

On the Cameron Bands (${}^3\Pi - {}^1\Sigma$) of Carbon Monoxide

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The 0-0 and 1-0 Cameron bands of CO are investigated in absorption with high dispersion. Three *P*, three *Q* and three *R* branches are observed for each band. New accurate values for the rotational constants of the ground state of CO are derived: $B_0=1.9310\text{ cm}^{-1}$, $\alpha=0.01744\text{ cm}^{-1}$ and, using Bearden's values for e , h and N , we obtain the moment of inertia $I_0=14.456\cdot 10^{-40}\text{ g cm}^2$, $I_1=14.521\cdot 10^{-40}\text{ g cm}^2$, the nuclear distance $r_0=1.127\text{ \AA}$, $r_1=1.129\text{ \AA}$. From the way in which the Λ doublets of the $a^3\Pi$ state combine with the ${}^1\Sigma^+$ ground state it can be definitely shown that the upper state of the third positive group of CO (whose lower state is $a^3\Pi$) is ${}^3\Sigma^+$ not ${}^3\Sigma^-$. For the electronic excitation energy of the $a^3\Pi$ level a value 48473.7 cm^{-1} is obtained which differs to some extent from the values at present used in the literature.

A. INTRODUCTION

THE Cameron bands of CO have been discovered by Cameron¹ in emission in a discharge through Ne with traces of CO, and have subsequently been observed in absorption by Hopfield.² As was first concluded by Johnson³ they constitute the transition from the lower state of the third positive group $a^3\Pi$ to the ground state $X^1\Sigma$ of the CO molecule. As a singlet-triplet inter-combination the bands are very weak in absorption compared to the 4th positive group ${}^1\Pi - {}^1\Sigma$.

Since thus far no example of the fine structure of ${}^3\Pi - {}^1\Sigma$ bands has been analyzed, and since an analysis would also supply better values than now available, for the rotational constants of the ground state and the electronic energy of the triplet levels it seemed to us worth while to study the Cameron bands under high dispersion in absorption.

B. EXPERIMENTAL

With an absorbing layer of 1 m and 6 m respectively of CO, spectrograms were independently taken at Budapest and at Darmstadt. At Budapest the first order of a 6 m grating with 30,000 lines per inch was used (dispersion 1.15 \AA/mm); at Darmstadt the third order of a

3 m grating with 15,000 lines per inch (dispersion 1.7 \AA/mm). After finding out that both at Budapest and at Darmstadt the same spectrograms had been taken we decided to evaluate the plates and publish the results together.

A hydrogen discharge tube was used to supply the continuous background.⁴ Only the 0-0 and the 1-0 bands lie in the region accessible without the use of a vacuum spectrograph. The 1-0 band could not be measured on the Budapest plates because of over-lapping by the oxygen absorption bands which of course in a 6 m spectrograph appear much stronger than in a 3 m spectrograph. The 0-0 band was measured only on the Budapest plates except for the weakest lines which appeared more intense on the Darmstadt plates because of the longer absorbing layer.

In Budapest Fe lines of the first order were used as comparison spectrum; in Darmstadt, Fe lines of the second order, and some silicon lines of the H_2 discharge tube in the third order. The lines of the 0-0 band measured both on the Budapest and on the Darmstadt plates showed a constant difference of 0.094 \AA corresponding to 2.2 cm^{-1} . Consequently half this shift (in wavelength) was added to all measurements of the Budapest plates and subtracted from those of the Darmstadt plates. The absolute values of the

¹ W. H. B. Cameron, *Phil. Mag.* **1**, 405 (1926).

² J. J. Hopfield, *Phys. Rev.* **29**, 356 (1927).

³ R. C. Johnson, *Nature* **117**, 376 (1926).

⁴ At Darmstadt in order to cut out the strong second order continuous spectrum that over-laps the third order, the method given by Curry and Herzberg (*Ann. d. Physik* **19**, 800 (1934)) was used.

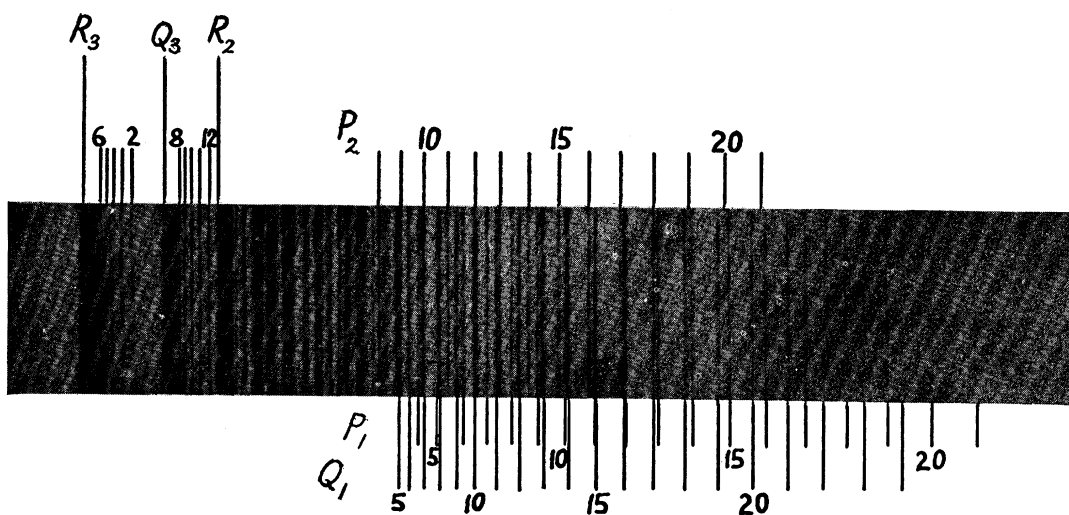


FIG. 1. The 0-0 band of the Cameron system in absorption.

wave numbers given may therefore be in error by 1-2 cm^{-1} but the relative accuracy is of course better (a few tenths of a cm^{-1}).

Figure 1 is a reproduction of the 0-0 band from a Budapest plate.

C. ROTATIONAL ANALYSIS

According to the selection rule $\Delta J=0, \pm 1$ nine branches are to be expected for a ${}^3\Pi-{}^1\Sigma$ transition: a P, Q and R branch for each component ${}^3\Pi_0-{}^1\Sigma, {}^3\Pi_1-{}^1\Sigma$ and ${}^3\Pi_2-{}^1\Sigma$. Some lines of these branches are indicated in Fig. 2. The branches are designated as $P_1, Q_1, R_1; P_2, Q_2, R_2; P_3, Q_3, R_3$. Since the ${}^3\Pi$ state is, at least for larger J values, near to case b the quantum number K has a meaning for the rotational levels of both the upper and lower states. For the above mentioned branches ΔK takes the values $\pm 2, \pm 1, 0$. Therefore the branches have, at least for larger K , the form of O, P, Q, R , and S branches. According to Mulliken⁵ they may also be designated by

$$\begin{array}{ccccccccc} P_1 & Q_1 & R_1 & P_2 & Q_2 & R_2 & P_3 & Q_3 & R_3 \\ oP & pQ & qR & pP & qQ & rR & qP & rQ & sR \end{array}$$

Table I gives the wave numbers of the branches of the 0-0 and 1-0 bands. Unresolved lines used in two or even three different places are indicated by an asterisk in Table I. Their accuracy is of course less than that of the unblended lines.

⁵ R. S. Mulliken, Phys. Rev. 36, 611 (1930).

In Table II the combination differences

$$R_i(K-1) - P_i(K+1) = \Delta_2 F''(K)$$

are given which should coincide for the two bands. The last column contains the average $\Delta_2 F''(K)$. In forming the average values the $\Delta_2 F''$ values obtained from blended lines (marked by *) have been given half the weight of the unblended $\Delta_2 F''$ values. From the average $\Delta_2 F''$

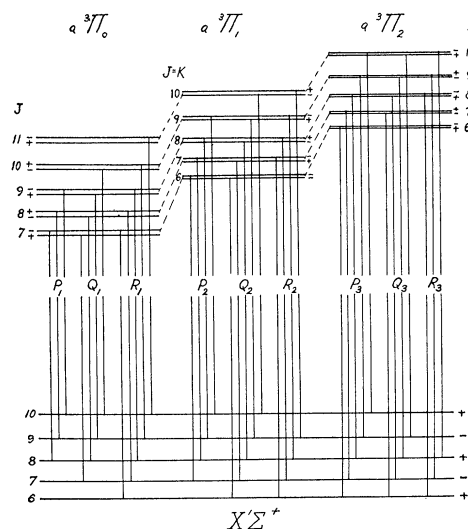


FIG. 2. Energy level diagram for the Cameron bands showing the nine branches. The J values on the right for $a^3\Pi_2$ should be lowered by one unit. In order to represent the relations as actually found by the following analysis the designations + and - in the upper state should be interchanged and the end points of the lines representing the transitions should be changed correspondingly.

TABLE I. Wave numbers of the lines in the 0-0 and 1-0 Cameron bands.

0-0 BAND									
$\lambda_H = 2059.6\text{\AA}$ $\nu_0 = 48473.7$									
K	P ₁	Q ₁	R ₁	P ₂	Q ₂	R ₂	P ₃	Q ₃	R ₃
0	—	—	—	—	—	48479.42*	—	—	48511.13
1	—	—	—	—	—	482.28*	—	—	516.23
2	—	—	—	48467.55	—	484.56*	—	—	520.42
3	—	—	—	463.01*	—	486.16*	—	48509.33*	524.21
4	48415.98*	48428.59*	48442.51*	457.70*	—	487.01*	48494.06	509.33*	526.99
5	408.32*	424.18*	441.50	451.34	—	—	489.24*	507.99	529.49
6	400.24*	419.21*	440.09	444.62	48465.17*	488.44	484.56*	506.77	531.75
7	390.52	414.22*	438.10*	438.10*	461.44	—	479.42*	504.84	533.78
8	382.21	408.33*	435.17	430.57	457.70*	487.01*	474.20	503.03	535.45
9	372.51	402.25	432.70	422.80	453.08	486.16*	468.56	500.67	536.65
10	362.03	394.64	428.59*	414.22*	448.17	484.56*	463.01*	498.60	537.97
11	351.57*	387.71	424.18*	405.42	442.51*	482.28*	455.94	495.55	538.77
12	340.56	379.40	419.21*	395.88	436.52	479.42*	449.48	492.30	539.29*
13	328.41	370.45	—	386.35	430.57*	476.95	442.51*	489.24*	539.29*
14	315.68	361.28	—	376.02	424.18*	472.88	—	—	—
15	302.86	351.57*	—	365.21	415.98*	469.41	—	—	—
16	288.94	341.45	—	353.87	408.33*	465.17*	—	—	—
17	275.09	330.21*	—	342.41	400.24*	—	—	—	—
18	259.90	318.90	—	330.21*	—	—	—	—	—
19	244.57	306.86	—	317.08	—	—	—	—	—
20	229.30	294.35	—	304.34	—	—	—	—	—
21	212.74	281.55	—	290.62	—	—	—	—	—
22	196.56	267.68	—	—	—	—	—	—	—
23	178.66	253.23	—	—	—	—	—	—	—
24	160.01	238.80	—	—	—	—	—	—	—
25	142.55	223.46	—	—	—	—	—	—	—
26	124.13	208.60	—	—	—	—	—	—	—
27	—	192.24	—	—	—	—	—	—	—
28	—	175.55	—	—	—	—	—	—	—

1-0 BAND									
$\lambda_H = 1989.4\text{\AA}$ $\nu_0 = 50188.3$									
K	P ₁	Q ₁	R ₁	P ₂	Q ₂	R ₂	P ₃	Q ₃	R ₃
0	—	—	—	—	—	—	—	—	—
1	—	—	—	—	—	—	—	—	50229.30
2	—	—	—	—	—	50198.67*	—	—	233.21
3	—	—	—	—	—	—	—	—	237.40
4	—	—	—	—	—	—	—	—	240.40
5	—	50138.13	—	—	—	—	50202.35	—	242.88
6	50113.58	133.88	—	—	50178.18	—	198.67*	50220.09	244.90
7	105.07	126.82*	—	—	174.83	—	193.74*	218.13	246.66
8	097.59	122.10	—	—	171.16	—	187.45*	216.01	—
9	086.85*	115.69	—	50136.27	165.74	198.67*	—	213.41	—
10	075.94	108.38	50141.57*	126.82*	160.84	196.41	174.83*	210.76	—
11	064.49	100.08*	—	118.23	154.62	193.74*	167.93*	207.31	—
12	052.91	091.77	131.39*	108.38	148.54	189.97*	160.84*	204.06	—
13	040.61	082.44	—	097.59	141.57*	187.45*	—	198.67*	—
14	027.62*	072.63	118.23	086.85*	133.88	182.71	—	193.74*	246.66
15	014.48	062.23	111.65	075.94*	126.82*	178.18*	—	189.97*	244.90
16	49999.75	051.73	103.74	064.49	118.23*	—	—	184.80	242.88
17	984.95	039.66	095.98	—	108.38*	167.93	—	178.18*	240.40
18	969.64	027.62*	086.85*	039.66*	100.08*	—	—	171.16*	—
19	952.89	014.48*	077.77	—	089.36	154.62*	—	164.72	—
20	937.25	001.51	067.72	—	079.05	148.54*	—	—	—
21	919.25	49988.42	056.84	—	067.72*	140.04	—	—	—
22	903.21	974.16	045.54	—	056.84*	131.39*	—	—	—
23	—	958.86	034.03	—	045.54*	—	—	—	—
24	—	944.31	—	—	034.03*	—	—	—	—
25	—	—	—	—	019.51	—	—	—	—
26	—	910.11	—	—	005.11	—	—	—	—

 λ_H is the wave-length in air of the most refrangible head formed by the R₃ branch.

TABLE II. $\Delta_2 F''(K) = R_i(K-1) - P_i(K+1)$.

K	$R_1(K-1)$ $-P_1(K+1)$		$R_2(K-1)$ $-P_2(K+1)$		$R_3(K-1)$ $-P_3(K+1)$		WEIGHTED AVERAGE
	0-0	1-0	0-0	1-0	0-0	1-0	
1	—	—	11.87*	—	—	—	11.87
2	—	—	19.27*	—	—	—	19.27
3	—	—	26.86*	—	26.36	—	26.53
4	—	—	34.82*	—	34.97*	—	34.97
5	42.27*	—	42.39*	—	42.43*	41.73*	42.21
6	50.98	—	—	—	50.07*	49.14*	50.29
7	57.88	—	57.87*	—	57.55	57.45*	57.70
8	65.59*	—	—	—	65.22	—	65.34
9	73.14	—	72.79*	—	72.44*	—	72.88
10	81.13*	—	80.74*	80.44*	80.71	—	80.75
11	88.03*	88.66*	88.68*	88.03	88.49	—	88.34
12	95.77*	—	95.93*	96.15*	96.26*	—	96.03
13	103.53*	103.77*	103.40*	103.12*	—	—	103.46
14	—	—	111.74	111.51*	—	—	111.66
15	—	118.48	119.01	118.22*	—	—	118.64
16	—	126.70	127.00	—	—	—	126.85
17	—	134.10	134.96*	—	—	—	134.39
18	—	143.09	—	—	—	—	143.09
19	—	149.60*	—	—	—	—	149.60
20	—	158.52	—	—	—	—	158.52
21	—	164.51	—	—	—	—	164.51

values the rotational constant B_0'' for the vibrationless ground state can be obtained in the usual way. Taking $D'' = 6 \cdot 10^{-6} \text{ cm}^{-1}$ (see Schmid and Gerö)⁶ a value

$$B_0'' = 1.9228 \pm 0.0010 \text{ cm}^{-1}$$

was obtained. The only other direct determi-

⁶ R. Schmid and L. Gerö, Zeits. f. Physik **101**, 343 (1936).

nation of B_0 for the ground state of CO was obtained by Amaldi⁷ from the Raman effect. He obtained $1.925 \pm 0.020 \text{ cm}^{-1}$ which agrees with our value within the accuracy given by Amaldi. Our value however is much more accurate. Schmid and Gerö, by an extrapolation of the higher B_v values derived from an analysis of the 4th positive group have obtained the value of $B_0'' = 1.9213$ which, considering the uncertainty of the extrapolation, agrees very well with the above value.

The new B_0'' , with Schmid and Gerö's B_v values, leads to the following slightly altered B_v formula for the ground state of CO

$$B_v = 1.9310 - 0.01744(v + \frac{1}{2}).$$

That is $B_e = 1.9310$ and $\alpha = 0.01744$. There seems to be a very slight curvature in the B_v curve but the data are too scarce to evaluate a quadratic term for B_v .

The values of the moments of inertia I_0 and I_e and the nuclear distances r_0 and r_e of the CO molecule in its ground state following from the above B_0 and B_e are (depending on the choice of

⁷ E. Amaldi, Zeits. f. Physik **79**, 492 (1932).

TABLE III. $\Delta_1 F_1(K) = F_1(K+1) - F_1(K)$ for ${}^3\Pi_0$.

K	$v=0$				$v=1$			
	CAMERON BANDS		3. POSITIVE GROUP		CAMERON BANDS		3. POSITIVE GROUP	
	$R_1(K+1)$ $-Q_1(K+1)$	$Q_1(K+2)$ $-P_1(K+2)$	$R_1(K)$ $-Q_1(K+1)$	$Q_1(K)$ $-P_1(K+1)$	$R_1(K+1)$ $-Q_1(K+1)$	$Q_1(K+2)$ $-P_1(K+2)$	$R_1(K)$ $-Q_1(K+1)$	$Q_1(K)$ $-P_1(K+1)$
1	—	—	—	—	—	—	—	—
2	—	12.61*	—	—	—	—	—	—
3	13.92*	15.86*	—	—	—	—	—	—
4	17.32*	18.97*	17.11	20.06	—	20.30	16.82	—
5	20.86*	23.70*	20.43	23.28	—	21.75	20.12	23.23
6	23.88*	26.12*	23.60	26.28	—	24.51	23.47	26.15
7	26.84*	29.74	26.91	29.55	—	28.84*	26.59	29.11
8	30.45	32.61	30.34	32.72	—	32.44	29.74	32.54
9	33.95*	36.14*	33.38	36.14	33.19*	35.59*	32.94	35.29
10	36.47*	38.84	36.64	38.96	—	38.86	36.13	38.67
11	39.81	42.04	39.97	42.52	39.62*	41.83	39.46	42.00
12	—	45.60	—	45.43	—	45.01*	42.77	45.10
13	—	48.71*	—	48.74	45.60	47.75	46.09	48.41
14	—	52.51	—	51.99	49.42	51.98	49.40	51.47
15	—	55.12*	—	55.31	52.01	54.71	52.62	54.78
16	—	59.00	—	58.70	56.32	57.98*	56.05	57.93
17	—	62.29	—	61.76	59.23*	61.59*	59.26	61.13
18	—	65.05	—	65.13	63.29*	64.26	62.62	64.35
19	—	68.81	—	68.21	66.21	69.17	65.95	67.57
20	—	71.12	—	71.58	68.42	70.95	69.33	70.85
21	—	74.57	—	74.80	71.38	—	72.51	—
22	—	78.79	—	78.05	75.17	—	75.74	—
23	—	80.91	—	81.36	—	—	—	—
24	—	84.47	—	84.78	—	—	—	—

the old Birge or the new Bearden values for the atomic constants e , h and N):

$$\begin{aligned} I_0 &= 14.383 \text{ or } 14.521 \cdot 10^{-40} \text{ g cm}^2 \text{ resp.,} \\ I_e &= 14.318 \text{ or } 14.456 \cdot 10^{-40} \text{ g cm}^2 \text{ resp.,} \\ r_0 &= 1.128 \text{ or } 1.129\text{A resp.,} \\ r_e &= 1.125 \text{ or } 1.127\text{A resp.} \end{aligned}$$

In Table III the combination differences

$$\Delta_1 F_1 = F_1(K+1) - F_1(K)$$

for the ${}^3\Pi_0$ component of the upper state are given, calculated from the differences $R_1(K+1) - Q_1(K+1)$ and $Q_1(K+2) - P_1(K+2)$ in the Cameron bands for both $v=0$ and $v=1$. Table III shows that $R_1(K+1) - Q_1(K+1)$ and $Q_1(K+2) - P_1(K+2)$ do not exactly coincide. As can be seen from Fig. 2 this is to be expected because of the Λ type doubling which is particularly strong for the ${}^3\Pi_0$ component of $a^3\Pi$. In Table III are also given the $\Delta_1 F_1$ values as calculated from the data of Dieke and Mauchley⁸ and Gerö⁹ for the third positive group of CO which has the same $a^3\Pi$ state as lower state. The differences $R_1(K) - Q_1(K+1)$ and $Q_1(K) - P_1(K+1)$ in the third positive group give $\Delta_1 F_1$, apart from Λ -type doubling.

It can be seen from Table III that $R_1(K) - Q_1(K+1)$ of the third positive group coincides very well with $R_1(K+1) - Q_1(K+1)$ of the Cameron bands, and $Q_1(K) - P_1(K+1)$ of the third positive group with $Q_1(K+2) - P_1(K+2)$ of the Cameron bands for both $v=0$ and $v=1$. This agreement is definite proof that the lower state of the third positive group is identical with the upper state of the Cameron bands.

The upper state of the third positive group is a ${}^3\Sigma$ state.⁸ From the analysis of the third positive group ($b^3\Sigma - a^3\Pi$) alone it cannot be decided whether the upper state is ${}^3\Sigma^+$ or ${}^3\Sigma^-$. However, this can now be decided from Table III if the assumption is made that the ground state of CO is ${}^1\Sigma^+$ (not ${}^1\Sigma^-$). The correctness of this assumption follows from the fact that the ground state

has closed electron shells only.¹⁰ In the ground state therefore the even rotational levels are positive, the odd negative, as indicated in Fig. 2. If in the $b^3\Sigma$ state the odd rotational levels were positive and the even negative, that is, if it were a ${}^3\Sigma^-$ level, $Q_1(K) - P_1(K+1)$ of the third positive group should coincide with $R_1(K+1) - Q_1(K+1)$ of the Cameron bands, and not with $Q_1(K+2) - P_1(K+2)$ as it actually does. It therefore follows that the upper state of the third positive group is a ${}^3\Sigma^+$ level. This is in agreement with the fact that the ground state ${}^1\Sigma^+$ combines, though very weakly, with the $b^3\Sigma^+$ state.¹¹ A ${}^3\Sigma^- - {}^1\Sigma^+$ combination would be expected to be much weaker still.

To save space the data for the combination differences $\Delta_1 F$ for the ${}^3\Pi_1$ and ${}^3\Pi_2$ components are not given here. The agreement with the corresponding values from the third positive group is about as good as for ${}^3\Pi_0$, and the conclusions as to the symmetry are the same. By a mistake in drawing Fig. 2 (noticed only in the proof) the + and - characters of the rotational levels of the ${}^3\Pi$ state indicated there are just opposite to the correct ones.

The *zero lines* ν_0 of the two Cameron bands, given in Table I, were obtained by extrapolating $\frac{1}{3}(Q_1 + Q_2 + Q_3)$ to $J=0$. It can be easily seen from a paper by Budó¹² that this procedure supplies the correct zero lines apart from Λ -doubling. The difference of the two zero lines 1714.6 is the ΔG_1 value of the $a^3\Pi$ state. Due to the fact that hitherto only the heads of the Cameron bands have been measured the values for the electronic excitation energy of the $a^3\Pi$ states given in recent tables deviate appreciably from the above ν_0 value 48473.7 cm^{-1} for the 0-0 band. The values for the electronic energies of the other triplet states of CO have to be changed correspondingly.

¹⁰ Quite generally the + and - character of the Σ states of a molecule can be determined only relatively from a band analysis alone. To determine it absolutely the + and - character of one state has to be known from other evidence, such as electron configurations.

¹¹ J. J. Hopfield and R. T. Birge, Phys. Rev. **29**, 922 (1927).

¹² A. Budó, Zeits. f. Physik **98**, 437 (1936).

⁸ G. H. Dieke and J. W. Mauchley, Phys. Rev. **43**, 12 (1933).

⁹ L. Gerö, Zeits. f. Physik **101**, 311 (1936).

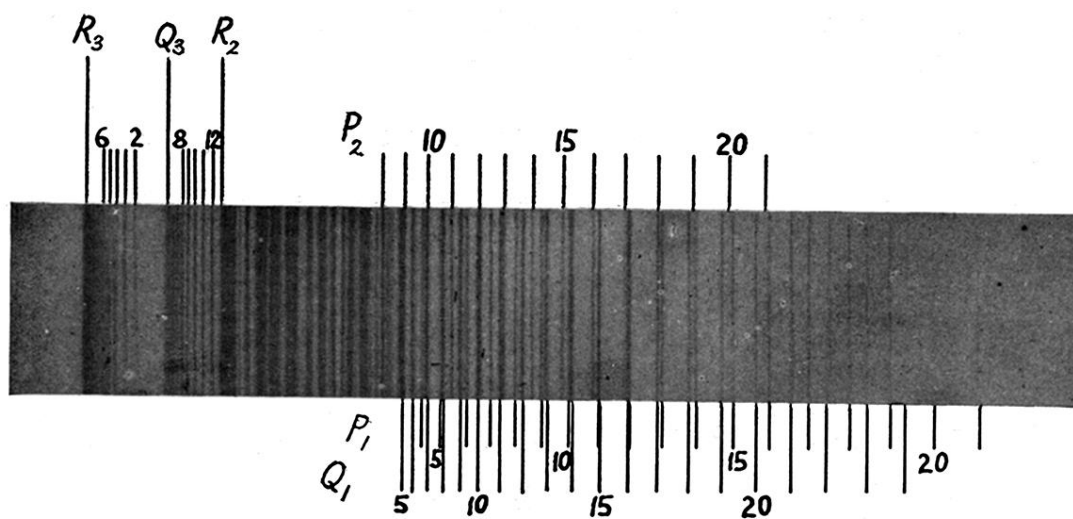


FIG. 1. The 0-0 band of the Cameron system in absorption.