the third positive bands (68·3). The final state is the same as that of these latter bands. It seems likely from this equality of electronic separation that the upper level is either a D or S level. Of course it may be argued that these bands really constitute the $n' = 1$ progression of the third positive bands. But though their fine structure analysis has not been attempted by the writer, still he is inclined to the view that because their superficial structure is different from that of the third positive bands, they form a new system by themselves.

New Bands.

A number of bands degraded towards the red have been photographed under small dispersion, and their wave-lengths determined by the measurement of three independent plates. These bands are of a complex structure probably having five heads ; but under the low dispersion used it has been possible to measure only the two extreme heads with any certainty. Some of these bands could be identified with the triplet carbon bands of Merton and Johnson.[*] It was therefore thought that the rest of the bands also belonged to the triplet system. But they could not be arranged on that basis. The intensity of the triplet bands as produced here is very weak as compared to their intensity when produced in helium or argon. The triplet band at λ 6464·6 which has an intensity 10 in helium, has an intensity of only 2 as produced here. Other triplet bands were so mixed up with the rest of the bands that it has not been possible to effect a complete separation of the bands of the two systems below λ 5700. The bands of wave-lengths higher than λ 5700 have been separated and it has been possible to give the following vibrational analysis, assuming the band at λ 8592 to be the 1–0 band.

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

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n' \ n''	0.		1.		2.		3.	
	λ (air).	ν (vac.).	λ (air).	ν (vac.).	λ (air).	ν (vac.).	λ (air).	ν (vac.).
1	8592	11636						
2	7833·9 88·0	12761·8 674·0						
3	7210·4 57·0	13864·5 776·0	8222·5 81·0	12158·5 072·5				
4	6685·7 6726·3	14953·2 ·862·9	7552·5 98·0	13237·0 157·7				
5	6244·0 75·0	16011·0 15931·8	6990·2 ——	14301·8 ——				
6	5861·0 89·0	17057·2 16976·1	6513·5 51·0	15348·5 260·6	7314·0 59·0	13668·4 13585·1		
7			6105·2 ——	16375·0 ——	6804·0 41·5	14693·2 612·7		
8			5749·1 75·9	17389·2 17308·5	6366·9 ——	15702·0 ——	7116·5 ——	14048·0 ——

The equation representing these band heads is :—

$$\nu = 10491 + (1154\cdot4\, n' - 9\cdot5\, n'^2) - (1721\cdot5\, n'' - 13\cdot7\, n''^2).$$

Hopfield and Birge (*loc. cit.*) have discovered a new level at 58927 ν, for the CO molecule. Assuming a transition to exist between this as the initial level and the final level (48438 ν) of the third positive carbon bands as the final level it will give rise to bands whose heads can be represented by

$$\nu = 10489 + (1155\, n' - 9\, n'^2) - (1726\cdot5\, n'' - 14\cdot4\, n''^2).$$

The equation representing the new bands is very close to this. There is a possibility of considerable error in the measurement of the bands of higher wave-lengths because the dispersion of the instrument falls rapidly in that region. Therefore the discrepancy between the two equations may be taken to be within the limits of experimental error. Experiments are in progress using instruments of higher dispersion and a detailed account of this band system must therefore be reserved for a future communication.

Fine Structure of the Third Positive Carbon Bands at $\lambda\lambda$ 2833 *and* 2977.

The structure of these bands is very complicated there being no obvious

regularity such as we find in less complicated bands. This arises from the fact that each band consists of five P, five Q and five R branches. At first sight it seemed almost a hopeless task to analyse the bands from plates taken in the first order of the grating, but subsequent measurements of the plates showed that in the case of the band at λ 2977, even the second order measurements recorded by Wolter in no way simplify the task. This indicated that the complexity of structure may not be avoided even if the third order of the grating was used. This, coupled with the fact that no line recorded by Wolter was missed in the λ 2977 band, on the first order plates, led me to attempt an analysis of the bands on the data of the first order plates. Measurements were taken on two independent plates and they agreed to $0\cdot02$ A. This introduces an error of $0\cdot2$ to $0\cdot3$ cm.$^{-1}$ in the absolute measurements.

Each band consists of five sub-bands. The first high frequency band will be called the $^5P_1$ band, the second $^5P_2$ band and so on. Each of these consists of a P, a Q and R branch, the intensity distribution being $Q > P > R$, thus indicating that the transition involved is an $S \to P$.* On account of the complexity of structure and the crowding together of lines in all except the $^5P_5$ bands, it is not possible to say with certainty how many lines are missing in each sub-band. Therefore an evaluation of σ on this basis is out of the question and consequently the theoretical significance which arises out of a knowledge of the values of σ accompanying a transition, is unfortunately not forthcoming.

Table I gives the wave-number data of all the 15 branches and the initial term differences in each of the two bands analysed. The initial term differences should be the same for the same sub-band in the two bands analysed, though theoretically they may differ in values from the initial term differences for the other sub-bands. But this change in the value of the term differences both in the initial and final states is so small for the different sub-bands, that we have assumed it to be negligible. So that in Table II are collected the initial term differences for all the 10 sub-bands and their weighted mean. Table III similarly gives the final term differences and their weighted means for the two bands.

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* Mulliken, ' Phys. Rev.,' vol. 29, p. 410 (1927).

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Table I.

Note.—The letter D before a line indicates that the line is a close double, d a diffused line, and b a blend with another line.

Band at $\lambda\, 2833$.

j''.	P.		Q.		R.
			$^5P_5$.		
1·5	35295·6	2·8	35298·4d		—
2·5	292·9	7·6	300·5	12·3	35312·8
3·5	290·9	11·9	302·8	16·6	319·4
4·5	289·3	15·8	305·1d	21·0	326·1
5·5	287·8	20·9	308·7	24·6	333·3
6·5	287·0d	25·8	312·8	30·1	342·9D
7·5	287·0	30·1	317·1	34·3	351·4b
8·5	287·0	34·5	321·5	38·8	360·3b
9·5	287·8	39·0	326·8	43·8	370·6d
10·5	289·3	44·0	333·3D	—	—
11·5	290·9	47·1	338·0	52·2	390·2b
12·5	292·9	52·4	345·3	56·5	401·8D
13·5	295·6	57·0	352·6	60·5	413·1
			$^5P_4$.		
1·5	35325·3	3·2	35328·5	7·8	35336·3
2·5	324·2	6·8	331·0	13·1	344·1D
3·5	323·4	—	—	—	—
4·5	323·4	16·8	340·2	20·1	360·3b
5·5	323·4	20·7	344·1b	26·5	370·6d
6·5	323·4	25·4	348·8	30·3	379·1D
7·5	324·2	29·6	353·8b	—	—
8·5	325·3	33·9	359·2b	38·9	398·1b
9·5	326·8	38·4	365·2D	—	—
			$^5P_3$.		
2·5	35342·9D	6·9	35349·8		
3·5	341·4	12·4	353·8b	16·8	35370·6d
4·5	341·4	16·3	357·7	21·4	379·1D
5·5	343·7	21·5	365·2D	26·0	391·2b
6·5	344·1D	26·5	370·6d	30·5	401·1
7·5	346·5	29·7	376·2	34·4	410·6D
8·5	348·8	35·2	384·0b	39·0	423·0
9·5	351·4b	39·8	391·2b		
10·5	354·4	43·7	398·1b		

Table I—(continued).

Band at λ 2833.

j''.	P.		Q.		R.
			$^5P_2$.		
6·5	35359·2b	24·8	35384·0b	30·9	35414·9b
7·5	360·3b	29·9	390·2b	34·9	425·1D
8·5	361·8	35·1	396·9	38·8	435·7b
9·5	—	—	—	—	—
10·5	365·2D	—	—	—	—
11·5	367·5	48·8	416·3	51·6	467·9
12·5	370·6d	—	—	—	480·6
13·5	374·4	57·1	431·5b	61·5	493·0
			$^5P_1$.		
4·5	35391·2b	16·1	35407·3	20·2	35427·5
5·5	390·2b	20·4	410·6	25·1	435·7b
6·5	389·5	25·4	414·9b	—	—
7·5	389·5	29·9	419·4	34·9	454·3
8·5	391·2	33·9	425·1D	38·9	464·0
9·5	392·7	38·8	431·5b	43·7	475·2
10·5	394·9	43·6	438·5	—	—
11·5	398·1b	47·9	446·0	52·9	498·9
12·5	401·8D	52·6	454·4		
13·5	406·3	56·4	462·7		
14·5	410·6D	61·3	471·9		

Band at λ 2977.

j''.	P.		Q.		R.
			$^5P_5$.		
1·5	33585·3	3·0	33588·3		
2·5	582·7	7·7	590·4	12·0	33602·4
3·5	580·6	11·9	592·5	17·0	609·5b
4·5	578·9	16·2	595·1	21·5	616·6b
5·5	577·6	20·9	598·5	25·6	624·1b
6·5	576·8	25·6	602·4	30·3	632·7D
7·5	—	—	606·5	34·8	641·3b
8·5	576·8	34·5	611·3b	—	—
9·5	577·6	39·0	616·6b	43·8	660·4b
10·5	578·9	43·5	622·4D	48·0	670·4b
11·5	580·6	47·5	628·1	—	—
12·5	582·7	52·2	634·9D	57·2	692·1
13·5	585·3	56·8	642·1		

Table I—(continued).

Band at λ2977.

j''.	P.		Q.		R.
			$^5P_4$.		
1·5	—	—	33616·6b	7·5	33624·1b
2·5	33611·3	8·0	619·3	—	—
3·5	610·5	11·9	622·4D	16·0	638·4D
4·5	609·5b	16·4	625·9	20·8	646·7
5·5	609·5	20·4	629·9	24·5	654·4
6·5	610·5	24·4	634·9D	30·0	664·9
7·5	611·3b	30·0	641·3b	34·0	675·3
8·5	612·9	34·2	647·1	38·9	686·0b
9·5	614·6	39·1	653·7b	43·4	697·1D
10·5	616·6	43·8	660·4b		
11·5	619·3				
12·5	622·4D				
			$^5P_3$.		
2·5	33630·8	7·6	33638·4D		
3·5	629·2	12·1	641·3b	16·8	33658·1
4·5	628·1	16·9	645·0	21·5	666·5
5·5	—	—	649·1d	26·1	675·2
6·5	—	—	653·7b	30·0	683·7
7·5	628·1	30·0	658·1	34·9	693·0
8·5	629·2	34·3	663·5	39·6	704·1D
9·5	630·8	39·6	670·4b	43·6	714·0b
10·5	632·7	43·8	676·5	48·0	724·5b
11·5	634·9D	47·7	682·6b	52·7	735·3
			$^5P_2$.		
6·5	33647·1	24·8	33671·9	29·3	33701·2b
7·5	649·1d	30·7	679·8d	34·2	714·0b
8·5	652·2	33·8	686·0b	38·5	724·5b
9·5	656·3	38·6	694·9b	42·6	737·5
10·5	660·4b	43·7	704·1D	47·9	752·0D
11·5	665·0	47·1	712·1d		
12·5	670·4b	52·1	722·5		
13·5	676·5				
			$^5P_1$.		
4·5	33677·6	15·9	33693·5	20·5	33714·0b
5·5	676·5	20·6	697·1D	25·4	722·5
6·5	676·0	25·2	701·2b	28·9	730·1
7·5	676·5	29·5	706·0	33·7	739·7
8·5	677·6	34·5	712·1d	39·9	752·0D
9·5	679·8d	39·0	718·8	42·8	761·6
10·5	682·6b	43·7	726·3	—	—
11·5	686·0b	48·1	734·1	52·7	786·8
12·5	690·2	52·6	742·8	—	—
13·5	694·9b	57·1	752·0	61·2	813·2
14·5	700·1	61·5	761·6	65·2	826·8

Table II.—Initial Term Differences. $\Delta F'j$.

j'	0–0 band.										0–1 band.									Weighted mean.
0·5	2·8										3·0									3·0
1·5	7·6										7·7									7·6
2·5	11·9			3·2							11·9		7·6							12·1
3·5	15·8	12·3		6·8			7·8			16·8	16·2	12·0	12·1	8·0	7·5					16·5
4·5	20·9	16·6	16·8	16·8			13·1			21·4	20·9	17·0	16·9	11·9	16·0		16·8	15·9	20·5	20·9
5·5	25·8	21·0	20·7	20·7	16·8		20·1			26·0	25·6	21·5		16·4	20·8		21·5	20·6	25·4	25·3
6·5	30·1	24·6	25·4	25·4	21·4		26·5			30·5		25·6		20·4	24·5		26·1	25·2	29·9	30·0
7·5	34·5	30·1	29·6	29·6	26·0	24·8	30·3			34·4	34·5	30·3	30·0	24·4	30·0		30·0	29·5	33·7	34·5
8·5	39·0	34·3	33·9	33·9	30·5	29·9		30·9		39·0	39·0	34·8	34·3	30·0	34·0		34·9	34·5	39·9	39·0
9·5	44·0	38·8	38·4	38·4	34·4	35·1		34·9			43·5		39·6	34·2	38·9		39·6	39·0	39·9	43·6
10·5	47·1	43·8	43·7		39·0		38·9	38·8			47·9	43·8	43·8	39·1	43·4		43·6	43·7	42·8	47·9
11·5	52·4	52·2				48·8				51·6	52·2	48·0	47·7	43·8			48·0	48·1	52·7	52·4
12·5	57·0	56·5									56·8						52·7	52·6		56·8
13·5		60·5				57·1				61·5		57·2						57·1	61·2	61·3
																		61·5		

Table III.—Final Term Differences. $\Delta F''j$.

j''	0–0 band.									Weighted mean.	0–1 band.								Weighted mean.
1·5	5·5									5·0	5·6		4·8	5·3					5·3
2·5	9·6			5·3						9·0	9·8	9·9	9·2	8·8					9·2
3·5	13·5	10·0		14·3		8·4				13·3	13·6	14·4	13·2	12·9			13·1	16·9	13·2
4·5	17·3	14·3		17·4	16·2	12·4	12·9			17·1	17·5	18·1		16·4	12·5		17·4	21·3	17·1
5·5	21·7	17·4	16·8	20·7	21·8	21·1		20·6		21·1	21·7	21·7	19·5	19·4	16·8		21·5	24·1	21·1
6·5	25·8	20·5	20·7	24·6	25·3	24·1		24·9	16·9	25·0		26·2	23·6	23·6	19·5	22·8	25·6	27·6	25·0
7·5	30·1	25·8	24·6	28·5		27·4		26·6	20·8	29·0	29·7	30·0	28·4	28·4	23·6		29·5	28·4	28·9
8·5	33·7	29·9	28·5	32·4		32·6		31·8	29·2	32·7	33·7		32·5	32·5	23·7	29·7	33·7	32·3	33·0
9·5	37·5	33·5	32·4		32·9	36·8	23·7		32·5	36·9	37·7	38·0	37·1	32·3		34·5	37·5	36·2	36·9
10·5	42·4	37·3					28·2		36·7	41·0	41·8	42·3		36·7	29·6		41·9	40·3	41·0
11·5	45·1	44·9								44·0	45·4	50·0			33·4			43·9	44·7
12·5	49·7	49·2					45·7		44·5	44·9	49·6					21·4		47·9	48·6
13·5							49·1			49·0									—

x

Application of the Combination Principle and Term Formulation.

According to the quantum theory of molecular spectra the lines of the P, Q and R branches are given, as is well-known, by the following expressions :—

$$R(j) = \nu_0 + F'(j+1) - F''(j), \tag{1}$$

$$Q(j) = \nu_0 + F'(j) - F''(j), \tag{2}$$

$$P(j) = \nu_0 + F'(j-1) - F''(j). \tag{3}$$

The following combination relations deduced from these, give us the spacing of the rotational levels in the initial and final states :—

$$Q(j+1) - P(j+1) = R(j) - Q(j) = \Delta F'(j), \tag{4}$$

$$Q(j) - P(j+1) = R(j) - Q(j+1) = \Delta F''(j). \tag{5}$$

Using old quantum mechanics, the rotational energy can be expressed in the simplest case by

$$F(j) = Bm^2 = B(j-\rho)^2,$$

where j takes half-integral values for the even electron molecule CO.

Now

$$\Delta F(j) = F(j+1) - F(j) = (B - 2B\rho) + 2B(j). \tag{6}$$

If therefore the set of spacing of rotational levels obtained from observational data by relations given in (4) and (5) are expressed by an equation

$$\Delta F(j) = a + bj,$$

then

$$a = B - 2B\rho \quad \text{and} \quad b = 2B,$$

or

$$B = b/2 \quad \text{and} \quad \rho = -\frac{a - (b/2)}{2}.$$

In this way one can calculate B and ρ for the initial and the final states. The $\Delta F'j$ and $\Delta F''j$ values were fitted to a linear equation because the experimental accuracy did not warrant the use of a higher degree polynomial. Moreover, the linear equations derived, represented the data sufficiently well and within the limits of experimental error. Table IV gives the equations derived and the observed and calculated $\Delta F(j)$ values.

Table IV.

0–0 band. $\Delta F'j = 4 \cdot 485j - 3 \cdot 673.$			0–0 band. $\Delta F''j = 3 \cdot 985j - 0 \cdot 895.$			0–1 band. $\Delta F''j = 3 \cdot 948j - 0 \cdot 636.$		
Calc.	Obs.	O − C.	Calc.	Obs.	O − C.	Calc.	Obs.	O − C.
3·06	3·0	−0·06	5·08	5·0	−0·08	5·29	5·3	+0·01
7·54	7·6	+0·06	9·07	9·0	−0·07	9·23	9·2	−0·03
12·03	12·1	+0·07	13·05	13·2	+0·15	13·18	13·2	+0·02
16·51	16·5	−0·01	17·04	17·1	+0·06	17·13	17·1	−0·03
21·00	20·9	−0·10	21·02	21·1	+0·08	21·08	21·1	+0·02
25·48	25·3	−0·18	25·01	25·0	−0·01	25·03	25·0	−0·03
29·97	30·0	+0·03	28·99	29·0	+0·01	28·97	28·9	−0·07
34·45	34·5	+0·05	32·98	32·8	−0·18	32·92	33·0	+0·08
38·94	39·0	+0·06	36·96	36·9	−0·06	36·87	36·9	+0·03
43·42	43·6	+0·18	40·95	41·0	+0·05	40·82	41·0	+0·18
47·91	47·9	−0·01	44·93	44·9	−0·03	44·77	44·7	−0·07
52·39	52·4	+0·01	48·92	49·0	+0·08	48·71	48·6	−0·11
56·88	56·8	−0·08						
61·36	61·3	−0·06						

The initial and final states are represented by the following equations :—

$$F_0'(j) = 2 \cdot 243 \, (j - 0 \cdot 32)^2 \qquad \text{(initial)}$$
$$F_0''(j) = 1 \cdot 993 \, (j - 0 \cdot 72)^2 \qquad \text{(final for 0–0)}$$
$$F_1''(j) = 1 \cdot 974 \, (j - 0 \cdot 68)^2 \qquad \text{(final for 0–1).}$$

The existence of large values of ρ is genuine. Their theoretical significance is not clear, we having no definite information about such higher multiplet levels. It is clear, however, that they are characteristic of the quintet level in both states. The same values for ρ persist if a higher degree polynomial is used to represent the data and also if the rotational energy function is derived from the new quantum mechanics.

Band Origins.

These were calculated by using equation (3) on the lines of the P branches and sometimes by equation (2) on Q lines. The values deduced from the various chosen lines did not differ among themselves by more than $0 \cdot 5$ cm.$^{-1}$. The following table gives the five origins of the two bands :—

	0–0.	0–1.
P$_5$	35296·3 \	33586·2 \
	\ 30·0	\ 28·9
P$_4$	326·3 / \	615·2 / \
	\ 20·0	\ 19·8
P$_3$	346·3 / \	635·0 / \
	\ 21·1	\ 20·5
P$_2$	367·4 / \	655·5 / \
	\ 30·5	\ 29·1
P$_1$	397·9 /	684·6 /

x 2

It will be seen that there is a marked contraction in the electronic separations of the 0–1 band. While this may partly be due to experimental errors, the systematic manner in which the contraction proceeds from level to level indicates that perhaps it is genuine. The contraction appears to be more pronounced in the two extreme levels where it is $1 \cdot 1$ and $1 \cdot 4$ ν. Similar contraction of electronic levels with higher vibration states is also observed in the case of the β bands of NO.* The theory of the rotational distortion of electronic multiplets has been developed by Kemble and others.† It would be very desirable to have also a theory of the vibrational distortion of electronic multiplets.

Molecular Constants.

The following table gives the molecular constants of CO for this band system. As previously noted it has not been possible to evaluate ω_0 and $\omega_0 x$. The latest values of the fundamental units have been used.

Initial state.	Final state.
$B_0' = 2 \cdot 243$ $I_0' = 12 \cdot 33 \times 10^{-40}$ g. cm.^{2} $r_0' = 1 \cdot 10 \times 10^{-8}$ cm.	$B_0'' = 1 \cdot 993, \quad B_1'' = 1 \cdot 974$ $I_0'' = 13 \cdot 91 \times 10^{-40}$ g. cm.^{2} $r_0'' = 1 \cdot 24 \times 10^{-8}$ cm.

The moment of inertia for the final state is thus $13 \cdot 91 \times 10^{-40}$ g. cm.^{2}. The Cameron bands which have this level for their initial state and the final level of the fourth positive carbon bands for their final state are degraded towards the red, thus indicating that I_0'' for this latter level must be smaller than this value. The value now commonly accepted is $14 \cdot 9 \times 10^{-40}$.‡ This value has been indirectly obtained by measurements of the infra-red absorption doublet band by Lowry§ using the Kemble equation, $\Delta \nu = \dfrac{1}{\pi} \sqrt{\dfrac{KT}{I}}$. Burmeister's values by the same method‖ give $14 \cdot 7 \times 10^{-40}$. Unfortunately this band has not been resolved into its fine-structure. But in cases where the moments of inertia calculated by measurements on the doublet using the above equation are compared with those obtained by fine structure analysis using the equation $\nu_z = mh/4\pi^2 I$, the agreement is qualitative,¶ the values

* 'Phys. Rev.,' vol. 30, p. 150 (1927).
† 'Phys. Rev.,' vol. 30, p. 387 (1927); *ibid.*, vol. 32, p. 250 (1928).
‡ 'Report on Molecular Spectra,' p. 225.
§ 'J. Opt. Soc. Am.,' vol. 8, p. 647 (1924).
‖ 'Report on Molecular Spectra,' p. 12.
¶ *Vide*, International Critical Tables.

obtained by fine structure analysis being lower than those obtained by the Kemble equation. Another indirect qualitative method has also been used for computing the I_0 for this level from the relation between ω_0 and I_0.* This relation observed by Mecke† and others which indicates that for similar electronic states the product $\omega_0 \times I_0$ is constant, is only qualitatively true. On the other hand, the I_0 associated with the initial state of the Ångström bands which is a $2\,^1S$ level is $14 \cdot 26 \times 10^{-40}$, and the final level of the fourth positive carbon bands and the Cameron bands being a $1\,^1S$ level, one would expect a much lower value than this for its moment of inertia. It thus appears that the value now accepted is very high. It would be very valuable to have a fine structure analysis of the fourth positive carbon bands. But since most of these bands lie in the far ultra-violet, the prospect of a complete analysis appears to be remote. The present writer has, however, analysed some of the bands in the near ultra-violet taken in the first order of the 21-foot grating. The bands are not resolved near the head and the P branch is very weak. A preliminary analysis, however, gives $B_{18}'' = 1 \cdot 60$ with $\alpha = 0 \cdot 023$. Assuming a linear change in the values of B'', we get by extrapolation $B_0'' = 2 \cdot 01$, which gives $I_0'' = 13 \cdot 8 \times 10^{-40}$. This value is lower than the value of I_0'' for the final of the third positive carbon bands, and thus fits in with the observed red degradation of the Cameron bands.

Mention must also be made of some recent remarks of Mulliken‡ on the electronic levels of CO. While theoretically he finds that CO can possess quintet levels, he rules out the possibility of such levels on energy considerations. But the foregoing experimental evidence shows that the levels of the third positive carbon bands are certainly quintet.

In conclusion, I should like to express my indebtedness to Dr. R. C. Johnson, for the unceasing kindness with which he has guided me throughout the investigation.

Summary.

1. The third positive carbon bands, the 3 A bands and the so-called Wolter spurious bands, have been photographed in the first order of a 21-foot grating.

2. The Wolter spurious bands are regarded as forming a new system of bands.

3. A complete vibrational analysis of these three systems is given, which shows that they have all got the same final electronic state.

* ' Report on Molecular Spectra,' p. 225.

† ' Z. Physik,' vol. 32, p. 823 (1925).

‡ ' Phys. Rev.,' vol. 32, p. 769 (1928).

4. A new band system, photographed under low dispersion, has been described. A vibrational analysis of these bands is given, which shows that their initial level is identical with the new level at $\nu = 58927$ found by Hopfield and Birge, and their final level is the same as the final level of the above three band systems of the CO molecule.

5. The fine structure analysis of the 0–0 and 0–1 bands of the third positive system is given and the usual molecular constants evaluated. This analysis shows that the final level of these bands is a quintet P level, the transition being $^5S \to {}^5P$. The 3 A bands are probably due to the transition $^5P \to {}^5P$.

<div align="center">DESCRIPTION OF PLATE 3.</div>

1. Third positive Carbon bands, $0 - 4, 0 - 3$, and $0 - 2$, enlarged 3·5 times.   2. Third positive Carbon bands, $0 - 1$ and $0 - 0$, enlarged 4·5 times.   3. New bands, enlarged three times.

<div align="center">———————</div>

Hydrodynamic Forces acting on a Cylinder in Motion, and the Idea of a " Hydrodynamic Centre."

By W. G. Bickley, M.Sc., Lecturer in Mathematics, Battersea Polytechnic.

There are two general methods of determining the forces acting on a cylinder due to the two-dimensional motion of a surrounding liquid. One is applicable to the case of a stationary cylinder in a stream, in the form*
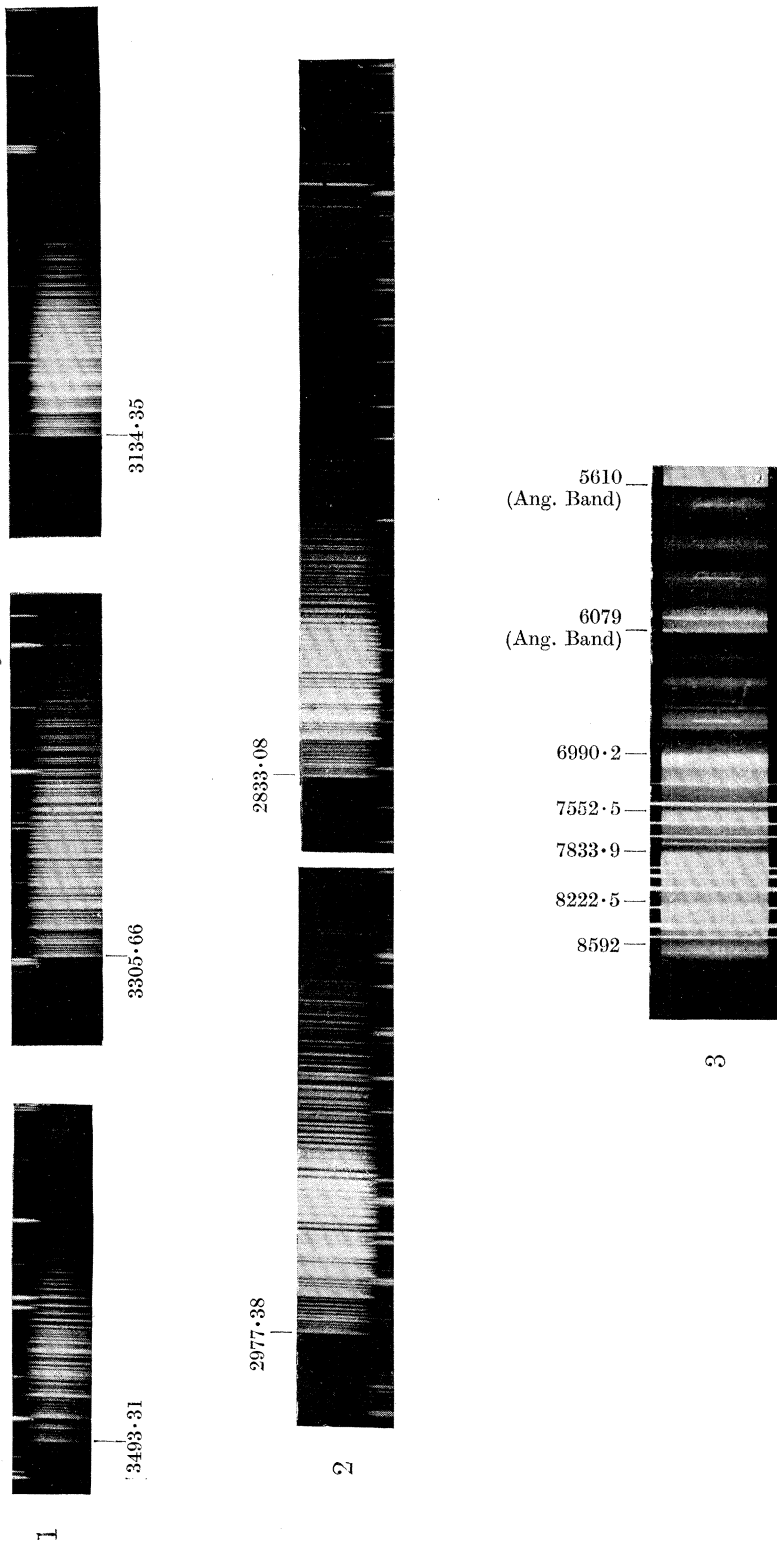
$$X - \iota Y = \tfrac{1}{2} \iota \rho \int \left(\frac{dw}{dz} \right)^2 dz. \tag{1.1}$$

$$M = -\tfrac{1}{2} \rho \mathfrak{R} \int \left(\frac{dw}{dz} \right)^2 z \, . \, dz, \tag{1.2}$$
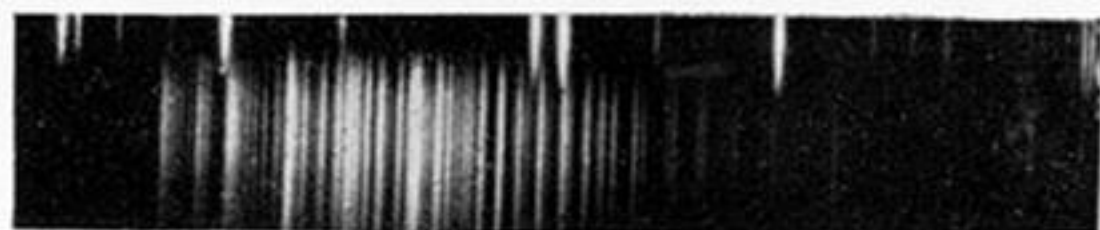
where X and Y are the components of the resultant force, parallel to the x and y axes, and M is its moment about the origin; ρ is the density of the fluid, and w is the velocity potential-stream-function for the fluid motion; z is as usual the complex variable $x + \iota y$. The other is that obtained from the general theory of the "impulse."† The first of these is unable to deal

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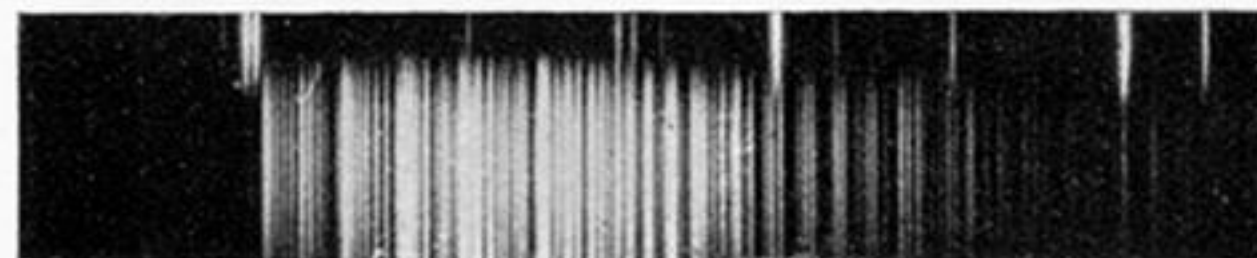* *Cf.* Glauert, 'Aerofoil and Airscrew Theory,' p. 81 (Cambridge, 1926).

† *Cf.* Lamb, 'Hydrodynamics' (4th ed.), ch. 6, especially p. 165 (Cambridge, 1916).
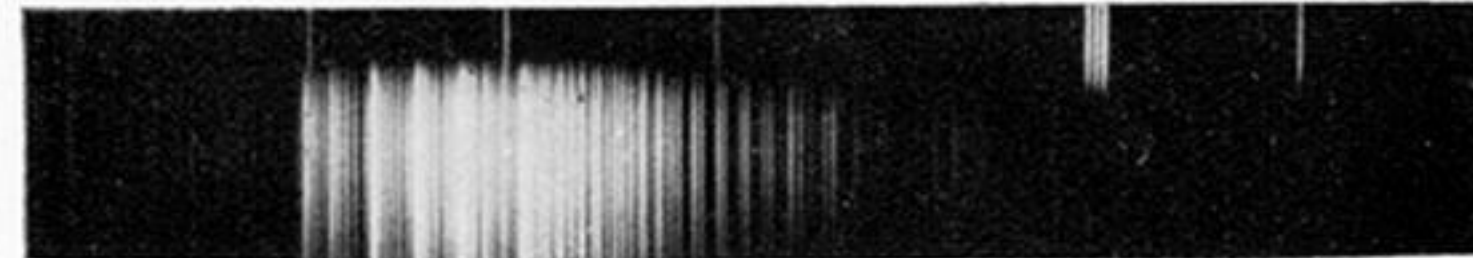
Asundi.

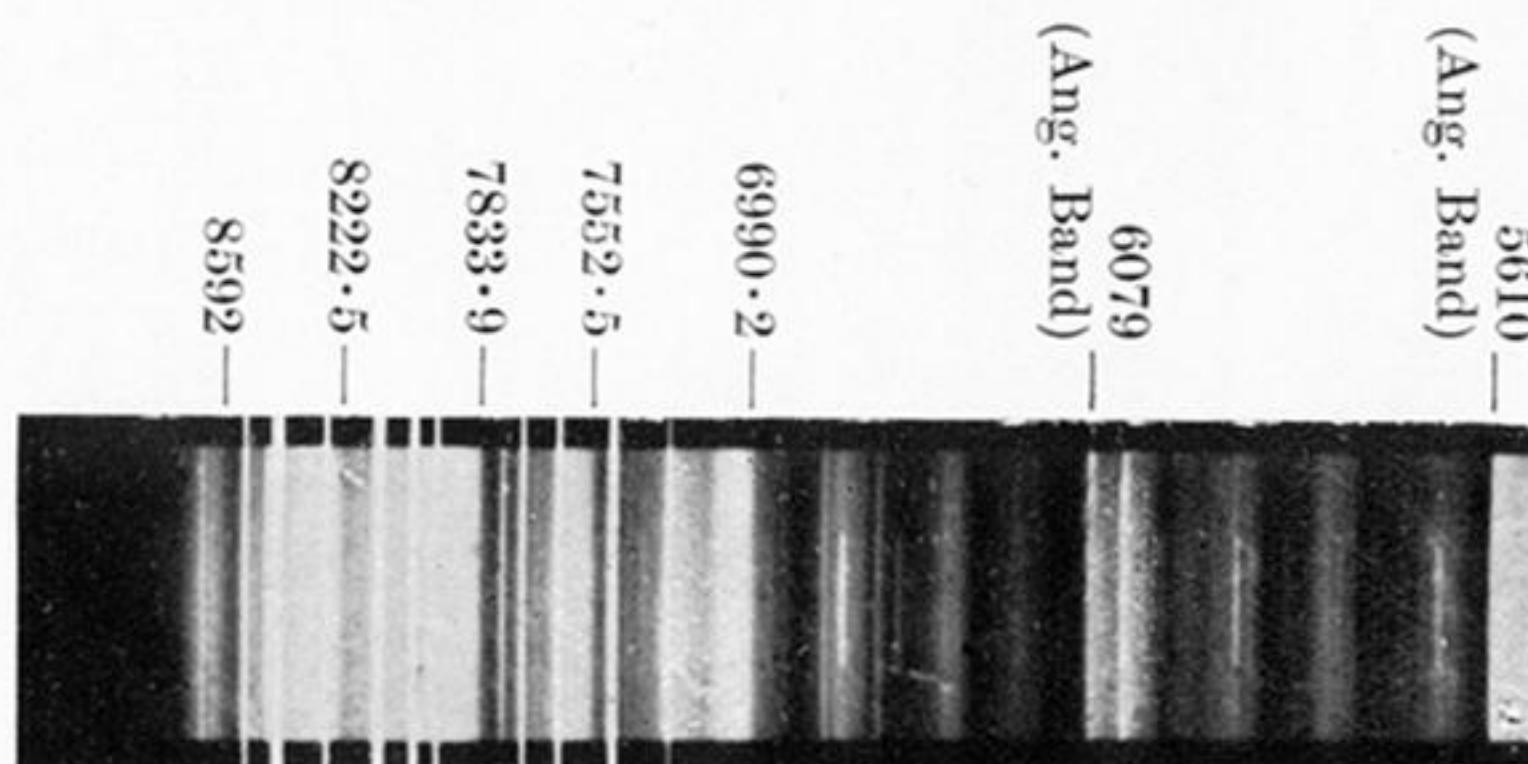*Roy. Soc. Proc., A, vol.* 124, *Pl.* 3.

DESCRIPTION OF PLATE 3.

1. Third positive Carbon bands, 0 — 4, 0 — 3, and 0 — 2, enlarged 3·5 times.   2. Third positive Carbon bands, 0 — 1 and 0 — 0, enlarged 4·5 times.   3. New bands, enlarged three times.