
Rotational Analysis of the First Negative Band Spectrum of Oxygen

Thomas E. Nevin

Phil. Trans. R. Soc. Lond. A 1938 **237**, 471-507

doi: 10.1098/rsta.1938.0014

Email alerting service

Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click [here](#)

To subscribe to *Phil. Trans. R. Soc. Lond. A* go to: <http://rsta.royalsocietypublishing.org/subscriptions>

ROTATIONAL ANALYSIS OF THE FIRST NEGATIVE BAND SPECTRUM OF OXYGEN

By THOMAS E. NEVIN
University College, Dublin

(*Communicated by A. W. Conway, F.R.S.—Received 6 April 1938*)

[Plates 7, 8]

INTRODUCTION

The first negative bands of oxygen, $\lambda 6856$, (0, 2), $\lambda 6419$, (0, 1), $\lambda 6026$, (0, 0), $\lambda 5632$, (1, 0) and $\lambda 5295$, (2, 0) appear in the negative glow when a discharge is passed through oxygen at low pressure. Under low dispersion the bands appear very diffuse, but each exhibits on the long-wave side a well-defined head degraded to the violet, to which the wave-lengths given above refer, accompanied by a less well-defined head about 30 cm.^{-1} towards shorter wave-lengths. Though they have no state in common with the ultra-violet negative bands they are generally attributed to the O_2^+ molecule.

References to earlier work are given by Frerichs (1926), who excited the spectrum with high intensity in a hollow-cathode discharge in oxygen and photographed it in the first order of a 21 ft. grating. In each band he found two branches, one of which formed the sharp head referred to above. On the basis of a combination relation between the branches he assigned vibrational quantum numbers to the bands. Bands additional to those given above have been discovered by Mulliken and Stevens (1933) and Bozoky and Schmid (1935). It was found by the latter workers that the bands given above, with the exception of $\lambda 6856$, were not single but formed the first band in each of the progressions $v' - v'' = -1, 0, +1, +2$, respectively. They excited the spectrum by a high-frequency discharge which seemed to have a lower effective temperature than the hollow-cathode discharge, so that the rotational structure was not well developed and the later bands in each progression were not masked by the overlapping rotational structure of the first band.

Very little is known about the rotational structure of the bands. From a study of the probable electronic configurations of the O_2^+ molecule, Mulliken (1932) considered that they might be due to a $^4\Sigma \rightarrow ^4\Pi$ transition. Bozoky and Schmid (1935) considered their observations on the Zeeman effect consistent with a doublet or quartet structure.

EXPERIMENTAL

The spectrum was excited by a discharge through helium mixed with a small amount of oxygen in the pyrex discharge tube shown in fig. 1. The electrodes were of aluminium, 25 cm. long, external diameter 3 cm. The capillary was 50 cm. long with an internal diameter of 7 mm. The oxygen prepared by heating potassium permanganate in a side tube was stored at a pressure of a few cm. of mercury in contact with phosphorus pentoxide in the bulb *A*, attached to one limb of the discharge tube with an internal seal which prevented the gas from entering the discharge tube except through the needle valve *V*. The tap *T* allowed the oxygen supply to be cut off without altering the adjustment of the valve. The tube was kept cool by immersing it up to the level of the bulb in a tank of running water.

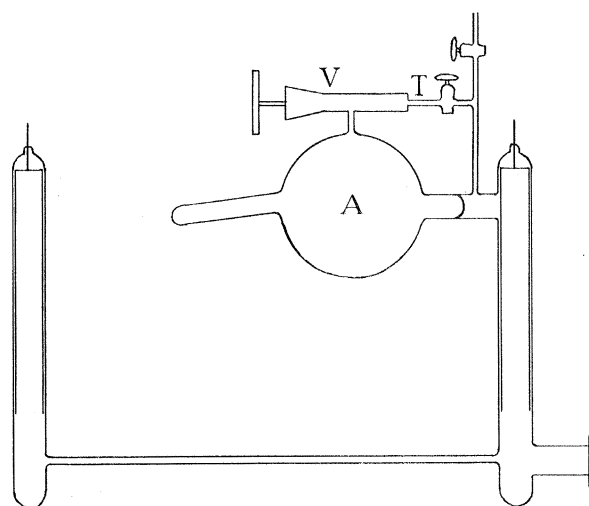


FIG. 1. The discharge tube.

It was found that the oxygen introduced into the discharge tube disappeared fairly rapidly, presumably combining with the electrodes. By proper adjustment of the valve, the rate of inflow could be adjusted so that the total amount in the tube remained very nearly constant, and the tube would run for about 2 hr. without attention. The pressure of helium in the tube was 3–4 mm. No attempt was made to measure the pressure of the oxygen, but it was probably about 0.1 mm. The amount was adjusted until the bands appeared with maximum intensity, judged by visual observation with a hand spectroscope. Under these conditions the discharge had a greyish yellow colour. The exciting current was between 0.8 and 1.2 amp., obtained from a 10 kVA transformer. With a current of 1.2 amp. the power dissipated in the tube was about 1.8 kW. The helium was pumped away about every 2 hr. during an exposure.

The bands were photographed in the second order of a 21 ft. grating in an Eagle mounting, which in the region in question has a dispersion of about 1.22 Å/mm. The bands λ 6419, 6026, 5632 and 5295 were photographed, though the analysis of

$\lambda 5295$ is not given in the present paper. With a plate-holder 75 cm. long two bands could be photographed at one time. The plates used were Ilford Astra III for the green and Ilford Special Rapid Panchromatic for the red, the latter hypersensitized in the usual manner by bathing in dilute ammonia. In the bright second order of the grating the exposures ranged from 5 to 12 hr. A resolving power of 180,000 for suitable lines was actually reached, slightly exceeding the theoretical resolving power of the grating (173,000). No unresolved groups of lines appeared on the plates.

An iron comparison spectrum was used and the international standard lines were used as far as possible in measuring the plates. However, it was found impossible to avoid small shifts of the order 0.02 \AA between the two spectra. Owing to the great difference between the two sources it was very difficult to be sure the grating was illuminated in exactly the same manner for the two spectra. A single plate of the $\lambda 6026$ and $\lambda 6419$ bands was taken with a neon comparison produced by a small trace of neon in the tube during the exposure, so that there was no possibility of a shift between the two spectra. The wave-lengths were calculated from this plate by a cubic formula. The wave-lengths obtained from the iron plates were reduced to agree with those obtained from the neon plate by adding or subtracting a small constant amount. When this had been done there remained no systematic difference between the wave-lengths deduced from the various plates. In the case of the $\lambda 5632$ band, a plate was obtained on which a couple of neon lines appeared, the wave-lengths of which agreed with the accepted values to 0.005 \AA . The remaining plates were reduced to agree with this. Most of the lines have been measured on three plates, and it is considered that the absolute values of the wave-lengths are correct to at least 0.01 \AA , while the accuracy of the relative values in the case of sharp lines should be a good deal higher. The intensities were estimated from the plates during measurement and checked from large-scale enlargements of the bands.

On account of the enormous over-exposure of the line, He $\lambda 5876$, there was considerable blackening of the plates of the $\lambda 6026$ band, sufficient to obscure faint lines below $\lambda 5910$ and making it impossible to follow the band at all below $\lambda 5890$, though it certainly extends below this point. Some lines in this region too may be obscured by ghosts.

STRUCTURE OF ${}^4\Sigma \rightarrow {}^4\Pi$ BANDS

The analysis shows that the bands are due to a transition ${}^4\Sigma \rightarrow {}^4\Pi$. As this appears to be the first time this type of transition has been observed it seems advisable to consider briefly the structure the bands may be expected to show.

In Σ states the component, A , of the electronic angular momentum along the internuclear axis is zero, and the resultant electron spin, S , is coupled loosely to the rotational axis of the molecule. In a ${}^4\Sigma$ state $S = \frac{3}{2}$, and each rotational level consists of four closely spaced components corresponding to $J = K + \frac{3}{2}$, $J = K + \frac{1}{2}$, $J = K - \frac{1}{2}$,

474 THOMAS E. NEVIN ON ROTATIONAL ANALYSIS OF THE

$J = K - \frac{3}{2}$, where J is the quantum number corresponding to the total angular momentum of the molecule and K is the quantum number corresponding to the angular momentum exclusive of spin. These four components are denoted respectively $F_1(K + \frac{3}{2})$, $F_2(K + \frac{1}{2})$, $F_3(K - \frac{1}{2})$, $F_4(K - \frac{3}{2})$. The energy levels are given by the expression

$$F_i(J) = F_e + G(v) + B_v K(K+1) + D_v K^2(K+1)^2 + f_i(K, J-K). \quad (1)$$

For a given vibrational level $F_e + G(v)$ is constant. The term $f_i(K, J-K)$ takes four values corresponding to the four values of J for a given K and consists of two parts, the first arising from the interaction of K and S and the second from the mutual interaction of the individual electron spins. The values calculated by Budó (1937) by a method due to Kramers are as follows:

$$\left. \begin{aligned} f_1(K) &= -\frac{3}{2}\epsilon \left(1 - \frac{3}{2K+3}\right) + 3\gamma K, \\ f_2(K) &= +\frac{3}{2}\epsilon \left(1 + \frac{3}{2K+3}\right) + \gamma(K-3), \\ f_3(K) &= +\frac{3}{2}\epsilon \left(1 - \frac{3}{2K-1}\right) - \gamma(K+4), \\ f_4(K) &= -\frac{3}{2}\epsilon \left(1 + \frac{3}{2K-1}\right) - 3\gamma(K+1). \end{aligned} \right\} \quad (2)$$

When $A > 0$ we get Hund's case a when S is coupled to the internuclear axis and case b when it is coupled to the rotational axis. In case a the energy is given by the expression

$$F(J) = F_e + G(v) + AA\Sigma + B_v\{S(S+1) - \Omega^2 - \Sigma^2\} + B_v J(J+1) + D_v J^2(J+1)^2. \quad (3)$$

Here Σ is the component of S along the internuclear axis and $\Omega = |A + \Sigma|$. J takes the values $\Omega, \Omega + 1, \Omega + 2, \dots$. For a given vibrational level $AA\Sigma + B_v\{S(S+1) - \Omega^2 - \Sigma^2\}$ represents the variable part of the electronic energy. In a ${}^4\Pi$ state, $A = 1$ and Σ takes the values $\pm\frac{3}{2}, \pm\frac{1}{2}$, so the molecular multiplet consists of four components denoted ${}^4\Pi_{-\frac{3}{2}}, {}^4\Pi_{-\frac{1}{2}}, {}^4\Pi_{\frac{1}{2}}, {}^4\Pi_{\frac{3}{2}}$, where the suffix denotes $A + \Sigma$.

In practice it is often found that the observed terms approximate to case a for the lower rotational levels and gradually approach case b for the higher levels. In case b we denote the levels corresponding to a given K as $F_1(K + \frac{3}{2})$, $F_2(K + \frac{1}{2})$, $F_3(K - \frac{1}{2})$, $F_4(K - \frac{3}{2})$ as in the ${}^4\Sigma$ state.

In the intermediate case the notation of either case a or case b can be used. If the state is normal F_4 corresponds to ${}^4\Pi_{\frac{3}{2}}$ and F_1 to ${}^4\Pi_{-\frac{3}{2}}$, while if the state is inverted the correspondence is reversed. The energy expressions for an intermediate ${}^4\Pi$ state have been worked out by Brandt (1936) and slightly less accurate expressions have been given by Budó (1937). To a sufficiently high degree of approximation for the present

purpose Brandt's expressions may be written as follows, omitting a common constant term:

$$\left. \begin{aligned}
 F_4(J) &= B_v \left[J(J+1) + \frac{3}{2} \left\{ y_1 + 4J(J+1) + \frac{23}{9} + \frac{2\delta}{9} \right\}^{\frac{1}{2}} - 2 \frac{y_2 - 2J(J+1)}{y_1 + 4J(J+1)} \right] \\
 &\quad + D_v \left(J + \frac{3}{2} \right)^2 \left(J + \frac{5}{2} \right)^2, \\
 F_3(J) &= B_v \left[J(J+1) + \frac{1}{2} \left\{ y_1 + 4J(J+1) - 5 - 2\delta \right\}^{\frac{1}{2}} + 2 \frac{y_2 - 2J(J+1)}{y_1 + 4J(J+1)} \right] \\
 &\quad + D_v \left(J + \frac{1}{2} \right)^2 \left(J + \frac{3}{2} \right)^2, \\
 F_2(J) &= B_v \left[J(J+1) - \frac{1}{2} \left\{ y_1 + 4J(J+1) - 5 - 2\delta \right\}^{\frac{1}{2}} + 2 \frac{y_2 - 2J(J+1)}{y_1 + 4J(J+1)} \right] \\
 &\quad + D_v \left(J - \frac{1}{2} \right)^2 \left(J + \frac{1}{2} \right)^2, \\
 F_1(J) &= B_v \left[J(J+1) - \frac{3}{2} \left\{ y_1 + 4J(J+1) + \frac{23}{9} + \frac{2\delta}{9} \right\}^{\frac{1}{2}} - 2 \frac{y_2 - 2J(J+1)}{y_1 + 4J(J+1)} \right] \\
 &\quad + D_v \left(J - \frac{3}{2} \right)^2 \left(J - \frac{1}{2} \right)^2,
 \end{aligned} \right\} \quad (4)$$

where $y_1 = Y(Y-4)$ with $Y = \frac{A}{B_v}$, $y_2 = Y(Y-1)$ and $\delta = \frac{6Y(Y+4)}{2y_1 + 8J(J+1) + 56}$.

To each of the above expressions it is necessary to add a term $\Phi_c(\Sigma, J)$ or $\Phi_d(\Sigma, J)$ which arises from the interaction between the magnetic field due to the rotation of the molecule and the field along the internuclear axis. This causes each of the rotational levels to become double, one level of the doublet being classified as a c level and the other as a d level. This doubling of the rotational levels is spoken of as A -type doubling.

In a homonuclear molecule, on account of its symmetry properties, alternate levels have different statistical weights. When, as in O or O⁺, the nuclear angular momentum is zero, alternate rotational levels are missing in the ⁴ Σ state and alternate c and d levels in the ⁴ Π state. Fig. 2 shows a diagram of the transition ⁴ $\Sigma \rightarrow$ ⁴ Π for O₂⁺. In case a the branches are given by the selection principle $\Delta J = 0, \pm 1$, so that altogether 48 branches are to be expected. In case b , in addition, $\Delta K = 0, \pm 1$, so that the total number of branches is reduced to 27. No attempt has been made to illustrate the differing intensities of the branches on the diagram. The combination relations which give certain term differences in the initial and final states can be read off from the heads of the columns in Tables XIII–XIX. Owing to the fact that alternate lines are missing in each branch only alternate values of these differences can be derived from the analysis.

ANALYSIS OF THE BANDS

The appearance of the bands under high dispersion can be seen from Plates 7, 8, which show an enlargement of part of the (0, 0) band. Examination of the spectrum on large-scale enlargements showed that of the two branches found by Frerichs, each

line of the one which did not form the head was accompanied on the low-frequency side by a fainter line at a distance of about 0.45 cm.^{-1} . It was also noticed that the second head was formed by two branches, corresponding members of which had this same separation. In the (0, 0) and (0, 1) bands the lines running up to the head coincided exactly with the returning lines. This blending did not occur in the (1, 0) band

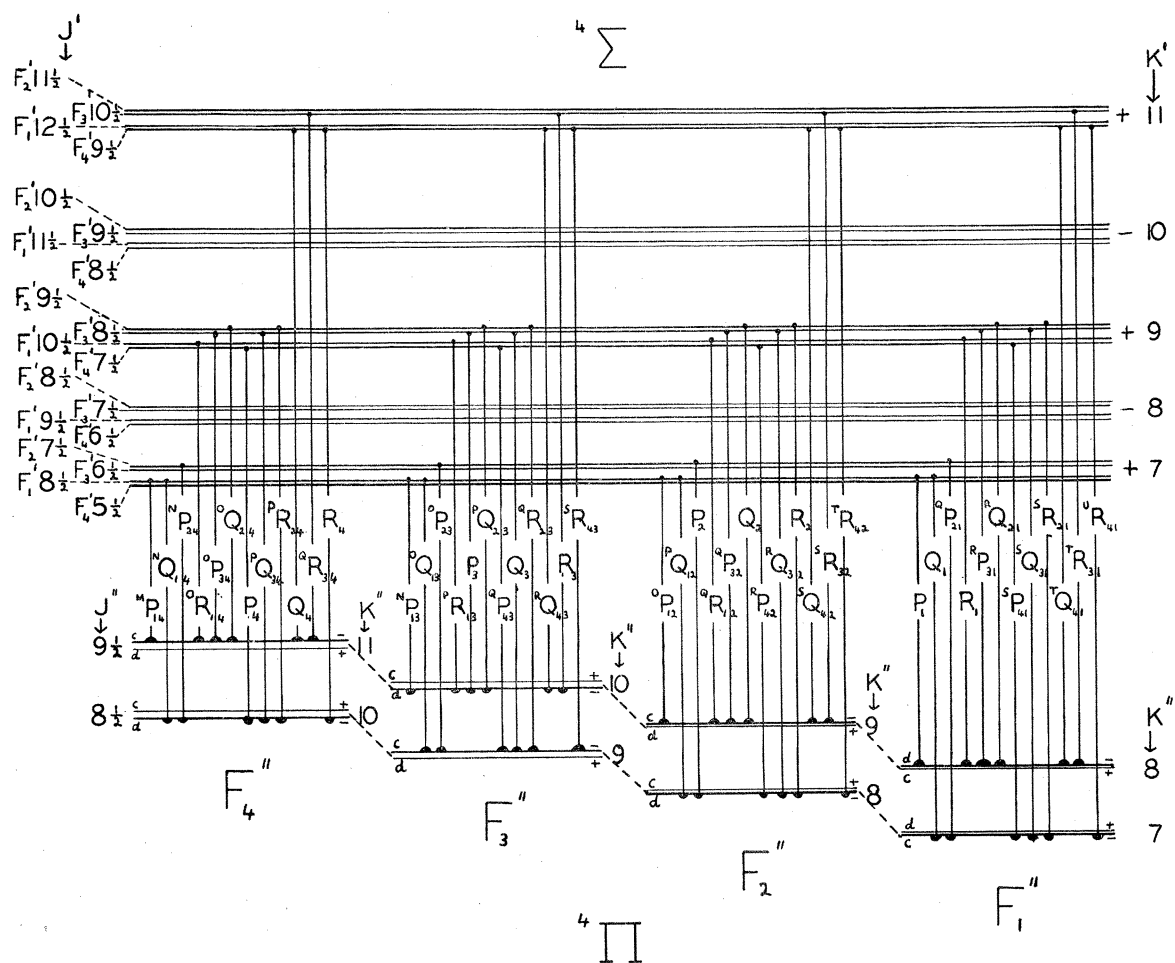


FIG. 2. Structure of the rotational levels in the initial ${}^4\Sigma$ state and final ${}^4\Pi$ state of the first negative bands of oxygen. The diagram shows the transitions to be expected in case *a*. The lightly drawn horizontal lines correspond to the missing levels.

which enabled the distance between the origins of the two components to be estimated at approximately 50 cm.^{-1} . To find additional branches it was necessary to adopt the tedious procedure of marking off on the enlargements lines which satisfied the condition that the second wave number difference between consecutive lines should be approximately constant. With so many lines close together the possibility that this procedure might give rise to spurious branches could not be ignored. On this account the existence of a branch could not be regarded as definitely established till it had been found in all three bands. In this way two branches with a separation of 0.45 cm.^{-1}

were found starting from the same sub-origin as Frerichs' two and additional branches starting from the second sub-origin. A search next showed a number of branches commencing at a point 50 cm.^{-1} above the second sub-origin and five strong branches commencing at a point 50 cm.^{-1} higher still. In a number of cases the branches seemed to be in pairs with the separation already noticed.

The existence of four components established the quartet structure of the band, and it seemed reasonable to assume, in accordance with Mulliken's suggestion, that the transition was ${}^4\Sigma \rightarrow {}^4\Pi$. The separation of 0.45 cm.^{-1} should then be connected with the spin fine structure of the ${}^4\Sigma$ state. From this point a search for additional branches and an attempt to identify those already found by means of the combination relations were carried on simultaneously. Fortunately, in many cases the probable J values of the lines could be established directly from the fact that the branches could be followed close up to the origin. When the analysis had been partly completed Budó's paper (1937) appeared confirming tentative conclusions on the structure of the ${}^4\Sigma$ state. With the confidence thus inspired it did not take long to identify the remaining branches found empirically and to calculate the positions of the lines of the weak branches with the aid of the combination relations.

The observed structure of the bands agrees with that to be expected for a ${}^4\Sigma \rightarrow {}^4\Pi$ transition with alternate lines missing in each branch. It will be shown in the next section that the initial level $F'_1(K)$ is blended with $F'_4(K)$ and $F'_2(K)$ with $F'_3(K)$. The effect of this is to reduce the total number of branches from 48 to 40, all of which have been observed in the (1, 0) and (0, 1) bands. The absolute J values of the lines of the branches were checked in the usual manner.

The wave number and intensities for the lines of the (0, 0), (1, 0) and (0, 1) bands are given in Tables I–XII. The assignment of the wave numbers to the branches is checked by the combination relations given in Tables XIII–XIX. To save space the $\Delta_1 F''(J + \frac{1}{2})$ values are given for the (0, 0) band only. On account of the complex structure of the bands blends of two lines and of more than two lines in some cases are common. The superscript following the wave number indicates the number of times the particular line has been used in the analysis.

For the observed branches, which, owing to the coincidence of $F'_2(K)$ with $F'_3(K)$, are really blends of two branches, the lines are counted as having been used once on that account. In a few cases the exact end-point of the branches could not be established, as strong lines of other branches fell in the calculated position. Up to the point at which the second band commences in each of the sequences of which the three analysed bands form the first members the analysis includes all but a very few lines of low intensity. Beyond this point unassigned lines nearly all of low intensity become more numerous. It seems reasonable to assume that these lines belong to the later bands in the sequences. The intensities of some of the lines in the analysed bands may be affected by blending with lines of these faint bands. In the (0, 0) band the intensities of some lines below $\lambda 5920$ may be affected by blending with faint ghosts of He $\lambda 5876$.

TABLE I. WAVE NUMBERS OF LINES IN THE (0, 0) BAND. $4\Sigma \rightarrow 4\Pi_{-3/2}$ TRANSITION

$J + \frac{1}{2}$	MP_{14}	NP_{24}	NQ_{14}	OP_{34} and OQ_{24}	OR_{14}	PR_{24} and PQ_{34}	P_4	QR_{34}	Q_4	R_4
1				16590.73 ² 5*		16594.20 ¹ 1†		16603.16 ¹ 2		
2				589.29 ² 6*		597.50 ¹ 1†		612.16 ¹ 3	16611.76 ¹ 1	
3				588.84 ³ 5*		601.74 ¹ 4†	16601.27 ³ 5	621.92 ² 5	621.50 ³ 6	
4				589.29 ² 6		606.94 ² 8	606.53 ¹ 00	632.67 ¹ 3	632.24 ¹ 3	
5	16565.41 ¹ 1	16578.91 ¹ 00	16578.41 ¹ 00	590.73 ² 5	588.46 ¹ 0	613.06 ¹ 7	612.61 ¹ 3	644.32 ¹ 3	643.88 ¹ 4	16649.80 ³ 6d
6		573.83 ¹ 1	573.34 ¹ 3	593.20 ¹ 4	588.84 ³ 5	620.12 ¹ 7	619.69 ¹ 2	656.94 ¹ 4	656.52 ¹ 5	666.19 ² 4
7		569.74 ¹ 0	569.34 ¹ 0d	596.69 ¹ 4		628.21 ¹ 7	627.77 ¹ 3	670.67 ² 8	670.18 ² 7	683.44 ¹ 2
8		566.63 ¹ 0d	566.23 ¹ 0	601.27 ³ 5		637.35 ¹ 7	636.91 ¹ 4	685.23 ³ 12	684.81 ⁶ 25	701.67 ¹ 2
9		564.46 ¹ 1	563.99 ¹ 0	606.94 ² 8		647.57 ¹ 6	647.14 ² 3	701.15 ¹ 2	700.69 ¹ 6	720.93 ¹ 3
10		563.49 ² 1		613.81 ¹ 3		658.92 ² 5	658.53 ³ 4	718.08 ¹ 2	717.65 ² 8	741.30 ¹ 6
11		563.49 ² 1		621.92 ² 5		671.50 ¹ 5	671.02 ¹ 4	736.31 ⁴ 10	735.78 ³ 10	762.72 ¹ 4
12		563.49 ² 1		631.15 ¹ 2		685.23 ³ 12	684.81 ⁶ 25	755.54 ¹ 4	755.15 ² 5	785.34 ¹ 4
13						700.10 ¹ 2	699.66 ² 6	776.18 ² 6	775.70 ² 6	809.12 ¹ 4
14						716.30 ¹ 2	715.86 ¹ 2	797.95 ² 9	797.52 ³ 10b	834.12 ¹ 3
15						733.82 ³ 8	733.31 ¹ 3	820.92 ¹ 3	820.51 ¹ 4	860.28 ¹ 5
16								845.28 ¹ 3	844.81 ¹ 5	887.63 ¹ 3
17								870.88 ¹ 1	870.36 ² 4	
18								897.23 ¹ 4	897.23 ¹ 4	
19								925.36 ¹ 1	925.36 ¹ 1	
20								954.77 ² 5†	954.77 ² 5†	
21										
22										
23										
24										
25										
26										
27										
28										
29										
30										
31										
32										
33										
34										
35										
36										
37										
38										
39										
40										

* OQ_{24} only. Corresponding lines in OP_{34} not observed.
 † PQ_{34} only. Corresponding lines in PR_{34} not observed.
 ‡ The Q_4 branch could not be followed beyond this point owing to blackening produced by He $\lambda 5876$.

TABLE II. WAVE NUMBERS OF LINES IN THE $(0, 0)$ BAND. $4\Sigma \rightarrow 4I_{3/2}$ TRANSITION

$J + \frac{1}{2}$	$^nP_{13}$	$^oP_{23}$	$^oQ_{13}$	P_3 and $^rQ_{23}$	$^rR_{13}$	Q_3 and $^eR_{23}$	$^eP_{43}$	R_3	$^rQ_{43}$	$^sR_{43}$
2		16634·67 ² 3	16634·16 ² 3	16640·11 ² 2*	16639·68 ² 1	16647·14 ² 3†	16646·58 ¹ 1		16652·25 ² 4d	16669·69 ² 2
3		629·36 ² 4	628·92 ² 4	639·51 ² 1*	639·09 ¹ 1	652·25 ² 4d†	651·78 ¹ 1		661·90 ² 5	684·81 ⁶ 25
4				640·11 ² 2*	639·68 ² 1	658·53 ³ 4	658·11 ¹ 4		672·74 ¹ 5	701·53 ¹ 2
5	16616·63 ¹ 0d	625·41 ² 4	624·98 ² 4	641·95 ¹ 4	641·45 ² 3d	666·19 ² 4	665·71 ¹ 3		684·81 ⁶ 25	719·25 ¹ 2
6		622·79 ² 5	622·36 ² 5	645·11 ¹ 5	644·56 ¹ 1	675·07 ¹ 3	674·58 ¹ 4		698·15 ¹ 6	738·31 ² 5
7	608·30 ¹ 1	621·50 ³ 6	621·03 ² 5	649·51 ² 6d	649·02 ³ 6	685·23 ³ 12	684·81 ⁶ 25	16713·26 ¹ 0	712·80 ¹ 7	758·63 ¹ 3
8	601·27 ³ 5	621·50 ³ 6	621·03 ² 5	655·28 ¹ 6	654·81 ¹ 0	696·65 ¹ 6	696·19 ¹ 4	729·09 ¹ 00	728·70 ¹ 5	780·24 ¹ 4
9	595·50 ¹ 0	622·79 ² 5	622·36 ² 5	662·32 ¹ 6	661·90 ² 5	709·42 ¹ 4	708·97 ¹ 3	746·31 ² 5	745·91 ¹ 6	803·15 ¹ 3
10	591·07 ¹ 0	625·41 ² 4	624·98 ² 4	670·67 ² 8	670·18 ² 7	723·51 ² 5	723·07 ² 4	764·83 ¹ 2	764·40 ¹ 5	827·34 ¹ 3
11		629·36 ² 4	628·92 ² 4	680·42 ¹ 4	679·97 ¹ 00	738·94 ¹ 5	738·48 ¹ 3	—	784·24 ³ 4	852·84 ¹ 3
12		634·67 ² 3	634·16 ² 3	691·46 ² 7		755·69 ² 4	755·15 ² 5	805·80 ¹ 2	805·37 ¹ 4	879·72§
13		641·45 ² 3d	640·91 ¹ 1	703·87 ¹ 5		773·83 ¹ 4c	773·39 ¹ 2	828·36 ² 4b	827·85 ² 4b	
14		649·51 ² 6d	649·02 ³ 6	717·65 ² 8		793·19 ² 8b	792·72 ¹ 3	852·12 ² 3d	851·61 ¹ 4	
15		658·92 ² 5	658·53 ³ 4	732·79 ² 8		814·00 ¹ 5	813·42 ² 2d	877·17 ¹ 1	876·75 ² 3	
16		669·69 ² 2		749·25 ¹ 4		836·19 ¹ 6	835·78 ¹ 1	903·56 ¹ 4	903·15 ² 4	
17		681·78 ¹ 0d		767·12 ¹ 4		859·64 ¹ 5	859·09 ¹ 2	931·36 ¹ 2	930·90 ¹ 2	
18		695·35 ¹ 00		786·32 ² 7		884·46 ¹ 3	883·96 ¹ 2	960·49 ¹ 4†	960·00 ¹ 4†	
19				806·93 ³ 8		910·66 ¹ 3	910·23 ¹ 1			
20				828·80 ¹ 2		938·24 ¹ 3	937·80 ¹ 4			
21				852·12 ² 3d						
22				876·75 ² 3						
23				902·77 ¹ 4						
24				930·03 ¹ 1						

* $^rQ_{23}$ only. Corresponding lines in P_3 not observed.
 † Branches could not be followed beyond this point owing to blackening produced by He λ 5876.
 ‡ Coincides with ghost of He λ 5876.

TABLE III. WAVE NUMBERS OF LINES IN THE (0, 0) BAND. ${}^4\Sigma \rightarrow {}^4\Pi_{3/2}$ TRANSITION

$J + \frac{1}{2}$	${}^oP_{12}$	P_2	${}^rQ_{12}$	Q_2 and ${}^oP_{32}$	${}^qR_{12}$	R_2 and ${}^rQ_{32}$	${}^rP_{42}$	${}^sR_{32}$	${}^sQ_{42}$	${}^tR_{42}$
2			16684·81 ⁶ 25	16690·19 ² 1*	16689·77 ² 1	16697·74 ¹ 1†	16697·24 ¹ 1			
3	16677·22 ² 1		680·32 ¹ 4	690·19 ² 1*	689·77 ² 1	703·58 ¹ 3†	703·14 ¹ 2	16724·95 ¹ 3	16724·53 ¹ 3	16736·31 ⁴ 10
4			677·50 ¹ 5	691·77 ¹ 2*	691·46 ² 7	711·02 ¹ 4	710·58 ² 5	738·31 ² 5	737·88 ¹ 4	753·96 ² 4
5	668·50 ¹ 2		676·31 ¹ 6	694·92 ¹ 4	694·54 ² 4	720·03 ¹ 4	719·62 ¹ 2	753·23 ¹ 3	752·80 ¹ 3	773·18 ¹ 1
6	661·39 ² 5	16677·86 ¹ 00	676·72 ³ 7	699·66 ² 6	699·27 ¹ 3	730·66 ² 7	730·31 ² 6	769·73 ¹ 3	769·29 ¹ 4	794·06 ¹ 0
7	655·95 ² 5	677·22 ¹ 1	676·72 ³ 7	705·98 ¹ 4	705·57 ¹ 4	742·89 ¹ 6	742·62 ² 5	787·75 ¹ 4	787·35 ¹ 3	816·49 ³ 6b
8	652·07 ² 4d	679·11 ¹ 00b	678·73 ¹ 7	713·87 ¹ 6	713·47 ² 7	756·61 ¹ 6	756·18 ¹ 0	807·33 ² 4	806·93 ³ 8	840·26 ¹ 2
9	649·80 ³ 6d	682·73 ¹ 00	682·30 ¹ 6	723·28 ¹ 4	722·87 ¹ 3	771·88 ¹ 6	771·48 ¹ 0	828·36 ² 4b	827·85 ² 4b	—
10	649·02 ³ 6	687·81 ¹ 0	687·43 ¹ 6	734·26 ² 6	733·82 ³ 8	788·67 ¹ 7	788·23 ¹ 1	851·00 ¹ 4	850·55 ¹ 1	892·52 ¹ 2
11	649·80 ³ 6d	694·54 ² 4	694·07 ¹ 5	746·74 ¹ 6	746·31 ² 5	806·93 ³ 8		875·02 ¹ 2	874·41 ¹ 3	920·56 ¹ 3
12	652·07 ² 4d	702·67 ¹ 2	702·23 ¹ 4	760·72 ² 5	760·31 ¹ 2	826·70 ¹ 6		900·58 ¹ 6	900·15 ¹ 1	
13	655·95 ² 5	712·38 ¹ 1	711·94 ¹ 4	776·18 ² 6	775·70 ² 6	847·92 ¹ 6		927·49 ¹ 1		
14	661·39 ² 5	723·51 ² 5	723·07 ² 4	793·19 ² 8b	792·72 ² 3	870·62 ¹ 6				
15	668·31 ¹ 0	736·31 ⁴ 10	735·78 ³ 10	811·52 ¹ 5	811·11 ¹ 2	894·71 ¹ 4				
16	676·72 ³ 7	750·25 ² 6	749·79 ² 8	831·35 ¹ 6	830·85 ² 3	920·28 ¹ 4				
17	686·49 ¹ 0	765·90 ¹ 2	765·43 ¹ 2	852·64 ¹ 4		§				
18	697·81 ¹ 0	782·82 ² 7	782·49 ¹ 0	875·36 ¹ 4		975·58 ¹ 3†				
19				899·48 ¹ 3						
20				924·98 ¹ 3						
21				951·88 ¹ 3†						

* Q_2 only. Corresponding lines in ${}^oP_{32}$ not observed.

† Branches could not be followed beyond this point owing to blackening produced by He λ 5876.

§ Obscured by ghost of He λ 5876.

† ${}^rQ_{32}$ only. Corresponding lines in R_2 not observed.

‡ Branches could not be followed beyond this point owing to blackening produced by He λ 5876.

§ Obscured by ghost of He λ 5876.

TABLE IV. WAVE NUMBERS OF LINES IN THE (0, 0) BAND. ${}^4\Sigma^+ \rightarrow {}^4\Pi_{3/2}^-$ TRANSITION

$J + \frac{1}{2}$	P_1	Q_1	${}^oP_{21}$	R_1	${}^RQ_{21}$ and ${}^RP_{31}$	${}^sR_{21}$ and ${}^sQ_{31}$	${}^sP_{41}$	${}^TR_{31}$	${}^TQ_{41}$	${}^vR_{41}$
3		16735·32 ¹ 00	16735·78 ³ 10							
4		731·61 ¹ 3	732·02 ¹ 4	16743·23 ¹ 00	16743·65 ¹ 5d§	16763·43 ¹ 5		16791·38 ¹ 1	16790·98 ¹ 2	
5	16720·28 ¹ 3	729·89 ¹ 3	730·31 ² 6	747·64 ¹ 2	748·07 ¹ 8	773·91 ¹ 3c		807·88 ¹ 2	807·33 ² 4	
6	714·45 ¹ 3	730·17 ¹ 6	730·66 ² 7	753·96 ² 4	754·39 ¹ 8	786·32 ² 7		826·27 ¹ 3	825·84 ¹ 2	
7	710·58 ² 5	732·34 ¹ 6	732·79 ² 8	762·16 ¹ 3	762·57 ¹ 6	800·50 ¹ 5	16800·05 ¹ 2	846·41 ¹ 2d		
8	708·56 ¹ 5	736·31 ⁴ 10	736·79 ¹ 6	772·14 ¹ 4	772·61 ¹ 8	816·49 ² 6b		868·42 ¹ 3		
9	708·45 ¹ 5	742·18 ¹ 8	742·62 ² 5	783·96 ¹ 4	784·40 ¹ 6	834·25 ¹ 7		—		
10	710·08 ¹ 4	749·79 ² 8	750·25 ² 6	797·52 ³ 10b	797·95 ² 9	853·72 ¹ 5		917·45 ¹ 0		
11	713·47 ² 7	759·10 ¹ 7	759·57 ¹ 4	812·76 ¹ 4	813·20 ¹ 6	874·83 ¹ 4				
12	718·58 ¹ 5	770·13 ¹ 6	770·58 ¹ 4	829·64 ¹ 6	830·08 ¹ 6	897·58 ¹ 4				
13	725·38 ¹ 4	782·82 ² 7	783·25 ¹ 4	848·16 ¹ 6	848·60 ¹ 7	921·96 ¹ 2				
14	733·82 ³ 8	797·10 ¹ 9	797·52 ³ 10b	868·28 ¹ 5	868·72 ¹ 7					
15	743·95 ¹ 5d	812·97 ¹ 6	813·42 ² 2d	*	890·38 ¹ 5					
16	755·69 ² 4	830·41 ¹ 7	830·85 ² 3	*	*					
17	768·73 ¹ 4	849·40 ¹ 6	849·86 ¹ 1							
18	783·44 ¹ 4	869·91 ¹ 7	870·36 ² 4	937·80 ² 4	938·24 ² 3					
19	799·75 ¹ 3	891·89 ¹ 6		964·07 ¹ 3b†	963·64 ¹ 1b†					
20	817·52 ¹ 5	915·34 ¹ 5								
21	836·77 ¹ 3	940·28 ¹ 3								
22	857·45 ¹ 5b	966·67 ¹ 5†								
23	879·72†									
24	903·15 ² 4									
25	928·31 ¹ 3d									
26	954·77 ² 5†									

* Obscured by ghost of He λ5876.

† Blend with ghost of He λ5876.

‡ Branches could not be followed beyond this point owing to the blackening produced by He λ5876.

§ ${}^RQ_{21}$ only. Corresponding line in ${}^RP_{31}$ not observed.

TABLE V. WAVE NUMBERS OF LINES IN THE (0, 1) BAND. ${}^4\Sigma \rightarrow {}^4\Pi_{-3/2}$ TRANSITION

$J + \frac{1}{2}$	${}^M P_{14}$	${}^N P_{24}$	${}^N Q_{14}$	${}^O Q_{24}$ and ${}^O P_{34}$	${}^O R_{14}$	${}^P R_{24}$ and ${}^P Q_{34}$	P_4	${}^Q R_{34}$	Q_4	R_4
1				15575.17 ² 1*	15574.66 ³ 6b	15579.42 ² 2 [†]				15605.31 ¹ 0
2				574.66 ³ 6b*	574.26 ² 00	582.75 ¹ 2 [†]		15597.63 ² 7	15597.11 ¹ 1	620.29 ³ 3
3				574.66 ³ 6b*	574.26 ² 00	587.39 ¹ 5 [†]		607.75 ¹ 4	607.38 ² 9	635.96 ² 1d
4		15564.58 ¹ 1	15564.08 ¹ 00			593.00 ¹ 7	15592.63 ¹ 2	618.94 ¹ 4	618.50 ¹ 4	652.74 ² 5
5		559.86 ¹ 1	559.45 ¹ 1			599.65 ¹ 8	599.19 ¹ 1	631.19 ¹ 4	630.78 ¹ 4	670.79 ² 6
6		556.31 ¹ 1	555.77 ¹ 1			607.38 ² 9	606.98 ¹ 2	644.57 ³ 6	644.14 ³ 9b	689.78 ¹ 2
7	15542.00 ¹ 2					616.35 ¹ 7	615.89 ¹ 2	659.09 ¹ 4	658.66 ¹ 5	710.00 ² 3
8		553.78 ² 1				626.41 ¹ 7	625.96 ³ 7	674.88 ¹ 2	674.40 ¹ 5	731.42 ¹ 2
9		552.55 ² 1				637.73 ² 8	637.31 ¹ 5	691.82 ¹ 2	691.39 ¹ 5	754.10 ¹ 3
10		553.78 ² 1				650.28 ¹ 5	649.84 ¹ 2	710.00 ² 3	709.61 ¹ 5	778.04 ¹ 2
11						664.12 ¹ 4	663.69 ³ 7	729.56 ¹ 1	729.15 ¹ 4c	803.34 ¹ 4c
12						679.29 ¹ 2	678.87 ¹ 2	750.41 ¹ 1	750.01 ¹ 5	829.82 ¹ 4
13						695.83 ¹ 2	695.41 ¹ 2	772.62 ³ 4	772.21 ¹ 4	857.71 ¹ 3
14						713.70 ¹ 2c	713.34 ¹ 4d	796.27 ² 4	795.80 ² 4d	886.99 ¹ 2b
15						733.02 ¹ 1	732.59 ¹ 1		820.69 ¹ 4	917.51 ² 3
16							753.14 ² 5		847.01 ¹ 3	949.49 ¹ 0
17									874.74 ² 5	982.87 ¹ 0
18									903.86 ¹ 3	16017.56 ¹ 2
19									934.37 ¹ 1	053.43 ¹ 0
20									966.07 ¹ †	
21										
22										
23										
24										
25										
26										
27										
28										
29										
30										
31										
32										
33										
34										
35										
36										
37										
38										
39										
40										

* ${}^O Q_{24}$ only. Corresponding lines in ${}^O P_{34}$ not observed.

† ${}^P Q_{34}$ only. Corresponding lines in ${}^P R_{24}$ not observed.

‡ Obscured by line 6261.6 OI.

FIRST NEGATIVE BAND SPECTRUM OF OXYGEN

483

TABLE VI. WAVE NUMBERS OF LINES IN THE (0, 1) BAND. ${}^4\Sigma \rightarrow {}^4\Pi_{3/2}$ TRANSITION

$J + \frac{1}{2}$	${}^N P_{13}$	${}^O P_{23}$	${}^O Q_{13}$	P_3 and ${}^P Q_{23}$	${}^P R_{13}$	Q_3 and ${}^Q R_{23}$	${}^Q P_{43}$	R_3	${}^R Q_{43}$	${}^S R_{43}$
3		15620-29 ³	15619-79 ²	15624-99 ¹	15624-50 ¹	15632-52 ¹			15647-48 ¹	15670-63 ¹
4		615-23 ³	614-82 ²	625-96 ³	625-45 ¹	637-92 ²			658-55 ¹	687-48 ¹
5		611-52 ²	611-04 ²	628-19 ¹	627-75 ¹	644-57 ³	15644-14 ³		671-07 ¹	705-79 ¹
6		609-35 ²	608-90 ²	631-95 ¹	631-46 ¹	652-74 ²	652-20 ¹		684-99 ³	725-43 ¹
7	15594-56 ¹	608-60 ¹	608-18 ¹	637-04 ¹	636-60 ¹	662-26 ¹	661-71 ¹		700-35 ²	746-53 ¹
8		609-35 ²	608-90 ²	643-63 ¹	643-27 ²	673-08 ¹	672-62 ¹	15717-48 ¹	717-03 ¹	768-92 ²
9		608-60 ¹	608-18 ¹	651-64 ¹	651-19 ¹	685-43 ¹	684-99 ³	735-63 ¹	735-19 ¹	792-95 ¹
10		609-35 ²	608-90 ²	661-08 ¹	660-54 ¹	699-22 ¹	698-73 ²	755-17 ¹	754-81 ¹	818-37 ²
11		611-52 ²	611-04 ²	671-99 ¹		714-46 ¹	714-02 ¹	776-22 ¹	775-82 ³	845-04 ¹
12		615-23 ³	614-82 ²	684-37 ¹		731-12 ¹	730-81 ²	798-70 ²	798-27 ¹	873-27 ¹
13		620-29 ³	619-79 ²	698-23 ¹		749-25 ⁴	748-80 ²	822-60 ¹	822-16 ¹	
14		626-87 ¹	626-41 ²	713-59 ¹		768-92 ²	768-49 ²	847-99 ¹	847-57 ¹	
15		634-93 ¹	634-48 ¹	730-38 ²		789-97 ¹	789-52 ¹	874-74 ²	874-40 ¹	
16		644-57 ³	644-14 ³	748-71 ¹		812-53 ¹	812-09 ¹	903-03 ¹	902-63 ¹	
17		655-53 ¹	655-14 ²	768-49 ²		836-56 ¹	836-16 ¹	932-79 ¹	932-37 ¹	
18		668-11 ¹	667-74 ¹	789-78 ¹		862-05 ¹	861-69 ¹	963-99 ¹	963-51 ¹	
19		682-23 ¹				889-02 ¹		996-68 ¹		
20		697-82 ¹				917-51 ²				
21						947-39 ²				
22						978-65 ¹				
23						16011-55 ¹				
24						045-74 ¹				
25										
26										
27										
28										
29										
30										
31										
32										
33										
34										
35										
36										
37										
38										
39										
40										
41										
42										
43										
44										
45										

* ${}^P Q_{23}$ only. Corresponding lines in P_3 not observed.† ${}^Q Q_3$ only. Corresponding lines in ${}^Q R_{23}$ not observed.

TABLE VII. WAVE NUMBERS OF LINES IN THE (0, 1) BAND. $4\Sigma \rightarrow 4I_{3/2}$ TRANSITION

$J + \frac{1}{2}$	$^oP_{12}$	P_2	$^rQ_{12}$	Q_2 and $^qP_{32}$	$^qR_{12}$	R_2 and $^rQ_{32}$	$^rP_{42}$	$^sR_{32}$	$^sQ_{42}$	$^rR_{42}$
2			15670.06 ¹ 1	15675.34 ¹ 1*		15683.03 ¹ 2†	15682.59 ¹ 1			
3	15662.69 ² 7		665.84 ¹ 4	675.58 ¹ 1*		689.13 ¹ 2†	688.69 ¹ 2	15710.63 ¹ 2	15710.22 ¹ 1	15721.90 ¹ 00
4			663.39 ¹ 5	677.45 ¹ 2*		696.98 ² 6	696.48 ¹ 0	724.24 ³ 12b	723.92 ¹ 0	739.87 ² 3
5	654.19 ¹ 2		662.69 ² 7	681.04 ¹ 2	15680.68 ¹ 2	706.43 ¹ 3	705.92 ² 3c	739.87 ² 3	739.36 ² 5b	759.33 ¹ 0
6	647.39 ¹ 3		663.69 ³ 7	686.33 ¹ 3	685.93 ¹ 3	717.65 ² 8	717.25 ³ 6	757.04 ¹ 3	756.61 ¹ 3	780.94 ¹ 1
7	642.57 ¹ 4		666.40 ¹ 6	693.29 ¹ 3	692.90 ¹ 2	730.55 ¹ 7	730.11 ¹ 0	775.82 ³ 9	775.36 ² 9	803.89 ² 6
8	639.33 ¹ 4		670.79 ² 6	701.95 ¹ 4	701.55 ¹ 2	745.12 ¹ 6	744.72 ¹ 0	796.27 ² 4	795.80 ² 4d	828.63 ¹ 0
9	637.73 ² 8		676.88 ¹ 5	712.29 ¹ 4	711.87 ¹ 2	761.38 ² 12	—	818.37 ² 4d	817.98 ¹ 0	855.13 ¹ 00
10	637.92 ² 6		684.62 ¹ 5	724.24 ³ 12b	723.78 ² 10b	779.22 ¹ 5	778.84 ¹ 0	842.15 ¹ 1	841.82 ² 5	
11	639.78 ¹ 4	15684.99 ³ 10b	694.42 ¹ 3	737.88 ¹ 5	737.42 ¹ 2	798.70 ² 6		867.47 ¹ 1	867.09 ¹ 1	
12	643.27 ² 4	694.42 ¹ 1	705.44 ¹ 1	753.14 ² 6	752.69 ¹ 1	819.75 ¹ 6		894.40 ¹ 1		
13	648.41 ¹ 2	705.44 ¹ 1	717.65 ² 8	769.98 ¹ 4	769.54 ¹ 1	842.47 ¹ 5		922.80 ¹ 0		
14	655.14 ² 2d	718.06 ¹ 1	731.83 ¹ 2	788.43 ² 5	787.93 ² 6	866.71 ¹ 4		952.85 ¹ 2		
15	663.69 ³ 7	732.28 ¹ 1	747.66 ¹ 1	808.42 ² 8		892.52 ¹ 4				
16	673.60 ¹ 0	748.14 ¹ 1	765.08 ¹ 1	830.07 ¹ 5		919.87 ¹ 3				
17		765.49 ¹ 1	784.01 ¹ 00	853.24 ¹ 4		948.78 ¹ 2				
18		784.51 ¹ 0		877.96 ¹ 5		979.26 ¹ 1				
19		804.96 ¹ 1		904.21 ¹ 3		16011.10 ¹ 2				
20		827.14 ¹ 00		932.01 ¹ 1		044.60 ¹ 2				
21		850.79 ¹ 00		961.31 ¹ 1		—				
22				992.11 ¹ 2		115.91 ¹ 1				
23				16024.42 ¹ 1						
24				058.19 ¹ 0						
25				093.51 ¹ 1						
26										
27										
28										
29										
30										
31										
32										
33										
34										
35										
36										
37										
38										
39										
40										
41										
42										
43										
44										
45										
46										
47										
48										

* Q_2 only. Corresponding lines in $^qP_{32}$ not observed.

† $^rQ_{32}$ only. Corresponding lines in R_2 not observed.

FIRST NEGATIVE BAND SPECTRUM OF OXYGEN

485

TABLE VIII. WAVE NUMBERS OF LINES IN THE (0, 1) BAND. ${}^4\Sigma \rightarrow {}^4\Pi_{3/2}$ TRANSITION

$J + \frac{1}{2}$	P_1	Q_1	$Q_{P_{21}}$	R_1	${}^RQ_{21}$ and ${}^RP_{31}$	${}^SP_{21}$ and ${}^SQ_{31}$	${}^SP_{41}$	${}^TR_{31}$	${}^TQ_{41}$	${}^UR_{41}$
4	15713.59 ¹ 3c	15716.79 ² 4	15717.25 ³ 6	15728.85 ¹ 00	15726.41 ¹ 1*	15749.25 ⁴ 20b	15748.80 ² 3c	15762.30 ¹ 00	15761.85 ² 3	
5	705.92 ² 3c	715.64 ¹ 4	716.08 ¹ 4	733.54 ¹ 1b	729.24 ¹ 4c*	760.14 ¹ 4	759.61 ¹ 0	—	776.87 ¹ 0	
6	700.35 ² 7b	716.35 ¹ 4	716.79 ² 4	740.37 ¹ 5	740.82 ¹ 7	773.05 ² 9	772.62 ³ 5	794.33 ¹ 1	793.91 ¹ 3d	
7	696.98 ² 6	719.05 ¹ 5	719.50 ¹ 5	749.25 ⁴ 20b	749.66 ² 12b	787.93 ² 6	787.56 ² 6	813.35 ¹ 00		
8	695.64 ¹ 3	723.78 ² 10b	724.24 ³ 12b	760.01 ¹ 4	760.40 ¹ 7	804.69 ¹ 5	804.32 ¹ 00	834.21 ¹ 0		
9	696.22 ¹ 4	730.38 ² 10	730.81 ² 3	772.62 ³ 5	773.05 ² 9	823.37 ¹ 5	822.89 ¹ 00			15917.04 ¹ 0
10	698.73 ² 7	738.88 ¹ 7	739.36 ² 5b	787.12 ¹ 5	787.56 ² 6*	843.84 ¹ 4				
11	703.10 ¹ 7	749.25 ⁴ 20b	749.66 ² 12b	803.42 ¹ 4c	803.89 ² 6	866.13 ¹ 2				
12	709.28 ¹ 4	761.38 ² 12	761.85 ² 3	821.54 ¹ 3	821.97 ¹ 5	890.13 ¹ 2				
13	717.25 ³ 6	775.36 ² 9	775.82 ³ 9	841.38 ¹ 5	841.82 ² 5	915.86 ¹ 3				
14	727.03 ¹ 3	791.03 ¹ 6	791.46 ¹ 2	862.93 ¹ 4	863.40 ¹ 4	943.26 ¹ 0				
15	738.54 ¹ 3	808.42 ² 8	808.84 ¹ 2	886.18 ¹ 3	886.63 ¹ 3					
16	751.76 ¹ 3	827.60 ¹ 5	827.94 ¹ 1	911.06 ¹ 4	911.55 ¹ 3					
17	766.67 ¹ 2	848.24 ¹ 5	848.66 ¹ 5	937.61 ¹ 1	938.06 ¹ 1					
18	783.23 ¹ 2	870.63 ¹ 5	870.63 ¹ 5	965.72 ¹ 0						
19	801.47 ¹ 1	894.62 ¹ 4	894.62 ¹ 4	995.51 ¹ 1						
20	821.30 ¹ 2	920.20 ¹ 3	920.20 ¹ 3	16026.81 ¹ 1						
21	842.73 ¹ 0	947.39 ² 4	947.39 ² 4							
22		976.17 ¹ 2	976.17 ¹ 2							
23		16006.43 ¹ 2	16006.43 ¹ 2							
24		038.30 ¹ 2	038.30 ¹ 2							
25		071.70 ¹ 1	071.70 ¹ 1							
26		106.51 ¹ 1	106.51 ¹ 1							
27		142.93 ¹ 1	142.93 ¹ 1							

* ${}^RQ_{21}$ only. Corresponding lines in ${}^RP_{31}$ not observed.

TABLE IX. WAVE NUMBERS OF LINES IN THE (1, 0) BAND. ${}^4\Sigma \rightarrow {}^4\Pi_{-1/2}$ TRANSITION

$J + \frac{1}{2}$	${}^M P_{14}$	${}^N P_{24}$	${}^N Q_{14}$	${}^O Q_{24}$ and ${}^O P_{34}$	${}^O R_{14}$	${}^P R_{24}$ and ${}^P Q_{34}$	P_4	${}^Q R_{34}$	Q_4	R_4
1				17753·26 ¹ 1*		17756·82 ¹ 2†		17765·59 ¹ 1	17765·22 ¹ 0	
2				751·71 ¹ 2*		759·78 ¹ 2†		774·21 ² 5	773·73 ² 6	
3				750·87 ¹ 3*		763·79 ¹ 5†	17763·28 ¹ 0	783·39 ¹ 4	782·93 ¹ 3	17795·94 ¹ 3
4		17741·26 ² 1	17740·91 ² 1	750·76 ² 4	17750·41 ³ 0	768·39 ¹ 6	768·01 ² 4	793·33 ² 4	792·91 ¹ 4	810·54 ¹ 2
5				751·42 ¹ 4	750·41 ³ 0	773·73 ² 6	773·27 ¹ 3	804·04 ¹ 4	803·60 ¹ 6	825·92 ¹ 3
6		735·83 ¹ 1	735·37 ¹ 1	752·95 ¹ 5		779·87 ¹ 6	779·43 ¹ 2	815·54 ² 5	815·12 ² 5	842·07 ¹ 4
7		731·11 ¹ 1	730·71 ¹ 0	755·33 ¹ 6		786·82 ¹ 4	786·39 ¹ 3	827·92 ¹ 4	827·49 ¹ 5	859·02 ¹ 3
8		727·25 ¹ 1	726·81 ¹ 1	758·59 ¹ 4		794·63 ¹ 6	794·22 ¹ 4	841·16 ² 3	840·72 ¹ 6	876·85 ¹ 3
9	17708·38 ¹ 1			762·80 ² 5		803·38 ² 6	802·97 ² 4	855·36 ¹ 3	854·92 ¹ 6	895·56 ¹ 3 ^c
10		699·92 ¹ 0	723·79 ¹ 00	768·01 ² 4		813·12 ¹ 5	812·70 ² 5	870·48 ¹ 2	870·07 ¹ 5	915·07 ³ 14
11				774·21 ² 5		823·87 ² 6	823·39 ² 5		886·13 ⁴ 12	935·71 ² 5
12						835·51 ¹ 5	835·11 ¹ 4		903·36 ² 6	957·33 ⁴ 8
13						848·30 ¹ 3	847·87 ¹ 3		921·55 ² 6	979·89 ² 4
14						862·15 ² 4	861·70 ¹ 2		940·78 ² 4	18003·54 ¹ 3
15							876·54 ² 4		961·13 ² 8	028·21 ¹ 1
16							892·40 ² 5		982·49 ² 3	053·92 ¹ 1
17									18004·96 ¹ 5	080·71 ¹ 1
18									028·47 ¹ 1	108·56 ² 1
19									053·09 ¹ 2	137·53 ¹ 1
20									078·83 ² 2	167·50 ¹ 0
21									105·72 ¹ 1	
22										
23										
24										
25										
26										
27										
28										
29										
30										
31										
32										
33										
34										
35										
36										
37										
38										
39										
40										
41										
42										

* ${}^O Q_{24}$ only. Corresponding lines in ${}^O P_{34}$ not observed.

† ${}^P Q_{34}$ only. Corresponding lines in ${}^P R_{34}$ not observed.

FIRST NEGATIVE BAND SPECTRUM OF OXYGEN

487

TABLE X. WAVE NUMBERS OF LINES IN THE (1, 0) BAND. ${}^4\Sigma \rightarrow {}^4\Pi_3$ TRANSITION

$J + \frac{1}{2}$	${}^N P_{13}$	${}^O P_{23}$	${}^O Q_{13}$	P_3 and ${}^P Q_{23}$	${}^P R_{13}$	Q_3 and ${}^Q R_{23}$	${}^Q P_{43}$	R_3	${}^R Q_{43}$	${}^S R_{43}$
2				17802.06 ² 3*	17801.62 ² 2	17809.76 ¹ 0d [†]			17814.69 ¹ 2	17831.69 ¹ 1
3				802.06 ² 3*	801.62 ² 2	814.30 ¹ 2 [†]			823.87 ² 6	846.40 ¹ 3
4				803.38 ² 6	802.97 ² 4	820.03 ¹ 1			834.27 ² 6	862.15 ² 4
5	17779.10 ¹ 2	17791.81 ¹ 1	17791.32 ¹ 3	805.75 ¹ 5	805.35 ¹ 4	826.85 ¹ 3			845.51 ¹ 5	879.05 ¹ 4
6		787.43 ¹ 2	786.95 ¹ 6	809.25 ¹ 4	808.84 ¹ 0	834.76 ¹ 5			857.93 ¹ 5	896.98 ¹ 3
7		784.25 ¹ 3	783.80 ¹ 4	813.84 ³ 7	813.44 ¹ 0	843.84 ² 7b			871.42 ¹ 6	916.02 ¹ 4
8		782.21 ² 4	781.69 ¹ 3	819.61 ² 6	819.19 ¹ 1	853.98 ¹ 4		17886.74 ¹ 3b	886.13 ⁴ 12	936.15 ¹ 3
9	762.80 ² 5	781.20 ¹ 3	780.75 ¹ 3	826.55 ¹ 5		865.31 ³ 8b		902.23 ¹ 00	901.80 ¹ 5	957.33 ⁴ 8
10	756.19 ¹ 2	781.38 ¹ 3	780.91 ¹ 3	834.61 ¹ 5		877.76 ¹ 5		919.08 ¹ 4	918.66 ¹ 5	979.89 ² 4
11		782.70 ¹ 4	782.21 ² 4	843.84 ² 7b		891.36 ⁴ 4		937.11 ¹ 2	936.64 ¹ 4	979.89 ² 4
12		785.20 ¹ 4	784.76 ¹ 1	854.27 ¹ 5		906.19 ¹ 5		956.17 ¹ 1	955.77 ² 4	18003.38 ³ 3
13		788.91 ¹ 3	788.42 ¹ 1	865.76 ² 8b		921.96 ² 6		976.70 ⁴ 6	976.06 ¹ 3	027.95 ¹ 3
14		793.74 ¹ 2	793.33 ² 4	878.58 ¹ 4		939.08 ² 5		997.87 ¹ 1	997.41 ² 8b	053.47 ¹ 4b
15		799.76 ¹ 3	799.29 ¹ 3	892.54 ¹ 5		957.33 ⁴ 8		18020.44 ¹ 0	18019.83 ¹ 1	080.39 ¹ 1
16		807.09 ² 4	—	907.62 ² 6		997.41 ² 8b		044.14 ¹ 0	043.72 ¹ 2	108.56 ² 1
17		815.54 ² 5	815.12 ² 5	923.98 ¹ 3		18019.03 ¹ 3		069.16 ¹ 2	068.61 ¹ 0	
18		825.05 ¹ 2				041.88 ¹ 1		094.93 ¹ 0	094.43 ² 2	
19						065.82 ¹ 3d		122.14 ¹ 0		
20						091.13 ¹ 1		150.35 ¹ 00		
21										
22										
23										
24										
25										
26										
27										
28										
29										
30										
31										
32										
33										
34										
35										
36										
37										
38										
39										
40										
41										

* ${}^P Q_{23}$ only. Corresponding lines in P_3 not observed.† Q_3 only. Corresponding lines in ${}^Q R_{23}$ not observed.

TABLE XI. WAVE NUMBERS OF LINES IN THE (1, 0) BAND. ${}^4\Sigma \rightarrow {}^4\Pi_{3/2}$ TRANSITION

$J + \frac{1}{2}$	${}^oP_{12}$	P_2	${}^pQ_{12}$	Q_2 and ${}^oP_{32}$	${}^oR_{12}$	R_2 and ${}^RQ_{32}$	${}^R P_{42}$	${}^S R_{32}$	${}^S Q_{42}$	${}^T R_{42}$
2				17852·592 2*			17860·13 ¹ 1 [†]			17897·93 ² 2
3	17839·87 ¹ 2		17847·37 ¹ 3	852·592 2*			—		17886·13 ⁴ 12	914·61 ³ 4
4			842·70 ¹ 5	853·77 ² 3*			872·49 ² 6		898·55 ¹ 4	932·88 ¹ 1 ^d
5	830·87 ¹ 3		839·48 ¹ 5	856·43 ² 6	17855·97 ¹ 3		880·71 ² 8	17898·98 ¹ 3	912·63 ² 4	952·63 ¹ 0
6	823·39 ² 5		837·76 ¹ 6	860·35 ¹ 3	859·98 ¹ 3		890·44 ² 6	913·11 ² 6	927·82 ² 6 ^b	973·83 ² 5
7	817·32 ¹ 4		837·40 ¹ 6	865·76 ² 8 ^b	865·31 ³ 8 ^b		901·55 ¹ 5	928·34 ¹ 4	944·69 ¹ 3	996·13 ² 5
8	812·70 ² 5		838·47 ¹ 6	872·49 ² 6	872·05 ³ 6		913·99 ¹ 6	945·11 ¹ 3	962·78 ¹ 1	18020·00 ¹ 1
9	809·43 ¹ 4		840·90 ¹ 6	880·71 ² 8	880·25 ² 4		927·82 ² 6 ^b	963·21 ¹ 3	—	044·90 ¹ 0
10	807·60 ¹ 4	17845·21 ¹ 0	844·76 ¹ 6	890·12 ² 6	889·73 ¹ 4		942·91 ¹ 6	982·76 ¹ 3	18003·38 ³ 3	
11	807·09 ² 4	850·39 ¹ 1	849·95 ¹ 5	900·97 ² 6 ^c	900·56 ¹ 3		959·36 ¹ 5	18003·38 ³ 3	025·53 ¹ 3	
12	807·99 ¹ 4	856·93 ² 2	856·43 ² 6	913·11 ² 6	912·63 ² 4		977·09 ¹ 6	025·53 ¹ 3	025·13 ¹ 1	
13	810·20 ¹ 2	864·83 ² 5	864·34 ¹ 5	926·61 ¹ 4 ^c	926·15 ¹ 2		996·13 ² 5	048·73 ¹ 1		
14	813·84 ³ 7	873·96 ¹ 1	873·49 ¹ 4	941·31 ² 7	940·78 ² 4		18016·48 ² 6	073·35 ¹ 1		
15	818·66 ¹ 2	884·42 ¹ 3	883·96 ¹ 3	957·33 ⁴ 8	956·87 ² 1		18016·48 ² 6	099·19 ¹ 1		
16	824·87 ¹ 2	896·12 ² 6	895·67 ¹ 3 ^c	974·64 ¹ 4	974·19 ¹ 00		037·96 ¹ 5	126·22 ² 2		
17	832·29 ¹ 0	909·14 ² 3	908·73 ¹ 2	993·16 ² 5	992·69 ² 6		060·81 ¹ 3			
18	841·16 ² 3	923·48 ¹ 1	923·07 ¹ 3	18013·00 ¹ 2	18012·70 ¹ 1		084·72 ¹ 4			
19		939·08 ² 5	938·59 ² 4	033·99 ¹ 3	033·50 ¹ 0		110·06 ¹ 3			
20		955·77 ² 4		056·33 ² 3 ^b	055·88 ¹ 0		136·54 ¹ 3			
21				079·66 ¹ 1			164·17 ¹ 1			
22				104·48 ¹ 2						

* Q_2 only. Corresponding lines in ${}^oP_{32}$ not observed.† ${}^RQ_{32}$ only. Corresponding line in R_2 not observed.

TABLE XII. WAVE NUMBERS OF LINES IN THE (1, 0) BAND. ${}^4\Sigma \rightarrow {}^4\Pi_{3/2}$ TRANSITION

$J + \frac{1}{2}$	P_1	Q_1	${}^oP_{21}$	R_1	${}^RQ_{21}$ and ${}^RP_{31}$	${}^sR_{21}$ and ${}^sQ_{31}$	${}^sP_{41}$	${}^TR_{31}$	${}^TQ_{41}$	${}^UR_{41}$
3	17890-44 ² 6	17897-52 ¹ 1d	17897-93 ² 2	17902-99 ¹ 00	17903-36 ² 6*	17910-64 ¹ 1d†	17910-11 ¹ 0d	17925-71 ¹ 2		
4		894-04 ¹ 3	894-48 ¹ 5	905-24 ¹ 0	905-68 ² 6*	916-92 ¹ 4†	916-48 ¹ 2	938-16 ¹ 0		
5	882-72 ¹ 3	892-00 ³ 6	892-40 ² 5	909-14 ² 3	909-54 ¹ 6	924-85 ² 8	924-39 ² 8	952-31 ¹ 0	17951-90 ¹ 2	
6	876-54 ² 4	891-60 ¹ 4	892-00 ³ 6	914-61 ³ 4	915-07 ³ 14	934-63 ¹ 5	934-23 ¹ 1			17986-76 ¹ 2
7	872-05 ³ 6	893-03 ¹ 7	893-46 ¹ 6	921-96 ² 6	922-36 ¹ 7	946-07 ¹ 5	945-75 ¹ 0			
8	869-28 ¹ 5	896-12 ² 6	896-55 ¹ 5	930-83 ¹ 4	931-26 ¹ 6	959-15 ¹ 5		984-93 ¹ 3	984-56 ¹ 2	
9	868-21 ¹ 5	900-83 ¹ 7	901-27 ¹ 4	941-31 ² 7	941-76 ¹ 6	973-83 ² 5	973-45 ¹ 2		18003-38 ³ 3	
10	868-72 ¹ 5	907-15 ² 6	907-62 ² 6	953-38 ¹ 4	953-84 ¹ 7	990-16 ¹ 4		18024-31 ¹ 0	023-97 ¹ 0	
11	870-84 ¹ 5	915-07 ³ 14	915-45 ¹ 3	966-97 ¹ 5	967-45 ¹ 6 ^v	18007-97 ¹ 4		046-32 ¹ 2	045-84 ¹ 2	
12	874-47 ¹ 5	924-39 ² 8	924-85 ² 8	982-04 ¹ 7	982-49 ² 3	027-22 ¹ 3				
13	879-61 ¹ 5	935-22 ¹ 6	935-71 ² 5	998-55 ¹ 3	998-99 ¹ 4	047-97 ¹ 4				
14	886-13 ⁴ 12	947-50 ¹ 7	947-93 ¹ 3	18016-48 ² 6	18016-94 ¹ 3	070-10 ¹ 1				
15	894-27 ¹ 5	961-13 ² 8	961-59 ¹ 2	035-75 ¹ 4	036-23 ¹ 3	093-70 ¹ 2				
16	903-73 ¹ 6	976-26 ² 8	976-70 ⁴ 6	056-33 ² 3b	056-85 ¹ 1	118-57 ² 3b				
17	914-61 ³ 4	992-69 ² 6	993-16 ² 5	078-33 ¹ 2	078-83 ² 2	144-71 ¹ 2				
18	926-74 ¹ 4c	18010-45 ¹ 4	18010-91 ¹ 0	101-64 ¹ 3	102-09 ¹ 2	172-19 ¹ 1				
19	940-27 ¹ 3	029-51 ¹ 5	030-06 ¹ 0	126-22 ² 2	126-66 ¹ 2					
20	955-17 ¹ 1	049-89 ¹ 2		152-00 ¹ 1						
21	971-32 ¹ 1	071-51 ¹ 2		179-05 ¹ 1						
22	988-66 ¹ 2b	094-43 ² 2								
23	18007-56 ¹ 0	118-57 ² 3b								

* ${}^RQ_{21}$ only. Corresponding lines in ${}^RP_{31}$ not observed.† ${}^sQ_{31}$ only. Corresponding lines in ${}^sR_{21}$ not observed.

TABLE XIII. $\Delta_2 F'(J)$ VALUES FOR $v' = 0$ LEVEL FROM $(0, 0)$ BAND

J	$\Delta_2 F'_1(J) = F'_1(J+1) - F'_1(J-1)$		$\Delta_2 F'_2(J) = F'_2(J+1) - F'_2(J-1)$		$\Delta_2 F'_3(J) = F'_3(J+1) - F'_3(J-1)$		$\Delta_2 F'_4(J) = F'_4(J+1) - F'_4(J-1)$									
	$4\Sigma \rightarrow 4\Pi_{3/2}$	$4\Sigma \rightarrow 4\Pi_{1/2}$	$4\Sigma \rightarrow 4\Pi_{3/2}$	$4\Sigma \rightarrow 4\Pi_{1/2}$	$4\Sigma \rightarrow 4\Pi_{3/2}$	$4\Sigma \rightarrow 4\Pi_{1/2}$	$4\Sigma \rightarrow 4\Pi_{3/2}$	$4\Sigma \rightarrow 4\Pi_{1/2}$								
1.5																
2.5																
3.5																
4.5																
5.5		12.55														
6.5	22.95	22.96	23.03	23.05												
7.5	33.19	33.15	33.15													
8.5	43.38	43.32	43.29													
9.5	53.60	53.50	53.52													
10.5	63.69	63.67	63.74													
11.5	73.88	73.85	74.00													
12.5	84.05	84.02	84.01													
13.5	94.18	94.06														
14.5	104.26	104.36														
15.5	114.34	114.31														
16.5	124.33	124.41														
17.5	—	134.39														
18.5	—	144.46														
19.5	154.36															
20.5	164.22															
21.5																
22.5																
23.5																
24.5																
25.5																
26.5																
27.5																
28.5																
29.5																
30.5																
31.5																
32.5																
33.5																
	$R_1(J)$ $-P_1(J)$	${}^oR_{12}(J)$ $-{}^oP_{12}(J)$	${}^pR_{13}(J)$ $-{}^nP_{13}(J)$	${}^oR_{14}(J)$ $-{}^mP_{14}(J)$	${}^sR_{21}(J)$ $-{}^qP_{21}(J)$	$R_2(J)$ $-P_2(J)$	${}^qR_{23}(J)$ $-{}^oP_{23}(J)$	${}^pR_{24}(J)$ $-{}^nP_{24}(J)$	${}^tR_{31}(J)$ $-{}^rP_{31}(J)$	${}^sR_{32}(J)$ $-{}^oP_{32}(J)$	$R_3(J)$ $-P_3(J)$	${}^qR_{34}(J)$ $-{}^oP_{34}(J)$	${}^vR_{41}(J)$ $-{}^sP_{41}(J)$	${}^tR_{42}(J)$ $-{}^rP_{42}(J)$	${}^sR_{43}(J)$ $-{}^oP_{43}(J)$	$R_4(J)$ $-P_4(J)$

TABLE XIV. $\Delta_2 F'(J)$ VALUES FOR $v' = 0$ LEVEL FROM $(0, 1)$ BAND

J	$\Delta_2 F'_1(J) = F'_1(J+1) - F'_1(J-1)$		$\Delta_2 F'_2(J) = F'_2(J+1) - F'_2(J-1)$		$\Delta_2 F'_3(J) = F'_3(J+1) - F'_3(J-1)$		$\Delta_2 F'_4(J) = F'_4(J+1) - F'_4(J-1)$	
	$4\Sigma \rightarrow 4\Pi_{3/2}$	$4\Sigma \rightarrow 4\Pi_{1/2}$	$4\Sigma \rightarrow 4\Pi_{3/2}$	$4\Sigma \rightarrow 4\Pi_{1/2}$	$4\Sigma \rightarrow 4\Pi_{3/2}$	$4\Sigma \rightarrow 4\Pi_{1/2}$	$4\Sigma \rightarrow 4\Pi_{3/2}$	$4\Sigma \rightarrow 4\Pi_{1/2}$
1.5	$R_1(J) - P_1(J)$		$R_2(J) - P_2(J)$		$R_3(J) - P_3(J)$		$R_4(J) - P_4(J)$	
2.5								
3.5								
4.5								
5.5								
6.5								
7.5								
8.5								
9.5								
10.5								
11.5								
12.5								
13.5								
14.5								
15.5								
16.5								
17.5								
18.5								
19.5								
20.5								
21.5								
22.5								
23.5								
24.5								
25.5								
26.5								
27.5								
28.5								
29.5								
30.5								
31.5								
32.5								
33.5								
34.5								
35.5								
36.5								
37.5								
38.5								

TABLE XV. $\Delta_2 F'(J)$ VALUES FOR $v'' = 1$ LEVEL FROM (1, 0) BAND

J	$\Delta_2 F'_1(J) = F'_1(J+1) - F'_1(J-1)$		$\Delta_2 F'_2(J) = F'_2(J+1) - F'_2(J-1)$		$\Delta_2 F'_3(J) = F'_3(J+1) - F'_3(J-1)$		$\Delta_2 F'_4(J) = F'_4(J+1) - F'_4(J-1)$	
	${}^4\Sigma \rightarrow {}^4\Pi_{3/2}$	${}^4\Sigma \rightarrow {}^4\Pi_{1/2}$	${}^4\Sigma \rightarrow {}^4\Pi_{3/2}$	${}^4\Sigma \rightarrow {}^4\Pi_{1/2}$	${}^4\Sigma \rightarrow {}^4\Pi_{3/2}$	${}^4\Sigma \rightarrow {}^4\Pi_{1/2}$	${}^4\Sigma \rightarrow {}^4\Pi_{3/2}$	${}^4\Sigma \rightarrow {}^4\Pi_{1/2}$
1.5	$R_1(J)$	${}^0R_{14}(J)$	${}^sR_{21}(J)$	${}^qR_{23}(J)$	${}^tR_{31}(J)$	${}^qR_{34}(J)$	${}^uR_{41}(J)$	${}^sR_{43}(J)$
2.5	$-P_1(J)$	$-{}^0P_{14}(J)$	$-{}^sP_{21}(J)$	$-{}^qP_{23}(J)$	$-{}^tP_{31}(J)$	$-{}^qP_{34}(J)$	$-{}^uP_{41}(J)$	$-{}^sP_{43}(J)$
3.5	12.55		22.44	22.49	32.48	32.52		32.56
4.5	22.42	22.52	32.45	32.60	42.77	42.57		42.54
5.5	32.60	—	42.63	42.60	—	52.62	52.53	52.66
6.5	42.56	42.55	52.61	52.55	62.57	62.59	52.53	62.71
7.5	52.68	52.65	62.60	62.64	—	72.55	72.86	72.64
8.5	62.62	62.68	72.56	72.60	—	82.31	82.58	82.63
9.5	72.59	72.61	82.54	82.61	82.55	92.53	92.77	92.54
10.5	82.54	72.61	92.52	92.56	92.48	102.50	102.45	102.37
11.5	92.50	92.57	102.37	102.43		112.33		112.32
12.5	102.44	102.43	112.26	112.26		122.43		122.22
13.5	112.42	112.31	122.17	122.17		132.11		132.05
14.5	122.21	122.12	132.11	132.06		141.86		141.84
15.5	132.06	132.00	141.87	141.84		151.58		151.69
16.5	141.71	141.90	151.55	151.67		161.54		161.67
17.5	151.59	151.53	161.28	161.24		170.95		170.95
18.5	161.37		170.98	180.77				
19.5	171.05							
20.5	180.68							
21.5	190.39							
22.5								
23.5								
24.5								
25.5								
26.5								
27.5								
28.5								
29.5								
30.5								
31.5								
32.5								
33.5								
34.5								
35.5								
36.5								
37.5								
38.5								
39.5								

FIRST NEGATIVE BAND SPECTRUM OF OXYGEN

493

TABLE XXVI. $\Delta_2 F''(J)$ VALUES FOR THE $v'' = 0$ LEVEL FROM THE $(0, 0)$ BAND

J	$4\Pi_{3/2}$ state		$4\Pi_{3/2}$ state		$4\Pi_{3/2}$ state		$4\Pi_{3/2}$ state		$4\Pi_{3/2}$ state	
	$\Delta_2 F''(J) = F''_{1c}(J+1) - F''_{1c}(J-1)$	$\Delta_2 F''(J) = F''_{1d}(J+1) - F''_{1d}(J-1)$	$\Delta_2 F''(J) = F''_{2a}(J+1) - F''_{2a}(J-1)$	$\Delta_2 F''(J) = F''_{2b}(J+1) - F''_{2b}(J-1)$	$\Delta_2 F''(J) = F''_{3c}(J+1) - F''_{3c}(J-1)$	$\Delta_2 F''(J) = F''_{3d}(J+1) - F''_{3d}(J-1)$	$\Delta_2 F''(J) = F''_{4c}(J+1) - F''_{4c}(J-1)$	$\Delta_2 F''(J) = F''_{4d}(J+1) - F''_{4d}(J-1)$	$\Delta_2 F''(J) = F''_{5c}(J+1) - F''_{5c}(J-1)$	$\Delta_2 F''(J) = F''_{5d}(J+1) - F''_{5d}(J-1)$
2.5										
3.5										
4.5										
5.5										
6.5										
7.5										
8.5										
9.5										
10.5										
11.5										
12.5										
13.5										
14.5										
15.5										
16.5										
17.5										
18.5										
19.5										
20.5										
21.5										
22.5										
23.5										
24.5										
25.5										
26.5										
27.5										
28.5										
29.5										
30.5										
31.5										
32.5										
33.5										
34.5										

J	${}^4\Pi_{3/2}$ state		${}^4\Pi_{3/2}$ state		${}^4\Pi_{3/2}$ state		${}^4\Pi_{3/2}$ state	
	$\Delta_2 F''_{1c}(J) = F''_{1c}(J+1) - F''_{1c}(J-1)$	$\Delta_2 F''_{1d}(J) = F''_{1d}(J+1) - F''_{1d}(J-1)$	$\Delta_2 F''_{2c}(J) = F''_{2c}(J+1) - F''_{2c}(J-1)$	$\Delta_2 F''_{2d}(J) = F''_{2d}(J+1) - F''_{2d}(J-1)$	$\Delta_2 F''_{3c}(J) = F''_{3c}(J+1) - F''_{3c}(J-1)$	$\Delta_2 F''_{3d}(J) = F''_{3d}(J+1) - F''_{3d}(J-1)$	$\Delta_2 F''_{4c}(J) = F''_{4c}(J+1) - F''_{4c}(J-1)$	$\Delta_2 F''_{4d}(J) = F''_{4d}(J+1) - F''_{4d}(J-1)$
2.5								
3.5								
4.5								
5.5	24.52	20.27						
6.5	32.85	28.70						
7.5	41.17	37.09						
8.5	49.42	45.33						
9.5	57.88	53.75						
10.5	66.21	62.11						
11.5	74.71	70.47						
12.5	83.12	78.91						
13.5	91.51	87.36						
14.5	100.04	95.91						
15.5	108.41	104.28						
16.5	117.00	112.75						
17.5	125.41	121.14						
18.5	133.80	129.59						
19.5	142.13	138.06						
20.5		146.47						
21.5		154.90						
22.5		163.34						
23.5		171.49						
24.5								
25.5								
26.5								
27.5								
28.5								
29.5								
30.5								
31.5								
32.5								
33.5								
34.5								
35.5								
36.5								
37.5								
38.5								
39.5								
40.5								

FIRST NEGATIVE BAND SPECTRUM OF OXYGEN

495

TABLE XVIII. $\Delta_2 F''(J)$ VALUES FOR THE $v'' = 1$ LEVEL FROM THE (0, 1) BAND

J	$^4\Pi_{3/2}$ state		$^4\Pi_{5/2}$ state		$^4I_{3/2}$ state		$^4I_{5/2}$ state		$^4\Pi_{1/2}$ state	
	$\Delta_2 F''(J) = F''_{1c}(J+1) - F''_{1c}(J-1)$	$\Delta_2 F''(J) = F''_{1d}(J+1) - F''_{1d}(J-1)$	$\Delta_2 F''(J) = F''_{2c}(J+1) - F''_{2c}(J-1)$	$\Delta_2 F''(J) = F''_{2d}(J+1) - F''_{2d}(J-1)$	$\Delta_2 F''(J) = F''_{3c}(J+1) - F''_{3c}(J-1)$	$\Delta_2 F''(J) = F''_{3d}(J+1) - F''_{3d}(J-1)$	$\Delta_2 F''(J) = F''_{4c}(J+1) - F''_{4c}(J-1)$	$\Delta_2 F''(J) = F''_{4d}(J+1) - F''_{4d}(J-1)$	$\Delta_2 F''(J) = F''_{4e}(J+1) - F''_{4e}(J-1)$	$\Delta_2 F''(J) = F''_{4f}(J+1) - F''_{4f}(J-1)$
2.5										
3.5										
4.5										
5.5										
6.5										
7.5	32.46		28.29		25.42		26.49		22.97	
8.5	40.64		—		33.95		35.28		32.16	
9.5	48.81		44.67		42.08		44.08		41.29	
10.5	57.12		52.95		50.83		52.81		50.31	
11.5	65.33		61.16		59.17		61.54		59.34	
12.5	73.71				—		70.19		68.28	
13.5	81.99				76.29		78.93		77.25	
14.5	90.31				84.80		87.56		86.03	
15.5	98.67				93.25		96.24		94.77	
16.5	107.02				101.69		104.78		103.60	
17.5	115.32				110.19		113.39		109.01	
18.5					118.57		121.96		117.61	
19.5					127.03		130.30		126.03	
20.5					135.36		138.74		134.54	
21.5					143.82		153.01		143.01	
22.5					152.12					
23.5					160.31					
24.5										
25.5										
26.5										
27.5										
28.5										
29.5										
30.5										
31.5										
32.5										
33.5										
34.5										
35.5										
36.5										
37.5										

TABLE XIX (cont.)

J	$4\Pi_1$ state					$4\Pi_{-1/2}$ state					
	$\Delta_1 F_{3ac}(J + \frac{1}{2}) = F_{3c}''(J+1) - F_{3c}''(J)$					$\Delta_1 F_{4ac}(J + \frac{1}{2}) = F_{4c}''(J+1) - F_{4c}''(J)$					
	$R_3(J) - Q_3(J+1)$	${}^R Q_{43}(J) - {}^R P_{43}(J+1)$	${}^P Q_{23}(J) - {}^P P_{23}(J+1)$	${}^P R_{13}(J) - {}^P Q_{13}(J+1)$	$Q_3(J) - P_3(J+1)$ ${}^Q R_{23}(J) - {}^Q P_{23}(J+1)$	${}^O Q_{13}(J) - {}^O P_{13}(J+1)$	${}^S R_{43}(J) - {}^S Q_{43}(J+1)$	$R_4(J) - Q_4(J+1)$	${}^P R_{24}(J) - {}^P Q_{24}(J+1)$ ${}^P Q_{34}(J) - {}^P P_{34}(J+1)$	${}^R R_{34}(J) - {}^R Q_{34}(J+1)$	${}^O Q_{24}(J) - {}^O P_{24}(J+1)$ ${}^O R_{14}(J) - {}^O Q_{14}(J+1)$
0.5									5.66		
1.5		5.67	5.44	5.52	7.63	7.79			10.49		
2.5		10.12	10.10	10.17	12.14	12.07			10.42		
3.5		14.63	14.70	14.68	16.58	16.72			14.97		
4.5		19.10	19.16	19.09	21.08	21.10			19.63		
5.5		23.57	23.61	23.53	25.56	25.51			24.19		
6.5		27.99	28.01	27.99	29.95	29.93			28.75		
7.5		32.51	32.49	32.45	34.33	34.33			33.27		
8.5		36.94	36.91	36.92	38.75	38.75			37.67		
9.5		41.33	41.31	41.26	43.09	43.10			42.16		
10.5	28.03	45.76	45.75	45.81	47.48	47.47			46.63		
11.5		50.11	50.01		51.82	51.87			50.97		
12.5		54.53	54.46		56.18	56.18			55.49		
13.5		58.93	58.89		60.40	60.40			59.84		
14.5		63.17	63.33		64.75	64.75			64.21		
15.5		67.37	67.47		69.07	69.07					
16.5		71.72	71.81		73.32	73.32					
17.5		76.03	76.04		77.53	77.53					
18.5					81.86	81.86					
19.5					85.12	85.12					
20.5											
21.5											
22.5											
23.5											
24.5											
25.5											
26.5											
27.5											
28.5											
29.5											
30.5											
31.5											
32.5											
33.5											
34.5											
35.5											
36.5											
37.5											
38.5											

* ${}^P Q_{34}(J) - {}^O P_{34}(J+1)$ only.

The letters which appear in some cases after the intensity figure have the following meanings: *b*, blend of two or more lines which appears comparatively sharp; *d*, diffuse line; *c*, line confused with another line which may affect both the wave-length and the intensity; *v*, line shaded towards the violet.

THE INITIAL 4Σ STATE

The combination differences for the initial state derived from equations 1 and 2 are as follows:

$$\left. \begin{aligned} \Delta_2 F'_1(K) &= 4B'_v(K + \frac{1}{2}) + 8D'_v(K + \frac{1}{2})^3 - \frac{18\epsilon}{(2K+1)(2K+5)} + 6\gamma, \\ \Delta_2 F'_2(K) &= 4B'_v(K + \frac{1}{2}) + 8D'_v(K + \frac{1}{2})^3 - \frac{18\epsilon}{(2K+1)(2K+5)} + 2\gamma, \\ \Delta_2 F'_3(K) &= 4B'_v(K + \frac{1}{2}) + 8D'_v(K + \frac{1}{2})^3 + \frac{18\epsilon}{(2K+1)(2K-3)} - 2\gamma, \\ \Delta_2 F'_4(K) &= 4B'_v(K + \frac{1}{2}) + 8D'_v(K + \frac{1}{2})^3 + \frac{18\epsilon}{(2K+1)(2K-3)} - 6\gamma. \end{aligned} \right\} \quad (5)$$

It is shown later that $\epsilon = 0.1487 \text{ cm.}^{-1}$ and $\gamma = -0.00033 \text{ cm.}^{-1}$, so that, except for the very lowest values of K , the sum of the third and fourth terms in these expressions can be neglected. Inspection of Tables XIII–XV shows that the four values of $\Delta_2 F'_i(K)$ which correspond to the same value of K are in fact equal when K is greater than four. Accordingly we can write

$$\Delta_2 F'(K) = 4B'_v(K + \frac{1}{2}) + 8D'_v(K + \frac{1}{2})^3. \quad (6)$$

Taking as $\Delta_2 F'(K)$ the average of the four values of $\Delta_2 F'_i(K)$ the graph of $\Delta_2 F'(K)/K + \frac{1}{2}$ against $(K + \frac{1}{2})^2$ is plotted. It is a straight line from the slope of which D'_v is found. B'_v is found by the method of Büttendörfer and Herzberg (1935). Taking an approximate value of B which we call \tilde{B} , the correction to give the true value of B is ΔB . A graph of the expression

$$\Delta_2 F'(K) - 8D'_v(K + \frac{1}{2}) - 4\tilde{B}(K + \frac{1}{2}) = 4\Delta B(K + \frac{1}{2})$$

against $K + \frac{1}{2}$ is a straight line passing through the origin with slope $4\Delta B$ from which

$$B'_v = \tilde{B}'_v + \Delta B'_v.$$

From equations (2) we get

$$\left. \begin{aligned} \Delta f'_{21}(K) &= F'_2(K) - F'_1(K) = 3\epsilon - 3\gamma - 3\gamma K, \\ \Delta f'_{23}(K) &= F'_2(K) - F'_3(K) = \frac{9\epsilon(2K+1)}{(2K+3)(2K-1)} + \gamma + 2\gamma K, \\ \Delta f'_{34}(K) &= F'_3(K) - F'_4(K) = 3\epsilon - \gamma + 2\gamma K. \end{aligned} \right\} \quad (7)$$

$\Delta f'_{21}(K)$ and $\Delta f'_{34}(K)$ are derived from the following relations between the lines of the branches

$$\begin{aligned}\Delta f'_{21}(K' = J - \frac{3}{2}) &= {}^oP_{21}(J) - Q_1(J) = {}^RQ_{21}(J-1) - R_1(J-1) = P_2(J) - {}^PQ_{21}(J) \\ &= Q_2(J-1) - {}^oR_{12}(J-1) = {}^oP_{23}(J) - {}^oQ_{13}(J) \\ &= {}^PQ_{23}(J-1) - {}^PR_{13}(J-1) = {}^NP_{24}(J) - {}^NQ_{14}(J) \\ &= {}^oQ_{24}(J-1) - {}^oR_{14}(J-1),\end{aligned}$$

$$\begin{aligned}\Delta f'_{34}(K' = J + \frac{3}{2}) &= {}^TR_{31}(J) - {}^TQ_{41}(J) = {}^SQ_{31}(J+1) - {}^SP_{41}(J+1) \\ &= {}^SR_{32}(J) - {}^SQ_{42}(J) = {}^RQ_{32}(J+1) - {}^RP_{42}(J+1) \\ &= R_3(J) - {}^RQ_{43}(J) = Q_3(J+1) - {}^oP_{43}(J+1) \\ &= {}^oR_{34}(J) - Q_4(J) = {}^PQ_{34}(J+1) - P_4(J+1).\end{aligned}$$

The average values of $\Delta f'_{21}(K)$ and $\Delta f'_{34}(K)$ derived from the initial levels $v' = 0$ and $v'' = 1$ are shown in fig. 3. The lines drawn through the points represent the theoretical curves with $\epsilon = 0.1487$ and $\gamma = -0.00033$. Bearing in mind the number of blends in the observed branches the agreement is as good as can be expected.

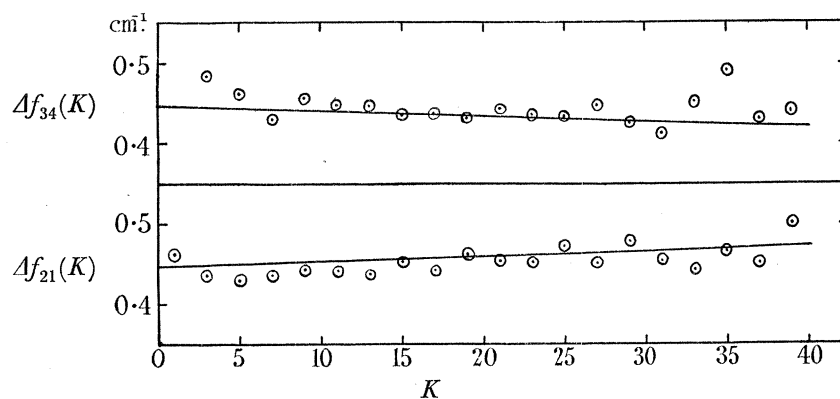


FIG. 3. Graphs showing the structure of the ${}^4\Sigma$ state. The points represent the average of the observed values of $\Delta f'_{21}(K)$ and $\Delta f'_{34}(K)$ for the levels $v' = 0$ and $v'' = 1$. The curves represent the theoretical values given by equations (7) where $\epsilon = 0.1487 \text{ cm.}^{-1}$ and $\gamma = -0.00033 \text{ cm.}^{-1}$.

Examination of the expression for $\Delta f'_{23}(K)$ shows that the separation of the levels $F'_2(K)$ and $F'_3(K)$ decreases rapidly with increasing K . Substitution of the values of ϵ and γ gives for the separation 0.81 cm.^{-1} , 0.21 cm.^{-1} and 0.13 cm.^{-1} for $K' = 1, 3$, and 5 respectively. For values of K' greater than 5 the branches which start from the levels $F'_2(K)$ and $F'_3(K)$ and which are listed together at the head of a single column in Tables I—XII should be blended together so that only one line results. This is confirmed by the manner in which the lines in the column are used in forming the combination relations in Tables XIII—XIX. For example, the lines in column seven

of Table I are treated in column nine of Table XIII as belonging to the ${}^P R_{24}$ branch and in column thirteen of Table XIX (cont.) as belonging to the ${}^P Q_{34}$ branch. The branches should be separated from one another, however, for $K' = 1$ and 3 and in favourable cases for $K' = 5$. In no case, however, has a doubling of the lines been observed for these values of K and the footnotes to the tables indicate the branch to which the observed lines have been assigned. It seems that the corresponding lines of the other branch involved are too faint to observe. It can readily be seen from equations (2) that $\Delta f'_{14}(K) = \Delta f'_{23}(K)$ so that the initial levels $F'_1(K)$ and $F'_4(K)$ are blended together for $K' > 5$.

THE FINAL ${}^4 I I$ STATE

In the (1, 0) and (0, 0) bands the first line in the ${}^P Q_{34}$ branch corresponds to $J = \frac{1}{2}$ and the first line in the ${}^Q R_{34}$ branch to $J = \frac{3}{2}$. In the (1, 0) band the first lines in the ${}^O Q_{24}$ and Q_4 branches correspond to $J = \frac{3}{2}$. These are the values of J at which these branches should begin if the ${}^4 I I$ state is inverted. None of the lines should be observed for a normal ${}^4 I I$ state the ${}^P Q_{34}$ branch beginning with $J = \frac{5}{2}$ and the ${}^O Q_{24}$, Q_4 and ${}^Q R_{34}$ branches with $J = \frac{7}{2}$. As all the lines in question have been used only once in the analysis we conclude that the ${}^4 I I$ level is inverted. The four components of each band are assigned to the transitions ${}^4 \Sigma \rightarrow {}^4 I I_{\frac{5}{2}}$, ${}^4 \Sigma \rightarrow {}^4 I I_{\frac{3}{2}}$, ${}^4 \Sigma \rightarrow {}^4 I I_{\frac{1}{2}}$, ${}^4 \Sigma \rightarrow {}^4 I I_{-\frac{1}{2}}$ as shown in Tables I–XII.

The expressions for the combination differences derived from equations (4) are very complicated. It can be shown however that $\Delta_2 F''_m(J)$, the average of the four values of $\Delta_2 F''_i(J)$, is given by

$$\Delta_2 F''_m(J) = 4B''_v(J + \frac{1}{2}) + 8D''_v(J + \frac{1}{2})^3. \quad (8)$$

It can be seen from Tables XVI–XVIII that if $\Delta_2 F''_{ic}(J)$ is present for a particular value of J , $\Delta_2 F''_{id}(J)$ is missing and vice versa. The missing values in both cases are obtained by interpolation and a complete table of values of $\Delta_2 F''_c(J)$ and $\Delta_2 F''_d(J)$ is formed for each of the four substates. The average of the eight values of $\Delta_2 F''(J)$ is taken as $\Delta_2 F''_m(J)$. The graph of $\Delta_2 F''_m(J)/J + \frac{1}{2}$ against $(J + \frac{1}{2})^2$ is a straight line for each of the levels $v'' = 0$ and $v'' = 1$. B''_v and D''_v are evaluated by the method described in the previous section.

To determine the constant $Y = A/B$ we use a method similar to that used by Budó (1935*a*) for triplet states. From equations (4)

$$\Delta F''_{41}(J) = F''_4(J) - F''_1(J) = 3B''_v \left\{ y_1 + 4J(J+1) + \frac{23}{9} + \frac{2\delta}{9} \right\}^{\frac{1}{2}} + 12D''_v(J + \frac{1}{2})^3, \quad (9a)$$

$$\Delta F''_{32}(J) = F''_3(J) - F''_2(J) = B''_v \{ y_1 + 4J(J+1) - 5 - 2\delta \}^{\frac{1}{2}} + 4D''_v(J + \frac{1}{2})^3. \quad (9b)$$

The analysis gives

$$\left. \begin{aligned} \Delta F_{41cd}(J) &= F''_{4c}(J) - F''_{1d}(J) = P_1(J) - {}^M P_{14}(J) = R_1(J) - {}^O R_{14}(J) = {}^R Q_{21}(J) - {}^O Q_{24}(J) \\ &= {}^R P_{31}(J) - {}^O P_{34}(J) = {}^T R_{31}(J) - {}^Q R_{34}(J) = {}^T Q_{41}(J) - Q_4(J), \\ \Delta F_{41dc}(J) &= F''_{4d}(J) - F''_{1c}(J) = Q_1(J) - {}^N Q_{14}(J) = {}^Q P_{21}(J) - {}^N P_{24}(J) = {}^S R_{21}(J) - {}^P R_{24}(J) \\ &= {}^S Q_{31}(J) - {}^P Q_{34}(J) = {}^S P_{41}(J) - P_4(J) = {}^U R_{14}(J) - R_4(J), \end{aligned} \right\} \quad (10)$$

$$\left. \begin{aligned} \Delta F''_{32cd}(J) &= F''_{3c}(J) - F''_{2d}(J) = P_2(J) - {}^O P_{23}(J) = {}^P Q_{12}(J) - {}^O Q_{13}(J) = R_2(J) - {}^Q R_{23}(J) \\ &= {}^R Q_{32}(J) - Q_3(J) = {}^R P_{42}(J) - {}^Q P_{43}(J) = {}^T R_{42}(J) - {}^S R_{43}(J), \\ \Delta F''_{32dc}(J) &= F''_{3d}(J) - F''_{2c}(J) = {}^O P_{12}(J) - {}^N P_{13}(J) = Q_2(J) - {}^P Q_{23}(J) = {}^Q P_{23}(J) - P_3(J) \\ &= {}^Q R_{12}(J) - {}^P R_{13}(J) = {}^S R_{32}(J) - R_3(J) = {}^S Q_{42}(J) - {}^R Q_{43}(J). \end{aligned} \right\} \quad (11)$$

From the expressions (10) a complete table of values of $\Delta F_{41c}(J)$ and $\Delta F_{41d}(J)$ can be calculated with the aid of the results for the A -type doubling which are given later using relations of the type

$$\Delta F''_{41c}(J) = F''_{4c}(J) - F''_{1d}(J) + [F''_{1d}(J) - F''_{1c}(J)].$$

The average of $\Delta F''_{41c}(J)$ and $\Delta F''_{41d}(J)$ is taken as $\Delta F''_{41}(J)$. By a similar method $\Delta F_{32}(J)$ is obtained from equations (11). The value of δ which in the present case is very small can be calculated with an approximate value of A obtained from the overall width of the band. From the values of y_1 given by equations (9a) and (9b) A can be calculated since $y_1 = Y(Y-4)$ and $Y = A/B$. There are two values of A for the one value of y_1 , one positive and one negative, the latter corresponding to an inverted 4I state. The results obtained for A are shown in fig. 4. For the level $v'' = 0$ the value of A obtained from $\Delta F''_{23}(J)$ is fairly constant and somewhat larger than the value obtained from $\Delta F''_{41}(J)$ which seems to increase almost linearly with J . The results for $v'' = 1$ are similar though there seems to be a slow increase in the value of A obtained from $\Delta F''_{32}(J)$.

From equations (4) we get

$$\begin{aligned} \Delta F''_{21}(J) - \Delta F''_{43}(J) &= F''_2(J) - F''_1(J) - [F''_4(J) - F''_3(J)] \\ &= 8 B''_v \frac{y_2 - 2J(J+1)}{y_1 + 4J(J+1)} - 24 D''_v J(J+1). \end{aligned} \quad (12)$$

$\Delta F''_{21}(J)$ and $\Delta F''_{43}(J)$ can be calculated from the branches by the method used for $\Delta F''_{41}(J)$. The observed values of the left-hand side of equation (11) completely fail to agree with the values calculated from the right-hand side. In Table XX are given the observed values of $\Delta F''_{21}(J)$, $\Delta F''_{32}(J)$ and $\Delta F''_{43}(J)$ for the level $v'' = 0$. The calculated values are derived from equations (4), the value of y_1 used in the calculations being the average of all the values derived from $\Delta F''_{32}(J)$ and $\Delta F''_{41}(J)$. It is clear that equations

(4) fail to represent the observed structure of the ${}^4\Pi$ state in O_2^+ . Roughly the interval $F_2''(J) - F_1''(J)$ is less than and the interval $F_4''(J) - F_3''(J)$ greater than the calculated value by $4B_v'' \frac{y_2 - 2J(J+1)}{y_1 + 4J(J+1)}$. It can be seen from Table XX that the observed values of $\Delta F_{21}''(J)$ and $\Delta F_{32}''(J)$ agree with one another and with the higher values of $\Delta F_{43}''(J)$ almost exactly. Exactly the same result holds good for the level $v'' = 1$. Incidentally it may be mentioned that the combination differences $\Delta_2 F_i''(J)$ are represented very well by equations (4) when the term $2B_v'' \frac{y_2 - 2J(J+1)}{y_1 + 4J(J+1)}$ is omitted.

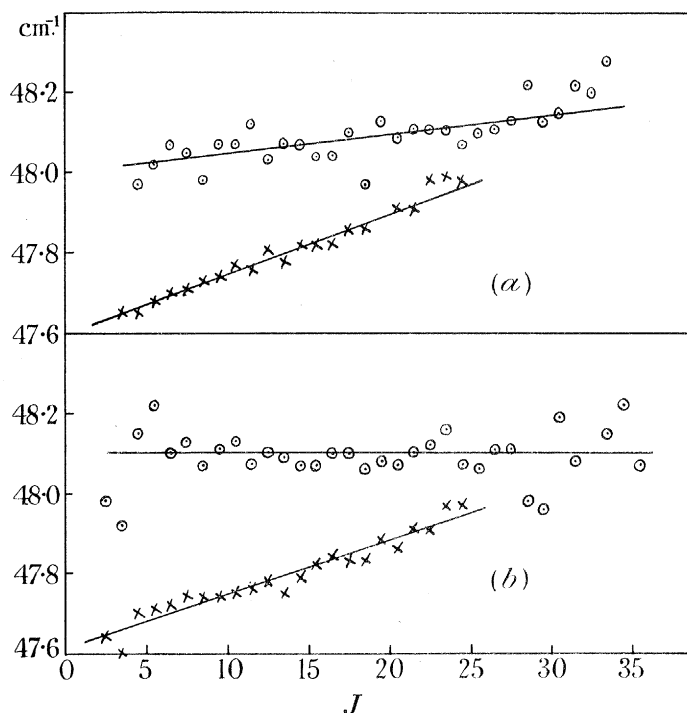


FIG. 4. Variation of A with J for the levels (a) $v'' = 1$ and (b) $v'' = 0$. The circles are values from $\Delta F_{32}(J)$ and the crosses are values derived from $\Delta F_{41}(J)$.

A -TYPE DOUBLING IN THE ${}^4\Pi$ STATE

The A -type doubling is given by the expression

$$\Delta v_{idc}(J) = F_{id}(J) - F_{ic}(J). \quad (13)$$

What is derived from the analysis, however, is the average of the doublings for two successive levels given by

$$\begin{aligned} \Delta_1 F_{idc}(J + \tfrac{1}{2}) - \Delta_1 F_{icd}(J + \tfrac{1}{2}) &= F_{id}(J+1) - F_{ic}(J+1) + F_{id}(J) - F_{ic}(J) \\ &= 2\Delta v_{idc}(J + \tfrac{1}{2}). \end{aligned}$$

FIRST NEGATIVE BAND SPECTRUM OF OXYGEN

503

Since the doubling is generally small this is practically the same as the value given by equation (13). The values of $\Delta_1 F_{idc}(J + \frac{1}{2})$ which are given by the analysis correspond to the missing values of $\Delta_1 F_{icd}(J + \frac{1}{2})$ and vice versa. In both cases the missing values

TABLE XX. OBSERVED AND CALCULATED VALUES OF $\Delta F''_{21}(J)$, $\Delta F''_{32}(J)$ AND $\Delta F''_{43}(J)$

$J + \frac{1}{2}$	$\Delta F''_{21}(J)$		$\Delta F''_{32}(J)$		$\Delta F''_{43}(J)$	
	Obs. cm.^{-1}	Calc. cm.^{-1}	Obs. cm.^{-1}	Calc. cm.^{-1}	Obs. cm.^{-1}	Calc. cm.^{-1}
2	—	—	—	—	49.35	46.29
3	—	—	50.42	50.42	49.86	46.60
4	50.61	54.87	50.74	50.75	50.12	47.03
5	51.28	55.19	51.34	51.18	50.60	47.55
6	51.78	55.58	51.82	51.69	51.12	48.17
7	52.42	56.04	52.40	52.32	51.78	48.88
8	53.11	56.58	53.11	52.97	52.45	49.74
9	53.86	57.18	53.83	53.73	53.28	50.65
10	54.68	57.85	54.70	54.56	54.14	51.64
11	55.63	58.58	55.63	55.47	55.08	52.74
12	56.57	59.37	56.55	56.46	56.12	53.88
13	57.63	60.25	57.62	57.51	57.20	55.10
14	58.71	61.24	58.72	58.67	58.31	56.38
15	59.87	62.17	59.87	59.78	59.55	57.71
16	61.09	63.20	61.11	61.00	60.81	59.11
17	62.36	64.29	62.39	62.27	62.11	60.55
18	63.68	65.40	63.71	63.56	63.47	62.02
19	65.07	66.65	65.03	64.95	64.93	63.55
20	66.46	67.90	66.45	66.36	66.31	65.11
21	67.89	69.17	67.88	67.79	67.78	66.71
22	69.41	70.52	69.39	69.28	69.31	68.33
23	70.86	71.86	70.91	70.79	70.87	69.98
24	72.47	73.24	72.46	72.31	72.41	71.63
25	74.01	74.70	74.00	73.91	73.97	73.31
26	75.61	76.17	75.59	75.50	75.60	75.06
27	77.19	77.69	77.23	77.12	77.19	76.75
28	78.90	79.21	78.88	78.76	78.84	78.52
29	80.55	80.78	80.49	80.43	80.54	80.32
30	82.25	82.34	82.16	82.11	82.36	82.26
31	83.92	83.96	83.96	83.81	—	—
32	85.66	85.60	85.62	85.54	—	—
33	87.21	87.25	87.28	87.27	—	—
34	89.01	88.93	89.20	89.03	—	—
35	90.88	90.56	90.94	90.79	—	—
36	92.77	92.26	92.63	92.55	—	—
37	—	—	94.56	94.34	—	—

had to be interpolated before $\Delta\nu_{idc}(J + \frac{1}{2})$ could be calculated. The results obtained for the width of the A -doublet can be regarded as those which would actually be found if both the c and d levels corresponding to a particular value of J were physically present. The results for the levels $v'' = 0$ and $v'' = 1$ are shown in fig. 5. The general trend of the observations are indicated by the lines drawn through the points. The doubling is very small in the ${}^4I_{\frac{3}{2}}$ and ${}^4I_{\frac{1}{2}}$ states. It appears to increase linearly with J in the ${}^4I_{\frac{3}{2}}$ state.

In the ${}^4\Pi_{-3/2}$ state it increases at first and finally decreases for the highest values of J . There is a systematic difference between the results for the doubling for $v'' = 0$ and $v'' = 1$.

There are no theoretical expressions available with which to compare the observations. They resemble, however, the results for ${}^2\Pi$ and ${}^3\Pi$ states in so far as the component of lowest $A - \Sigma$ has the largest doubling.

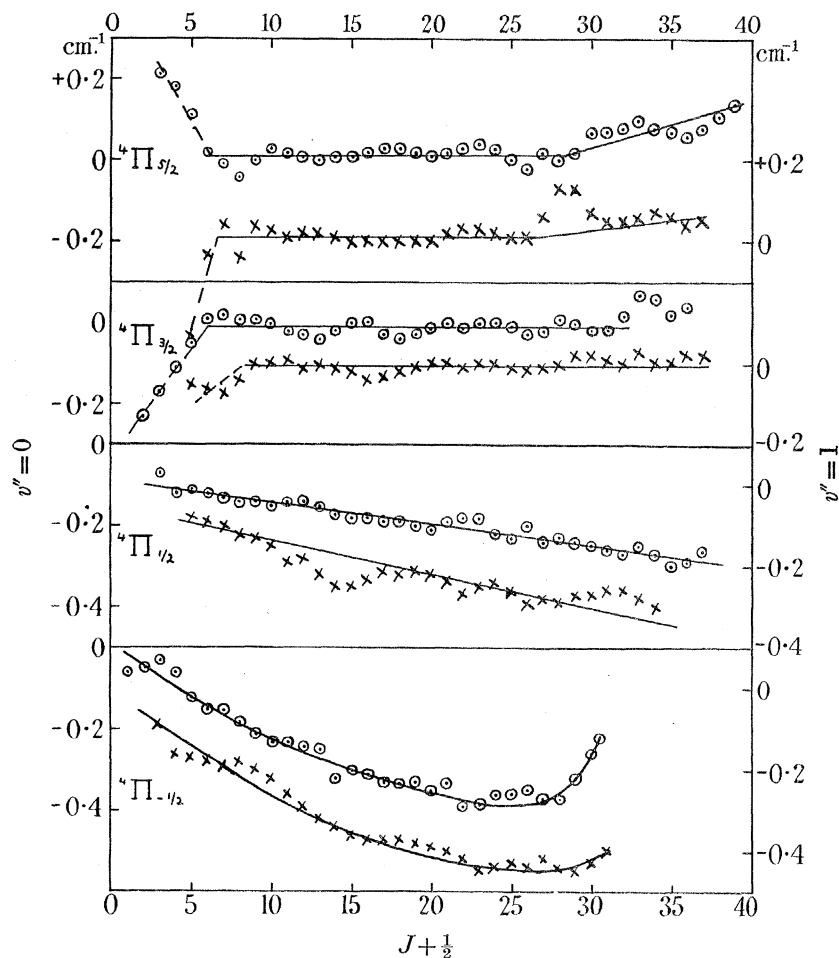


FIG. 5. A -type doubling in the ${}^4\Pi$ state. The circles refer to the level $v'' = 0$, the doubling being read off from the left-hand side of the graph. The crosses refer to the level $v'' = 1$, the doubling being read off from the right-hand side of the graph.

MOLECULAR CONSTANTS

The constants of the O_2^+ molecule in the initial ${}^4\Sigma$ and final ${}^4\Pi$ states obtained from the analysis are given in Table XXI. The values of B_e , α_e , D_e and β_e are determined with the aid of the relations

$$B_e = B_v + \alpha_e(v + \frac{1}{2}), \quad D_e = D_v - \beta(v + \frac{1}{2}).$$

FIRST NEGATIVE BAND SPECTRUM OF OXYGEN

505

The values of I_e and r_e are determined from the expressions

$$\mu r_e^2 = I_e = \frac{h}{8\pi^2 c B_e'}$$

where μ stands for the effective mass of the molecule which is equal to $M/2$, where M is the mass of the oxygen atom. In the calculation the values given by von Friesen (1937) for h , c and the mass of the hydrogen atom were used.

TABLE XXI. MOLECULAR CONSTANTS

	$^4\Sigma$ state	$^4\Pi$ state
$v = 0$	$B_0' = 1.2763 \text{ cm.}^{-1}$ $D_0' = -5.92 \times 10^{-6} \text{ cm.}^{-1}$	$B_0'' = 1.0967 \text{ cm.}^{-1}$ $Y \sim 43.8$ $D_0'' = -4.76 \times 10^{-6} \text{ cm.}^{-1}$ $A \sim 48.0$
$v = 1$	$B_1' = 1.2546 \text{ cm.}^{-1}$ $D_1' = -6.30 \times 10^{-6} \text{ cm.}^{-1}$	$B_1'' = 1.0811 \text{ cm.}^{-1}$ $Y \sim 44.4$ $D_1'' = -4.75 \times 10^{-6} \text{ cm.}^{-1}$ $A \sim 48.0$
	$B_e' = 1.2871 \text{ cm.}^{-1}$ $D_e' = -5.73 \times 10^{-6} \text{ cm.}^{-1}$ $\alpha_e' = 0.0217 \text{ cm.}^{-1}$ $\beta_e' = -0.38 \times 10^{-6} \text{ cm.}^{-1}$ $I_e' = 21.70 \times 10^{-40} \text{ g.cm.}^2$ $r_e' = 1.2732 \text{ \AA}$ $\epsilon = 0.1487 \text{ cm.}^{-1}$ $\gamma = -0.00033 \text{ cm.}^{-1}$	$B_e'' = 1.1046 \text{ cm.}^{-1}$ $D_e'' = -4.76 \times 10^{-6} \text{ cm.}^{-1}$ $\alpha_e'' = 0.0157 \text{ cm.}^{-1}$ β_e'' very small $I_e'' = 25.28 \times 10^{-40} \text{ g.cm.}^2$ $r_e'' = 1.3743 \text{ \AA}$

DISCUSSION

The analysis shows that in the initial state of the first negative bands of oxygen the levels with even values of K are missing. As the complete wave function of the molecule must be symmetrical the transition must be either $^4\Sigma_g^- \rightarrow ^4\Pi_u$ or $^4\Sigma_u^+ \rightarrow ^4\Pi_g$. Mulliken (1932) considers that the electron configuration of O_2 in the normal state is

$$1s\sigma^2 2p\sigma^2 2s\sigma^2 3p\sigma^2 3d\sigma^2 2p\pi^4 3d\pi^2.$$

By removal of a $3d\pi$ electron we get the normal state of $\text{O}_2^+ \dots 3d\sigma^2 2p\pi^4 3d\pi^2 \Pi_g$, the lower state of the second negative bands. By removal of a $2p\pi$ electron we get $\dots 3d\sigma^2 2p\pi^3 3d\pi^2 \Pi_u$ or $^2\Pi_u$, the former of which is identified with the lower state of the first negative bands and the latter with the upper state of the second negative bands. By removal of a $3d\sigma$ electron we get $\dots 3d\sigma 2p\pi^4 2d\pi^2 \Sigma_g^-$ which is identified with the upper state of the first negative bands. According to Mulliken, then, the transition is $^4\Sigma_g^- \rightarrow ^4\Pi_u$.

The failure of equations (4) to represent the observed structure of the $^4\Pi$ state is very surprising especially as the corresponding equations for $^3\Pi$ states are in excellent agreement with observation (Budó 1935 *a, b*). It appears probable that in the present case

the 4I state is perturbed, the rotational levels undergoing a displacement which varies with J in a regular manner. The interval $F_4(J) - F_1(J)$ is approximately three times as great as the interval $F_3(J) - F_2(J)$ as it should be according to equations (4). The main effect of the perturbation is to displace the F_4 levels away from the F_3 levels and the F_2 levels towards the F_1 levels by an amount which can be easily calculated from Table XX. Anomalous separations of the ${}^2I_{\frac{1}{2}}$ and ${}^2I_{\frac{3}{2}}$ components of the A 2I state of CO^+ have been observed by Bulthuis and Coster (1935), the band lines behaving apparently quite normally. They have been explained on the basis of Kronig's theory (1928) as a perturbation produced by the $X^2\Sigma$ state, this type of perturbation occurring when the vibrational levels of the two states do not approach each other too closely. From the rules given by Kronig the perturbing state in the present case must be either ${}^4\Sigma_u^-$, 4I_u or 4A_u . With the exception of ${}^4\Sigma_g^-$ the known states of the O_2^+ molecule dissociate into O in the 3P ground state and O^+ in the ${}^4S^\circ$ ground state ${}^4\Sigma_g^-$ dissociates into O in the first excited state 1D which lies about $15,700\text{ cm.}^{-1}$ above the 3P ground state and O^+ (${}^4S^\circ$). If we consider the possible molecular states which can dissociate into O 3P and O^+ in the first excited state ${}^2D^\circ$ which lies $26,800\text{ cm.}^{-1}$ above the ground state we find one ${}^4\Sigma_u^-$, three 4I_u states and two 4A_u states. Presumably it is one of these states which causes the perturbation. In the hope of throwing further light on the matter an analysis of the (0, 2) and (0, 3) bands is at present being attempted.

It will be observed from Tables II, III, VI, VII, X and XI, that the intensity of the R_3 and P_2 branches is very low. This is in accordance with the theoretical intensity factors given by Budó (1937). In general it may be said that the observed intensities of the various branches agree with the intensities to be expected theoretically when one assumes that the 4I state is intermediate between case a and case b .

In conclusion I should like to express my thanks to Professor J. J. Nolan for his interest in this work.

SUMMARY

The (1, 0), (0, 0) and (0, 1) bands of the first negative system of O_2^+ have been photographed in the second order of a 21 ft. grating.

Each of the bands has been analysed into forty branches, the transition involved being ${}^4\Sigma \rightarrow {}^4I$.

The fine structure of the ${}^4\Sigma$ level agrees with the theoretical structure predicted by Budó.

The 4I level is inverted. The structure of the level does not agree with that to be expected on theoretical grounds from formulae given by Brandt and Budó. It is suggested that this disagreement is caused by a perturbation similar to that observed by Bulthuis and Coster in the A 2I level of CO^+ .

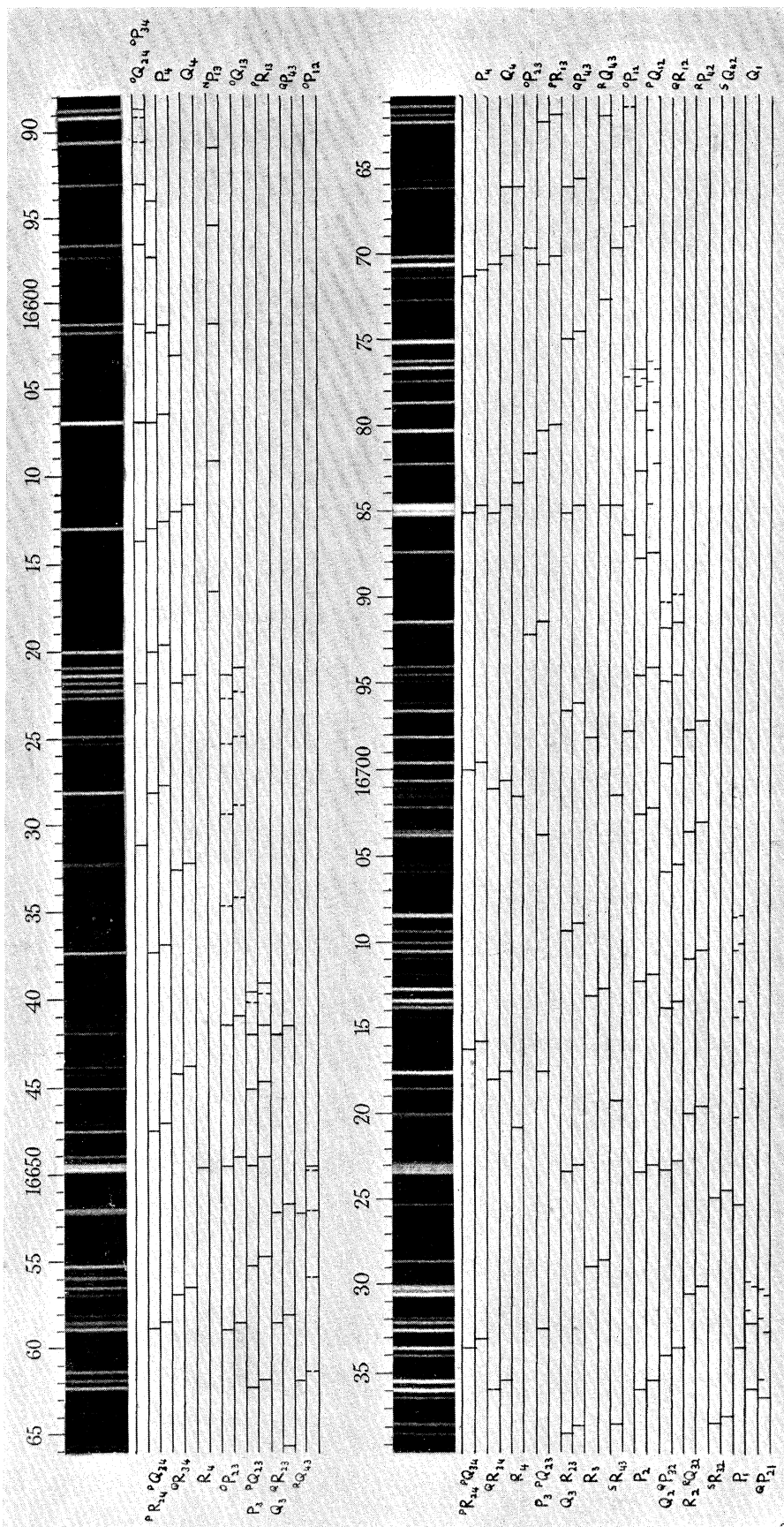
The constants of O_2^+ in the ${}^4\Sigma$ and 4I states are tabulated.

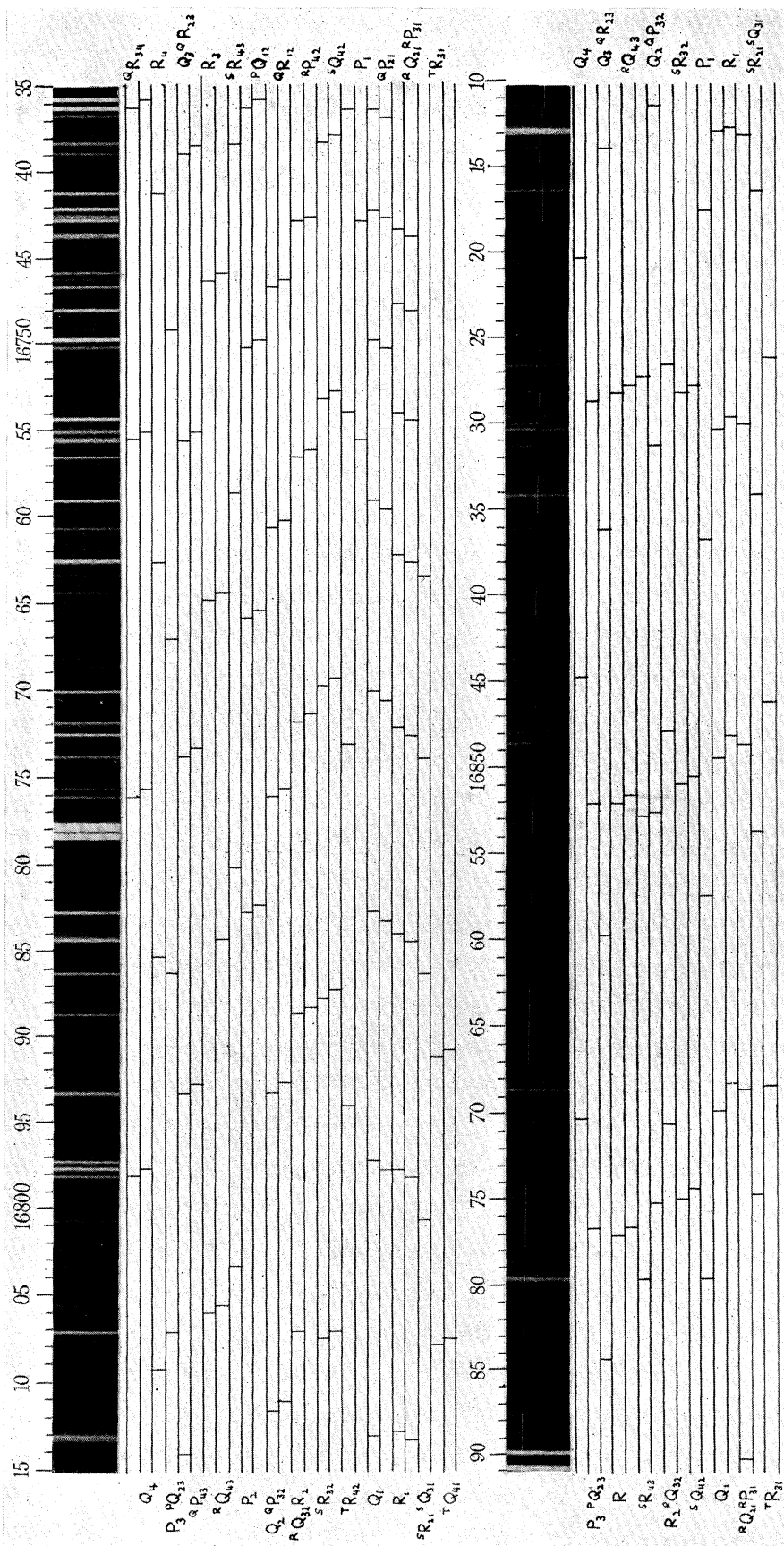
REFERENCES

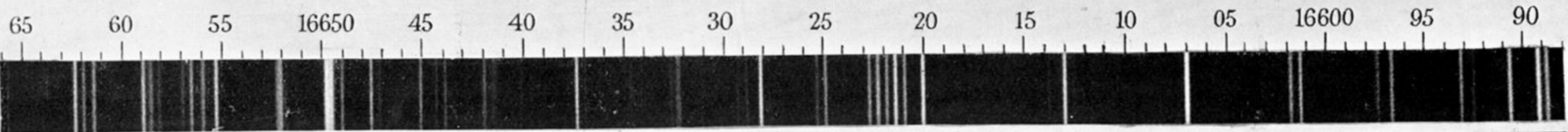
- Bozoky, L. and Schmid, R. 1935 *Phys. Rev.* **48**, 465.
Brandt, W. H. 1936 *Phys. Rev.* **50**, 778.
Budó, A. 1935*a* *Z. Phys.* **96**, 219.
— 1935*b* *Z. Phys.* **98**, 437.
— 1937 *Z. Phys.* **105**, 73.
Bulthuis, H. and Coster, D. 1935 *Verhandelingen op 25 Mei 1935*.
Aangeboden aan Prof. P. Zeeman, p. 135.
Büttenbender, G. and Herzberg, G. 1935 *Ann. Phys., Lpz.*, **21**, 577.
Frerichs, R. 1926 *Z. Phys.* **35**, 683.
von Friesen, S. 1937 *Proc. Roy. Soc. A*, **160**, 424.
Kronig, R. 1928 *Z. Phys.* **50**, 347.
Mulliken, R. S. 1932 *Rev. Mod. Phys.* **4**, 56.
Mulliken, R. S. and Stevens, S. 1933 *Phys. Rev.* **44**, 720.
-

DESCRIPTION OF PLATES 7–8

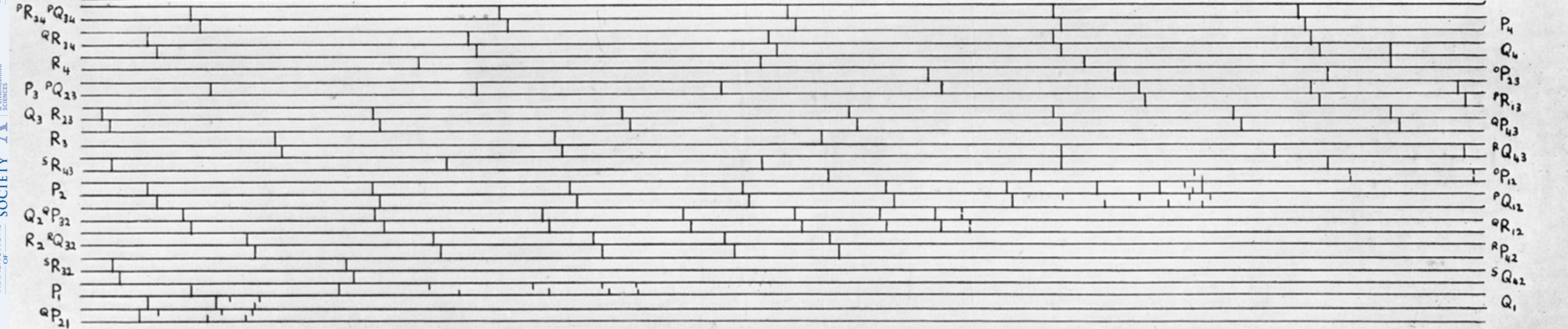
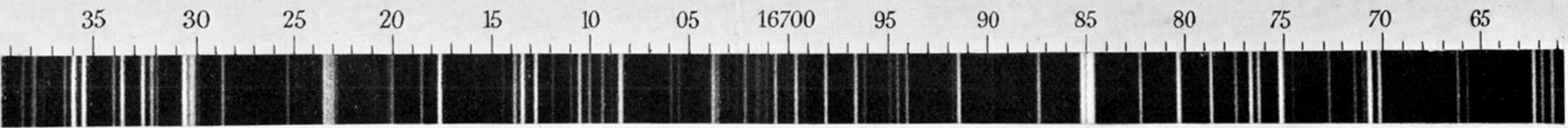
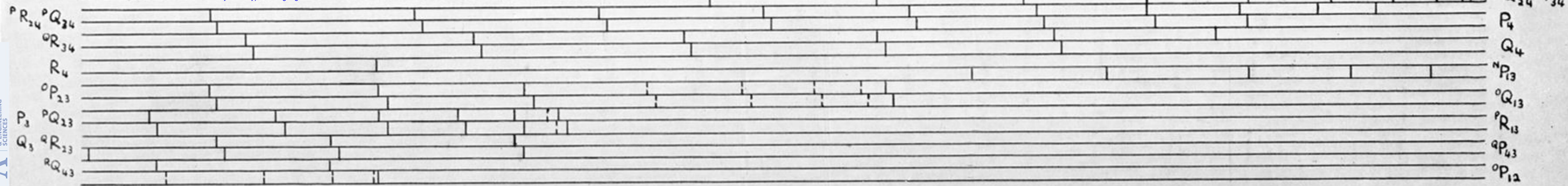
Plate 7 (*a, b*) and Plate 8 (*c, d*) show an enlargement of part of the $(0, 0)$ band. The scale is given in wave numbers. The key shows the assignment of the band lines to the various branches. Owing to lack of space all the branches are not represented on the key, the very weak ones being omitted. The branches which do not form heads are indicated on the key by lines drawn opposite the appropriate band lines on the picture. For the branches which form heads the lines running up to the head are represented by short lines depending from the horizontal lines and the lines returning from the head by short lines standing on the horizontal lines in the region where the two sets overlap. Beyond the region of overlap the lines are represented in the same manner as they are for the branches which do not form heads.







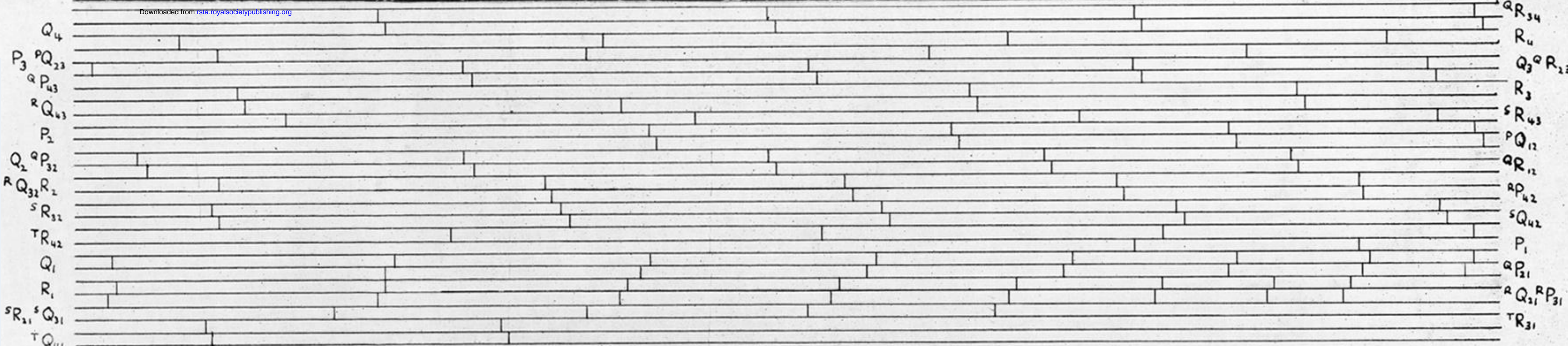
Downloaded from rsta.royalsocietypublishing.org



15 10 05 16800 95 90 85 80 75 70 65 60 55 16750 45 40 35



Downloaded from rsta.royalsocietypublishing.org



90 85 80 75 70 65 60 55 16850 45 40 35 30 25 20 15 10

