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XII—Rotational Analysis of the Band Spectrum of Zirconium Oxide

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[Plate 5]

Introduction

A previous paper by the author† contains an account of the analysis of the most characteristic bands of ZrO into three triplet systems, α, β, and γ, and the vibrational analysis of those systems. It also gives an account of the occurrence of ZrO bands in the S-type stars and of the previous work of other investigators on the subject. Plates 1 and 2 in that paper illustrate the spectrum from λ 4300 to λ 7700 A and show the very complicated nature of its structure. They are reproductions of spectrograms taken with a dense prism from λ 6200 to λ 7700 A and with the 10-foot grating in the first order from λ 4300 to λ 6585 A.

Experimental Procedure for Rotational Analysis

The source of the spectrum was chemically pure zirconium oxide on the positive pole of a Pfund arc, in which a current of five amperes was found to be the most effective in maintaining well-defined bands. Spectrograms of system α (the blue-violet region) were taken in the third order of the 10-foot grating, a solution of potassium ferrocyanide being used to filter out overlapping orders. Iron lines appeared within the band spectrum and served as standards; where these iron lines were not sufficiently strong, those of the adjacent comparison spectrum were used, any shift being checked and corrected by means of the iron lines which appeared in both band and comparison spectra. Eight-fold enlargements were made of the spectrograms of bands 1, 0; 0, 0; and 0, 1, and are reproduced on a reduced scale on Plate 5.

A small portion of the 0, 0 band, consisting of well-spaced lines, served as the starting place of the rotational analysis of that band and the two adjacent bands, 1, 0 and 0, 1. As the 0, 0 and 0, 1 bands have a common initial vibrational state and the 0, 0 and 1, 0 a common final vibrational state, the analysis could be tested by application of the combination principle, in consequence of which

$$\left.\begin{aligned} \mathrm{R}(\mathrm{J}) - \mathrm{P}(\mathrm{J}) &= \mathrm{F}'(\mathrm{J}+1) - \mathrm{F}'(\mathrm{J}-1) \equiv \Delta_2\mathrm{F}'(\mathrm{J}) \\ \text{and} \quad \mathrm{R}(\mathrm{J}-1) - \mathrm{P}(\mathrm{J}+1) &= \mathrm{F}''(\mathrm{J}+1) - \mathrm{F}''(\mathrm{J}-1) \equiv \Delta_2\mathrm{F}''(\mathrm{J}) \end{aligned}\right\} . \quad . \qquad (1)$$

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† 'Proc. Phys. Soc. Lond.,' vol. 44, p. 51 (1932).

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Thus, if the analysis is correct, we get from the bands 0, 0 and 0, 1 equal differences between two upper levels, and from bands 0, 0 and 1, 0 equal differences between two lower levels. From these equal differences, as is shown below, we obtain the molecular constants for the upper and lower states respectively. The present paper contains the rotational analysis of these three bands due to the most abundant molecule $Zr^{90}O$ and the isotope of next abundance $Zr^{94}O$.

Structure, Multiplicity, and Intensity

It has already been shown that system α arises from a transition $^3\Pi \rightarrow {}^3\Pi$; the separations in the lower substates, obtained from those of system γ, which are common to both systems, are $^3\Pi_0 - {}^3\Pi_1 = 292{\cdot}1$, $^3\Pi_1 - {}^3\Pi_2 = 313{\cdot}4$ cm^{-1}; the separations in the upper substates are $^3\Pi_0 - {}^3\Pi_1 = 304{\cdot}4$, $^3\Pi_1 - {}^3\Pi_2 = 397{\cdot}3$ cm^{-1}. *See* fig. 1.

The dispersion of the 10-foot grating in the third order is 1·7 A per mm; the definition is so fine that lines are resolved down to 0·03 A, its theoretical limit for an infinitely narrow slit at λ 4600 A. Nevertheless, none of the bands is completely resolved in the neighbourhood of the head, nor of the origin. Thus it is not possible to determine the number of " missing " lines, and hence the Ω-values of the substates cannot be determined thereby. However, in the 0, 1 band a Q branch has been found in substates previously designated as $^3\Pi_a$; hence in system α $^3\Pi_a$ is $^3\Pi_2$. (The discussion on this point will be found below.)

In regard to intensity it will be observed from the plate that in the three bands 1, 0; 0, 0 and 0, 1 the sub-bands (*a*) are the weakest, the (*a*) of the 1, 0 band being too weak for satisfactory analysis. With the exception of sub-band (*a*) of the 1, 0 band, the 0, 1 band is much weaker than the other two; the difference is greater than shown in Plate **5**, as the exposure for the 0, 0 band was three hours, while that for the 0, 1 band was five hours. Within the bands the relative intensities of the lines show insufficient regular differences to give much aid in the analysis; this may be due to the true intensities being masked by the overlapping of sub-bands and of other bands in the sequence. Little significance may be attached to the intensities of lines recorded in the tables, as they are eye-estimates and merely relative to those of lines within a comparatively small range. In the 0, 1 band, Plate 5, it will be observed that there are weaker heads of wave numbers about 3 cm^{-1} higher than those of the main heads due to $Zr^{90}O$; these weaker heads, as will be shown later, are the heads due to the isotopic molecule $Zr^{94}O$.

Observational Data

Measurements were made in the usual manner on over 2400 lines lying in the regions λ 4452 to λ 4737 and λ 4827 to λ 4914 A; these regions include the chief members of the sequences 0, + 1 and − 1. The wave-lengths of the lines were determined by reference to standard iron lines, those recommended by the I.A.U. (1932) being employed wherever available; otherwise, reference was made to the

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wave-lengths of lines determined by Burns and Walters.† From the wave-lengths the wave numbers were obtained from Kayser's table.‡ About one-half of the lines measured are assigned to the bands 1, 0 ; 0, 0 and 0, 1 of the molecules $Zr^{90}O$ and $Zr^{94}O$; the remainder belong to the other bands of the sequences not considered in the analysis. For the sake of economy in printing, the tables contain only the data appertaining to the lines included in the analysis and after the first fifteen lines, the data of only every fifth line.

In Tables I*a*, I*b*, I*c* are recorded the rotational quantum numbers, the wave numbers, the estimated intensities enclosed in brackets, and the differences, O — C, between the observed and calculated wave numbers of the lines forming the R and P branches of the 0, 0 band in all three substates of the molecules $Zr^{90}O$ and $Zr^{94}O$. Tables II*a*, . . . III*c* contain the corresponding data for the 0, 1 and 1, 0 bands respectively, excepting the data for the substate $^3\Pi_2$ of the 1, 0 band, which has not been analysed. Table II*d* contains the corresponding data of the Q branch of the 0, 1 band in the $^3\Pi_2$ substate for both molecules. Many lines are blends ; when a line has more than one assignment in the analysis, the number of them is indicated by a superscript to the brackets enclosing the intensity. The wave numbers are recorded to the second place of decimals, although in many cases they are probably not correct beyond the first place on account of the hazy character or close packing of the lines ; the second place is, however, retained in order to avoid inaccuracy, occasioned by the addition of the errors of two lines between which differences are taken.

Due to lack of resolution there is doubtless some uncertainty in the identification of the lines of very low J-values ; they have, nevertheless, been included in the tables, the uncertainty being indicated by the differences between the observed and calculated wave numbers (O — C).

Rotational Analysis

It has been shown by Hill and Van Vleck§ that in a molecular state classed by Hund as case *a* and comprised of three substates, the energy due to nuclear rotation and electronic spin is given (using present-day notation) by the equations :

$$\mathrm{W} = \pm \mathrm{A}\Lambda\,\Sigma + h\mathrm{B}_v\,[\mathrm{J}\,(\mathrm{J}+1) - \Lambda\,(\Lambda \pm 2)\,]$$
$$\pm\,(2h^2\mathrm{B}_v{}^2/\mathrm{A}\Lambda)\;[\mathrm{J}\,(\mathrm{J}+1) - \Lambda\,(\Lambda \pm 1)] + \mathrm{D}_v\,\mathrm{J}^2\,(\mathrm{J}+1)^2 + \ldots$$

when $\Sigma = \pm 1$, and

$$\mathrm{W} = h\mathrm{B}_v\,[\mathrm{J}\,(\mathrm{J}+1) - \Lambda^2 + 2] + 4h^2\mathrm{B}_v{}^2/\mathrm{A} + \mathrm{D}_v\,\mathrm{J}^2\,(\mathrm{J}+1)^2 + \ldots$$

when $\Sigma = 0$.

Λ is the quantum number for the component, along the internuclear axis, of the resultant of the electronic orbital momentum and is unity for Π states.

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† 'Publ. Allegheny Obs.,' vol. 8, No. 4 (1931).

‡ Kayser, "Tabelle d. Schwingungszahlen" (1925).

§ 'Phys. Rev.,' vol. 32, p. 261 (1928).

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The spin quantum number, S, is unity for all triple states.

Σ is the axial component of $\sqrt{S(S+1)}$, taking the values $-S$, $-S+1$, $-S+2$ and equalling $-1, 0, +1$ for the three substates ${}^3\Pi_0$, ${}^3\Pi_1$, ${}^3\Pi_2$, where the subscripts are the values of $\Omega = \Lambda + \Sigma$.

A is the coefficient of magnetic interaction of resultant electronic orbital and spin momenta.

$A\Lambda\,\Sigma$ represents the energy of magnetic interaction of Λ and Σ, $A\,\Lambda$ the separation of the electronic sub-levels.

B is an abbreviation for $h/8\pi^2 c\mu r^2 = 27{\cdot}66 \times 10^{-40}/\mu r^2$,

where r = the internuclear distance,
μ = the reduced or effective mass,
$= 22{\cdot}41 \times 10^{-24}$ gm.

D is the coefficient of a term required for the expansibility of the molecule under centrifugal force; Kratzer has shown that $D_e = -\dfrac{4B_e^3}{\omega_e^2}$.

The subscript v is the quantum number which designates the vibrational state and

$$B_v = B_e - \alpha\,(v + \tfrac{1}{2}) = B_o - \alpha v,$$
$$D_v = D_e + \beta\,(v + \tfrac{1}{2}) = D_0 + \beta v,$$

where the subscript e refers to the state of equilibrium, and α and β are small positive constants much smaller than B_e and D_e respectively.[†]

For the total energy term[‡] we must to W/h add T_e, the main electronic energy term, and $G(v)$ the vibrational energy term. If then we substitute for the Π state, $\Lambda = 1$ we obtain,

$$\left.\begin{array}{l}
\text{for } \Sigma = -1, \\
T(J) = T_e + G(v) - A + B_v + B_v(1 - 2B_v/A)\,J(J+1) + D_vJ^2(J+1)^2 + \ldots \\
\qquad = T_e + G(v) - A + B_v + B^*J(J+1) + D_vJ^2(J+1)^2 + \ldots; \\
\text{for } \Sigma = 0, \\
T(J) = T_e + G(v) + B_v + 4B_v^2/A + B_vJ(J+1) + D_vJ^2(J+1)^2 + \ldots; \\
\text{for } \Sigma = +1, \\
T(J) = T_e + G(v) + A - 3B_v - 4B_v^2/A + B^*J(J+1) + D_vJ^2(J+1)^2 + \ldots, \\
\text{where for convenience in printing we may write} \\
\qquad B_v^* = B_v(1 \pm 2B_v/A) \text{ according as } \Sigma = \pm 1.
\end{array}\right\} \quad . \quad (2)$$

[†] Jevons, "Report on Band Spectra of Diatomic Molecules," p. 25.

[‡] Jevons, p. 121 *et seq.*

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Thus in dealing with the rotation of a molecule in a given substate the only variable is J. The lines of a band which arise from a transition from one rotational state, J′, to another, J″, constitute different branches R, Q, P, according as J′ − J″ = + 1, 0 or − 1, where ′ and ″ refer to the upper and lower vibrational states respectively. The lines of the R branches of the three substates $^3\Pi_0 \rightarrow {}^3\Pi_0$, $^3\Pi_1 \rightarrow {}^3\Pi_1$, $^3\Pi_2 \rightarrow {}^3\Pi_2$ are denoted by R_1, R_2, R_3 and are expressed by the equations obtained by the application of the transition from J′ (= J″ + 1) to J″ to equations (2). Thus, letting $\nu_0 = T_e + G(v)$,

$$\left.\begin{aligned}
&\text{in } \Sigma = -1, {}^3\Pi_0:\\
&\quad R_1(J) = \nu_0 - A + (B' - B'') + (B'^* + B''^*)(J+1)\\
&\qquad\qquad + (B'^* - B''^* + D' - D'')(J+1)^2\\
&\qquad\qquad + 2(D' + D'')(J+1)^3 + (D' - D'')(J+1)^4 + \ldots,\\
&\text{in } \Sigma = 0, {}^3\Pi_1:\\
&\quad R^2(J) = \nu_0 + (B' - B'') + 4(B'^2 - B''^2)/A\\
&\qquad\qquad + (B' + B'')(J+1) + (B' - B'' + D' - D'')(J+1)^2\\
&\qquad\qquad + 2(D' + D'')(J+1)^3 + (D' - D'')(J+1)^4 + \ldots,\\
&\text{in } \Sigma = +1, {}^3\Pi_2:\\
&\quad R^3(J) = \nu_0 + A - 3(B' - B'') - 4(B'^2 - B''^2)/A\\
&\qquad\qquad + (B'^* + B''^*)(J+1) + (B'^* - B''^* + D' - D'')(J+1)^3\\
&\qquad\qquad + 2(D' + D'')(J+1)^3 + (D' - D'')(J+1)^4 + \ldots,
\end{aligned}\right\} \quad . \quad (3)$$

where for ease in printing J is used for J″, B for B_v and D for D_v.

Similarly the equations for the three Q and three P branches are obtained by applying to equations (2) the transitions from J′ (= J″) to J″ and from J′ (= J″ − 1) to J″, respectively. Thus we obtain :

$$\begin{aligned}
&\text{in } \Sigma = -1, {}^3\Pi_0:\\
&\quad Q_1(J) = \nu_0 - A + (B' - B'') + (B'^* - B''^*)J + (B' - B'' + D' - D'')J^2\\
&\qquad\qquad + 2(D' - D'')J^3 + (D' - D'')J^4 + \ldots;
\end{aligned} \qquad (4)$$

$$\begin{aligned}
&\text{in } \Sigma = -1, {}^3\Pi_0:\\
&\quad P_1(J) = \nu_0 - A + (B' - B'') - (B'^* + B''^*)J + (B'^* - B''^* + D' - D'')J^2\\
&\qquad\qquad - 2(D' + D'')J^3 + (D' - D'')J^4 + \ldots,
\end{aligned} \qquad (5)$$

With similar equations for Q_2 (J), Q_3 (J), P_2 (J) and P_3 (J), having the term independent of J the same as those of the corresponding R_2 and R_3 branches.

This modification of the B coefficients from B to B (1 ± 2 B/A) in the Π_0 and Π_2 substates is due to some uncoupling of the spin momenta from the internuclear axis, as the rotational momenta increase.

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Q Branches and Identification of Substates

It is well known that the Q branches in a $^3\Pi \rightarrow {}^3\Pi$ band are very much weaker than the R and P branches, and are only of appreciable intensity at comparatively low J-values. Further, in Hund's case *a*,[†] to which the $^3\Pi$ states of ZrO are a fair approximation, the intensity factors of the Q lines for a given J-value in the three sub-bands, $^3\Pi_0 \rightarrow {}^3\Pi_0$, $^3\Pi_1 \rightarrow {}^3\Pi_1$, $^3\Pi_2 \rightarrow {}^3\Pi_2$, are in the ratio of the squares of the subscripts, namely, 0 : 1 : 4 ; that is to say, that the first should have no Q branch, the second a weak one, and the third a rather stronger one, and even in this case only the earlier lines, such as Q (2) and Q (3), will be comparable in intensity with the corresponding R and P lines.

The wave numbers of the lines in possible Q branches in each of the three substates of the three bands 1, 0 ; 0, 0 and 0, 1 were calculated by substituting in equations (4) the values of ν_0, B′, B″, D′ and D″, previously determined from the R and P branches. The result of a comparison of these wave numbers with those in the catalogue of measured lines led to the conclusion that the only Q branch reasonably well established is that of the 0, 1 band in substate $^3\Pi_a \rightarrow {}^3\Pi_a$ for both molecules, $Zr^{90}O$ and $Zr^{94}O$. Hence the $^3\Pi_a$ substate is $^3\Pi_2$ and therefore $^3\Pi_c$ is $^3\Pi_0$.

Fig. 1 is an energy-level diagram for the three investigated bands and for the 0, 0 band of system γ. It shows that the separations of the substates due to electronic spin are greater in the upper than in the lower levels and that those in the upper states instead of being approximately equal to one another are roughly in the ratio of 3 : 4. This energy-level diagram differs from the *tentative* one in the author's

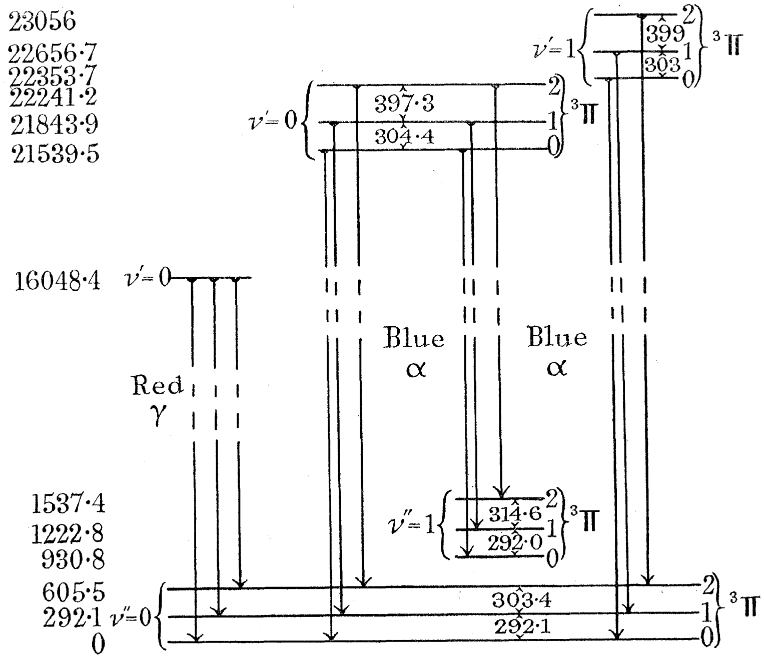

Fig. 1—Energy-level diagram for ZrO

[†] Jevons, "Report," p. 134.

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earlier paper, in that the $^3\Pi_a$ substates in the latter were provisionally assumed to be $^3\Pi_0$ and the spin separations were consequently smaller in the upper than in the lower levels. Since the presence of a Q branch in the $^3\Pi_a$ substate has shown $^3\Pi_a$ to be $^3\Pi_2$, the only alternative arrangement to that of fig. 1 would be one in which the upper and lower levels were inverted, the spin separations would be smaller in the upper than in the lower levels, but A would be negative and hence the lowest level for $v'' = 0$ could not be that of zero energy.

Application of Combination Principle and Calculation of Molecular Constants

From the well-known equations :

$$\left.\begin{aligned} R(J) - P(J) &= (4J+2)\{B' + 2D'(J^2+J+1)\} \equiv \Delta_2F'(J) \dots \\ R(J-1) - P(J+1) &= (4J+2)\{B'' + 2D''(J^2+J+1)\} \equiv \Delta_2F''(J) \dots \end{aligned}\right\}, \quad (6)$$

we obtain to a first approximation :

$$B' = \frac{R(J) - P(J)}{4J+2}, \quad B'' = \frac{R(J-1) - P(J+1)}{4J+2} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The B's were calculated by application of equations (7) to lines selected for their comparatively good definition, and of which the J-values were sufficiently low, so that errors greater than those due to measurement were not introduced by omission of the term in D in equations (6). The values of B thus obtained with J lying between 11 and 26 differed irregularly from one another by about 0·001. It was considered justifiable to ignore the term in D, because the second differences of the terms, namely,

$$\Delta_2F'(J) - \Delta_2F'(J+1),$$

and

$$\Delta_2F''(J) - \Delta_2F''(J+1),$$

were too irregular to indicate any reliable value of the D's. From the average of the B′'s from a given sub-band, and the value of ω' determined in the vibrational analysis, the D′'s were calculated from KRATZER's equation given on p. 358 ; the D″'s were similarly calculated. Substituting in equations (3) and (5) the average value of the B′'s and B″'s and the values of the D's therefrom, the ν_0's were calculated from selected lines and the mean taken. Then substituting these three constants for each sub-band in the appropriate equations (3) and (5), the wave numbers of the lines of the R and P branches were calculated from equations (8A) to (10C), given below. If any line employed in calculating the constants gave a large difference (O — C) between its observed and calculated values, that value of the constant was discarded and the process repeated until suitable values of (O — C) were obtained for all lines involved in determining the constants. The columns (O — C) in Tables I to III provide a test of the reliability of the method.

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TABLE I*a*—R_3, P_3, $R_3{}^i$ AND $P_3{}^i$ BRANCHES OF THE 0, 0 BAND

	Branches due to molecule $Zr^{90}O$				Branches due to molecule $Zr^{94}O$			
Substates :	$^3\Pi_2 \rightarrow {}^3\Pi_2$				$^3\Pi_2{}^i \rightarrow {}^3\Pi_2{}^i$			
	$\lambda_{\text{head}} = 4619\cdot823$ A,		$\nu_0{}^* = 21635\cdot70$ cm^{-1}					
J	R_3 (J)	O − C	P_3 (J)	O − C	$R_3{}^i$ (J)	O − C	$P_3{}^i$ (J)	O − C
2	21 638·55 (3)	+0·12	—	—	21 638·55 (3)	−0·01	↓ . . . . Blended with P_3 ↑	
3	(639·02)	—	21 631·52 (2)	−0·04	(639·18)	—		
4	639·36 (16)^2	−0·09	629·84 (3)	−0·02	639·57 (16)^3	+0·05		
5	639·81 (16)^5	+0·08	627·97 (2)	−0·03	639·81 (16)^5	−0·16		
6	639·81 (16)^5	−0·03	625·98 (2)	−0·01	(639·97)	—		
7	639·81 (16)^5	+0·01	623·81 (3)	−0·01	(639·97)	—		
8	639·57 (16)^3	−0·03	621·46 (2)	−0·03	639·81 (16)^5	+0·08		
9	639·36 (16)^2	+0·11	618·96 (2)	−0·04	639·57 (16)^3	+0·05		
10	(638·74)	—	616·29 (3)	−0·06	(638·91)	—		
11	(638·06)	—	613·48 (3)	−0·07	638·22 (3)	−0·01		
12	637·32 (2)	+0·09	610·50 (4)	−0·09	↓ Blended with R_3 ↑			
13	636·29 (2)	+0·05	607·41 (3)	−0·07				
14	635·15 (2)	+0·06	604·13 (4)	−0·07				
15	633·84 (1)	+0·05	600·70 (4)	−0·07				
20	624·88 (3)	−0·02	581·22 (4)	−0·03				
25	612·06 (4)	+0·01	557·83 (4)	+0·02				
30	595·26 (4)	−0·01	530·35 (6)^2	−0·11			531·38 (6)^3	+0·17
35	574·57 (5)	0·00	(499·22)	—			500·28 (6)^2	−0·02
40	550·00 (5)	+0·04	464·12 (Zr)^2	+0·03	550·55 (3)^2	−0·19	465·30 (3)	−0·11
45	521·33 (3)^2	−0·09	424·97 (ft)	−0·14	522·30 (4)^3	+0·05	(426·51)	—
50	(489·01)	—	382·25 (1)	−0·05	(490·14)	—	384·11 (2)	−0·05
55	452·76 (3)	+0·03	335·62 (4)	−0·04	(454·12)	—	(337·73)	—
60	412·76 (2)	+0·16	285·46 (5)	−0·21	—	—	288·02 (2)	+0·12

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TABLE I*b*—R_2, P_2, R_2^i AND P_2^i BRANCHES OF THE 0, 0 BAND

	Branches due to molecule $Zr^{90}O$				Branches due to molecule $Zr^{94}O$			
Substates :	$^3\Pi_1 \rightarrow {}^3\Pi_1$				$^3\Pi_1^i \rightarrow {}^3\Pi_1^i$			
	λ_{head} = 4637·888 A,		ν_0^* = 21551·84 cm^{-1}					
J	R_2 (J)	O − C	P_2 (J)	O − C	R_2^i (J)	O − C	P_2^i (J)	O − C
1	(21 553·78)							
2	554·42 (5)^2	−0·06	21 549·13 (4)^2	−0·05	(21 554·59)	—	(21 549·33)	—
3	555·10 (8)^2	+0·10	547·59 (5)^2	−0·02	555·30 (8)^5	+0·03	u^i	—
4	555·30 (8)^5	−0·06	545·76 (3)^2	−0·08	555·32 (10)^4	+0·05	u^i	—
5	555·52 (10)^4	−0·01	543·80 (4)^2	−0·10	555·80 (12)^2	+0·12	u^i	—
6	555·52 (10)^4	0·00	541·67 (6)^3	−0·11	555·80 (12)^2	+0·12	541·93 (8)^4	+0·01
7	555·30 (8)^5	−0·04	539·56 (5)	+0·07	555·52 (10)^4	+0·05	539·84 (3)^2	+0·01
8	555·10 (8)^2	+0·12	536·90 (5)^4	−0·12	555·30 (8)^5	+0·03	(537·18)	—
9	554·42 (5)^2	−0·03	534·47 (6)^3	+0·10	(554·59)	—	(534·77)	—
10	(553·74)	—	531·67 (6)^3	+0·13	553·98 (3)	+0·07	531·87 (6)	−0·12
11	553·00 (4)	+0·15	528·62 (5)^3	+0·08	u^i	—	529·10 (2)^2	+0·14
12	551·90 (3)	+0·12	525·49 (6)^4	+0·12	u^i	—	525·84 (2)^2	−0·01
13	550·55 (3)^2	+0·01	521·94 (3)^2	−0·08	u^i	—	522·30 (4)^3	−0·02
14	549·13 (4)^2	+0·01	518·51 (5)^3	+0·02	u^i	—	518·94 (5)	+0·03
15	547·59 (5)^2	+0·07	(514·78)	—	u^i	—	515·09 (5)^3	−0·12
20	536·90 (5)^4	+0·01	493·49 (2)^2	−0·13	(537·18)	—	493·97 (4)^3	−0·08
25	521·94 (3)^2	+0·08	468·05 (3)^2	−0·02	522·30 (5)^3	−0·02	468·89 (1)^3	+0·11
30	502·40 (6)^3	−0·03	438·09 (ft)^3	−0·06	(502·91)	—	—	—
35	478·67 (7)^3	+0·04	(403·88)	—	479·30 (4)^2	−0·03	—	—
40	(450·46)	—	365·19 (1)^2	−0·11	451·21 (2)	−0·09	—	—
45	417·89 (1)	−0·06	(322·41) (Zr)	—	—	—	—	—
50	381·01 (1)^2	−0·10	275·30 (2)	+0·04	—	—	—	—
55	(340·00)	—	—	—	—	—	—	—

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TABLE I*c*—R_1, P_1, $R_1{}^i$ AND $P_1{}^i$ BRANCHES OF THE 0, 0 BAND

	Branches due to molecule $Zr^{90}O$				Branches due to molecule $Zr^{94}O$			
Substates :	$^3\Pi_0 \to {}^3\Pi_0$				$^3\Pi_0{}^i \to {}^3\Pi_0{}^i$			
	$\lambda_{head} = 4640·636$ A,		$\nu_0{}^* = 21539·54$ cm^{-1}					
J	R_1 (J)	O − C	P_1 (J)	O − C	$R_1{}^i$ (J)	O − C	$P_1{}^i$ (J)	O − C
0	21 540·64 (4)^2	+0·08	—	—	21 540·64 (4)^2	−0·09	—	—
1	(541·42)	—	21 538·35 (4)	+0·04	541·67 (6)^4	+0·06	u^i	—
2	(542·06)	—	536·90 (5)^4	+0·02	(542·23)	—	u^i	—
3	(542·50)	—	535·30 (3)	+0·06	542·76 (20)^6	+0·08	u^i	—
4	542·76 (20)^6	+0·01	533·40 (4)	−0·02	543·11 (15)^2	+0·18	u^i	—
5	542·76 (20)^6	−0·04	531·38 (6)^3	−0·01	543·11 (15)^2	+0·18	21 531·67 (6)^3	+0·05
6	542·76 (20)^6	+0·11	529·10 (2)^2	−0·07	542·76 (20)^6	−0·17	529·42 (1)	+0·05
7	(542·30)	—	526·77 (4)	+0·03	(542·47)	—	527·06 (4)	+0·02
8	541·67 (6)^4	−0·09	524·04 (4)	−0·08	541·93 (8)^4	+0·09	(524·33)	—
9	541·13 (2)^2	+0·11	521·33 (3)^2	+0·02	541·13 (2)^2	−0·18	(521·64)	—
10	540·18 (2)^2	+0·10	518·31 (5)^2	+0·01	540·18 (2)^2	−0·18	518·51 (5)^3	−0·12
11	539·07 (5)^2	+0·13	515·09 (5)^3	0·00	539·31 (5)^2	+0·05	515·44 (5)^2	+0·01
12	537·62 (2)	+0·02	511·73 (3)	+0·05	(537·82)	—	512·16 (2)^2	+0·06
13	536·12 (4)^2	+0·05	508·07 (4)	−0·01	536·43 (2)	+0·10	(508·46)	—
14	534·27 (6)^3	−0·07	504·25 (5)	−0·02	534·47 (6)^2	−0·12	504·59 (3)	−0·07
15	532·43 (2)	+0·02	500·28 (6)	+0·01	(532·66)	—	(500·72)	—
20	519·78 (5)	−0·02	477·30 (3)	−0·03	520·14 (1)	+0·05	477·97 (2)	+0·08
25	502·40 (6)^3	+0·12	449·34 (5)	−0·14	502·56 (5)^3	−0·26	450·03 (ft)	−0·23
30	479·78 (4)^2	−0·06	416·70 (5)^3	−0·05	(480·35)	—	417·62 (1)	−0·06
35	452·40 (4)	−0·12	(379·16)	—	452·97 (1)	−0·18	380·53 (3)	+0·15
40	420·37 (6)	+0·06	(336·73)	—	421·47 (1)^3	+0·15	338·08 (1)^2	−0·15
45	383·40 (3)	+0·13	289·56 (2)	+0·05	384·59 (1)	0·00	291·40 (3)	+0·05
50	(341·43)	—	(237·50) (Fe)	—	—	—	239·44 (1)	−0·19
55	294·65 (1)^2	−0·13	(180·78)	—	—	—	—	—
60	—	—	119·39 (1)	+0·04	—	—	—	—

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PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

TABLE IIa—R_3, P_3, $R_3{}^i$ AND $P_3{}^i$ BRANCHES OF THE 0, 1 BAND

	Branches due to molecule $Zr^{90}O$				Branches due to molecule $Zr^{94}O$			
Substates :	$^3\Pi_2 \rightarrow {}^3\Pi_2$				$^3\Pi_2{}^i \rightarrow {}^3\Pi_2{}^i$			
	λ_{head} = 4827·525 A,		$\nu_0{}^*$ = 20703·82 cm^{-1}					
J	R_3 (J)	O − C	P_3 (J)	O − C	$R_3{}^i$ (J)	O − C	$P_3{}^i$ (J)	O − C
2	20 706·52 (12)^3 (Zr)	−0·05	—	—	20 709·79 (3)	+0·13	—	—
3	(707·20)	—	20 699·83 (1)	+0·08	(710·34)	—	20 703·10 (1)	+0·08
4	707·77 (1)^2	+0·09	698·16 (1)	+0·07	(710·90)	—	701·28 (1)	−0·08
5	(708·01)	—	696·20 (1)	−0·09	711·16 (2)^2	−0·02	699·27 (1)^2	−0·14
6	708·27 (2)^3	+0·08	694·26 (1)^2	−0·09	711·37 (2)^2	−0·03	(697·48)	—
7	708·27 (2)^3	+0·04	692·23 (1)^3	−0·02	711·37 (2)^2	−0·03	695·32 (1)^3	−0·14
8	(708·12)	—	690·03 (1)	+0·02	711·16 (2)^2	−0·12	693·30 (1)^3	+0·02
9	707·77 (1)^2	−0·09	687·63 (2)	0·00	(710·90)	—	691·05 (1)^2	+0·16
10	(707·45)	—	685·09 (2)	0·00	(710·59)	—	(688·37)	—
11	706·84 (1)	−0·07	682·38 (2)	−0·03	710·04 (1)	+0·06	685·71 (ft)	+0·03
12	706·07 (1)	−0·13	679·57 (2)	−0·02	709·39 (3)	+0·18	682·90 (ft)	+0·02
13	705·24 (1)^2	−0·11	676·64 (1)	+0·03	708·27 (4)^3	−0·12	680·04 (1)	+0·07
14	(704·36)	—	673·50 (1)^2	+0·01	(707·52)	—	(676·85)	—
15	703·35 (1)^2	+0·13	670·30 (1)	+0·07	706·52 (12)^3 (Zr)	+0·01	673·50 (1)^2	−0·17
20	695·32 (1)^3	+0·02	651·64 (4)	−0·06	698·56 (1)^2	+0·03	655·15 (1)	+0·02
25	683·72 (2)^2	−0·01	629·61 (1)	+0·08	687·00 (ft)^2	−0·01	633·26 (1)	+0·01
30	668·64 (1)	+0·14	603·67 (1)^2	−0·14	671·89 (1)^2	−0·14	607·44 (1)	−0·03
35	649·51 (1)	−0·08	574·23 (1)	−0·06	653·01 (1)	−0·01	578·14 (1)	−0·08
40	627·16 (1)	+0·11	541·33 (2)	+0·07	630·88 (1)^2	+0·07	545·39 (3)^3	−0·14
45	601·01 (2)^3	+0·13	(504·64)	—	604·74 (1)	−0·09	508·97 (1)	−0·11
50	(571·01) (Fe)	—	464·26 (1)	−0·19	575·11 (3)	0·00	468·84 (1)^2	−0·12
55	537·70 (4)	0·00	—	—	—	—	—	—
60	500·91 (3)^2	+0·19	—	—	—	—	—	—
65	460·15 (1)^3	−0·14	—	—	—	—	—	—

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TABLE II*b*—R_2, P_2, $R_2{}^i$ AND $P_2{}^i$ BRANCHES OF THE 0, 1 BAND

	Branches due to molecule $Zr^{90}O$				Branches due to molecule $Zr^{94}O$			
Substates :	$^3\Pi_1 \rightarrow {}^3\Pi_1$				$^3\Pi_1{}^i \rightarrow {}^3\Pi_1{}^i$			
	λ_{head} = 4847·182 A,		ν_0* = 20621·06 cm^{-1}					
J	R_2 (J)	O − C	P_2 (J)	O − C	$R_2{}^i$ (J)	O − C	$P_2{}^i$ (J)	O − C
1	20 622·97 (1)^2	−0·02	—	—	(20 626·12)	—	—	—
2	(623·70)	—	20 618·49 (1)^2	+0·05	(626·84)	—	20 621·72 (1)^2	+0·05
3	(624·23)	—	617·01 (1)^3	+0·14	(627·37)	—	620·10 (1)^2	−0·10
4	(624·60)	—	(615·13)	—	627·83 (1)^2	+0·09	618·49 (1)^2	−0·04
5	624·80 (4)^2	+0·01	613·30 (1)^2	+0·08	628·04 (2)^2	+0·10	(616·51)	—
6	624·80 (4)^2	0·00	610·99 (1)^2	−0·14	628·04 (2)^2	+0·10	614·45 (1)	+0·24
7	(624·65)	—	608·89 (1)	+0·01	627·83 (1)^2	+0·04	612·15 (5)^3	+0·02
8	(624·32)	—	(606·45)	—	(627·46)	—	(609·71)	—
9	(623·82)	—	603·87 (2)	+0·02	(626·96)	—	(607·15) (Zr)	—
10	622·97 (1)^2	−0·17	601·01 (1)^3	−0·06	626·12	—	604·49 (1)^3	+0·19
11	622·25 (1)^2	−0·05	(598·13)	—	(625·40)	—	601·31 (1)	+0·13
12	(621·29)	—	595·21 (1)^4	+0·20	(624·44)	—	598·49 (2)^2	−0·05
13	620·10 (1)^2	0·00	591·73	—	623·38 (1)^2	+0·11	595·21 (3)^4	+0·13
14	618·64 (1)^2	−0·10	588·08 (1)^2	−0·19	621·72 (1)^2	−0·10	591·36 (3)^2	−0·09
15	617·24 (1)	+0·03	584·57 (1)	−0·07	620·52 (1)	+0·09	588·08 (1)^2	+0·12
20	606·99 (Zr)	+0·03	(563·91)	—	(610·24)	—	567·53 (2)	+0·09
25	592·63 (3)^2	+0·20	538·94 (1)	+0·02	596·05 (1)^3	+0·08	542·77 (4)	+0·14
30	573·50 (1)^3	−0·10	509·92 (4)^2	+0·26	(576·96)	—	(513·80)	—
35	(550·51)	—	476·19 (2)	+0·02	554·32 (2)^2	+0·20	480·26 (2)	−0·02
40	(523·15) (Fe)	—	—	—	526·93 (3)^3	−0·01	—	—
45	491·56 (2)	−0·03	—	—	(495·55)	—	—	—
50	456·00 (1)^4	+0·20	—	—	—	—	—	—
55	415·97 (1)	+0·13	—	—	—	—	—	—

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TABLE IIc—R_1, P_1, $R_1{}^i$ AND $P_1{}^i$ BRANCHES OF THE 0, 1 BAND

Branches due to molecule Zr^{90}O — Branches due to molecule Zr^{94}O

Substates : $^3\Pi_0 \rightarrow {}^3\Pi_0$ — $^3\Pi_0{}^i \rightarrow {}^3\Pi_0{}^i$

$\lambda_{\text{head}} = 4850 \cdot 114$ A, $\nu_0{}^* = 20608 \cdot 73$ cm^{-1}

J	R_1 (J)	O − C	P_1 (J)	O − C	$R_1{}^i$ (J)	O − C	$P_1{}^i$ (J)	O − C
1	20 610·67 (2)	+0·05	—	—	20 613·85 (1)	+0·03	—	—
2	611·36 (1)^3	+0·05	20 606·14 (1)^3	+0·02	614·45 (1)^2	−0·05	20 609·29 (2)^4	−0·03
3	(611·79)	—	604·49 (1)^3	−0·05	(614·93)	—	607·72 (1)^2	+0·04
4	612·15 (5)^3	+0·04	602·76 (1)	−0·02	615·33 (2)^4	+0·04	606·14 (2)^3	+0·18
5	612·33 (5)^2	+0·09	(600·84)	—	615·33 (2)^4	−0·14	604·12 (1)	+0·07
6	612·15 (5)^3	−0·05	598·62 (2)^2	−0·11	615·33 (2)^4	+0·04	601·83 (2)^5	−0·02
7	(611·98)	—	596·42 (1)	0·00	(615·12)	—	599·60 (2)	−0·07
8	611·54 (1)^2	−0·03	594·00 (2)	+0·06	614·64 (1)^2	−0·04	597·23 (2)	−0·03
9	610·99 (1)^2	+0·01	591·36 (3)^2	+0·07	(614·14)	—	594·73 (1)	+0·10
10	610·02 (1)^3	−0·19	(588·45)	—	613·30 (1)^2	+0·13	591·78 (1)	+0·04
11	609·29 (2)^4	+0·02	585·49 (1)^3	+0·06	612·33 (5)^2	−0·12	588·66 (2)	−0·14
12	608·12 (2)	−0·02	582·31 (3)	+0·07	611·36 (1)^3	+0·06	585·49 (1)^3	−0·15
13	606·83 (Zr)	—	578·84 (2)	−0·01	610·02 (1)^3	+0·08	582·05 (2)	−0·14
14	605·35 (2)	+0·01	575·31 (3)	+0·01	608·41 (1)	−0·12	578·64 (3)	−0·04
15	603·67 (2)	0·00	(571·57) (Fe)	—	606·99 (Zr)	+0·13	574·76 (3)^2	−0·11
20	592·63 (3)^2	−0·01	550·25 (3)	+0·06	596·05 (1)^3	+0·16	553·70 (1)	−0·09
25	577·11 (1)^3	+0·01	524·22 (2)^2	−0·13	580·46 (3)^3	−0·01	528·01 (2)	+0·09
30	557·10 (6)	0·00	494·20 (1)^2	+0·14	560·55 (1)	−0·04	497·94 (2)	−0·16
35	532·49 (4)^2	−0·14	459·20 (1)	−0·13	536·05 (2)	−0·09	—	—
40	(503·71)	—	—	—	(507·55)	—	—	—
45	470·33 (1)	−0·15	—	—	474·37 (2)	−0·01	—	—

TABLE IId—Q_3 AND $Q_3{}^i$ BRANCHES OF THE 0, 1 BAND $^3\Pi_2 \rightarrow {}^3\Pi_2$

	Branch due to molecule					Branch due to molecule			
	Zr^{90}O		Zr^{94}O			Zr^{90}O		Zr^{94}O	
J	Q_3 (J)	O − C	$Q_3{}^i$ (J)	O − C	J	Q_3 (J)	O − C	$Q_3{}^i$ (J)	O − C
2	20 703·35 (1)^2	−0·03	(20 706·51) (Zr)	—	10	20 695·92 (2)	+0·18	20 699·27 (1)^2	+0·14
3	702·80 (1)^2	−0·14	705·94 (1)	+0·02	11	694·02 (1)	−0·10	697·26 (1)^3	+0·02
4	(702·35)	—	705·65 (1)	+0·14	12	692·23 (1)^3	−0·13	695·32 (1)^3	+0·14
5	701·49 (1)	−0·13	704·59 (1)	−0·07	13	690·31 (1)	−0·14	(693·55)	—
6	700·84 (1)	+0·11	704·04 (1)	+0·02	14	(688·39)	—	(691·65)	—
7	699·69 (1)	−0·01	702·80 (1)^2	−0·08	15	686·31 (2)^2	+0·12	689·53 (ft)^2	−0·05
8	698·56 (1)^2	+0·03	(701·75)	—	20	672·82 (1)	−0·15	(676·18)	—
9	697·26 (1)^3	+0·05	700·56 (1)^3	+0·10	25	656·03 (1)^2	−0·07	659·33 (1)^2	−0·17

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Table III*b*—R_2, P_2, R_2^i, P_2^i Branches of the 1, 0 Band

Branches due to molecule $Zr^{90}O$ — Branches due to molecule $Zr^{94}O$

Substates : $^3\Pi_1 \rightarrow {}^3\Pi_1$ — $^3\Pi_1^i \rightarrow {}^3\Pi_1^i$

$\lambda_{\text{head}} = 4469 \cdot 491$ A, $\nu_0^* = 22364 \cdot 58$ cm^{-1}

J	R_2 (J)	O − C	P_2 (J)	O − C	R_2^i (J)	O − C	P_2^i (J)	O − C
1	22 366·44 (3)^2	0·00	—	—	(22 364·02)	—	—	—
2	367·17 (4)^2	+0·11	(22 361·92)	—	(364·65)	—	(22 359·53)	—
3	(367·49)	—	(360·28)	—	365·12 (3)^2	+0·06	(357·90)	—
4	367·66 (4)^2	−0·05	(358·45)	—	(365·23)	—	356·05 (4)^3	−0·02
5	367·66 (4)^2	−0·07	356·51 (2)^4	+0·09	(365·23)	—	354·12 (5)^4	+0·03
6	(367·55)	—	354·12 (3)^5	−0·04	365·12 (1)^2	0·00	(351·82)	—
7	367·17 (4)^2	0·00	(351·72)	—	(364·74)	—	(349·39)	—
8	366·44 (3)^2	−0·14	(349·08)	—	(364·02)	—	346·91 (3)^3	+0·14
9	365·88 (3)	+0·09	(346·24)	—	363·53 (6) (Zr)	+0·07	(343·95)	—
10	(364·80)	—	343·15 (4)^3	−0·04	362·32 (12) (Zr)	−0·07	340·74 (4)^3	−0·14
11	363·53 (6)^2	−0·08	339·90 (3)	−0·04	361·16 (2)	+0·03	337·76 (3)^2	+0·11
12	362·32 (12) (Zr)	+0·10	336·39 (4)^2	−0·10	359·92 (1)	−0·01	(334·16) (Fe)	—
13	360·81 (2)	+0·18	332·73 (3)	−0·12	358·33 (1)	−0·10	330·51 (2)	−0·01
14	(358·84)	—	328·98 (1)	−0·02	356·51 (5)^4	+0·04	326·84 (4)	+0·04
15	356·84 (5)^2	0·00	324·99 (3)	+0·04	354·33 (4)^2	−0·15	322·83 (4)^2	0·00
20	(343·84)	—	301·69 (2)	+0·01	341·44 (3)	−0·12	(299·68)	—
25	325·92 (1)^2	+0·11	273·25 (2)	−0·16	(323·67)	—	(271·43)	—
30	302·71 (3)	−0·05	(240·15)	—	300·90 (1)	+0·20	238·16 (3)	−0·09
35	274·70 (1)^2	−0·03	202·20 (4)	+0·27	(272·87)	—	(200·83)	—
40	(241·72)	—	158·88 (3)	+0·11	(240·10)	—	—	—
45	203·96 (2)^2	+0·19	110·62 (5)	−0·09	202·69 (4)^2	+0·11	—	—
50	160·83 (4)^2	−0·07	(057·77)	—	(159·73)	—	—	—
55	113·40 (3)	+0·25	000·08 (3)	+0·08	112·58 (1)^2	−0·03	—	—
60	060·85 (4)	+0·31	21 937·22 (2)	−0·22	—	—	—	—
65	002·87 (4)^2	−0·26	—	—	—	—	—	—
70	21 940·70 (2)	−0·25	—	—	—	—	—	—

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TABLE III*c*—R_1, P_1, R_1^i AND P_1^i BRANCHES OF THE 1, 0 BAND

	Branches due to molecule $Zr^{90}O$				Branches due to molecule $Zr^{94}O$			
Substates :	$^3\Pi_0 \rightarrow {}^3\Pi_0$				$^3\Pi_0^i \rightarrow {}^3\Pi_0^i$			
	$\lambda_{head} = 4471\cdot652$ A,		$\nu_0^* = 22353\cdot73$ cm^{-1}					
J	R_1 (J)	O − C	P_1 (J)	O − C	R_1^i (J)	O − C	P_1^i (J)	O − C
0	22 354·78 (3)^2	+0·02	—	—	(22 352·36)	—	—	—
1	(355·57)	—	(22 352·49)	—	(353·15)	—	(22 350·09)	—
2	356·05 (4)^3	−0·12	(351·03)	—	353·52 (4)^2	−0·10	348·81 (4)	+0·17
3	356·51 (2)^4	−0·04	(349·36)	—	354·12 (5)^4	+0·04	346·91 (3)^3	−0·07
4	356·84 (5)^3	+0·13	347·57 (3)^2	+0·10	354·33 (4)^2	−0·08	(345·20)	—
5	356·84 (5)^3	+0·18	345·50 (3)	+0·13	354·33 (4)^2	−0·08	343·15 (4)^3	+0·01
6	356·51 (5)^4	+0·12	343·15 (4)^3	+0·10	354·12 (5)^4	+0·04	340·74 (3)^3	−0·07
7	356·05 (4)^3	+0·14	(340·52)	—	353·52 (4)^2	−0·11	337·27 (ft)	+0·07
8	355·12 (4)	−0·09	337·76 (3)^2	−0·01	352·70 (3)	0·00	(335·45) (Fe)	—
9	354·12 (5)^4	−0·18	(334·81) (Fe)	—	(351·71)	—	332·37 (3)	−0·15
10	(353·17)	—	331·71 (3)	+0·08	(350·76)	—	(329·44)	—
11	352·03 (3)	+0·21	328·29 (3)	+0·06	349·61 (3)^2	−0·02	325·92 (1)^2	−0·12
12	350·33 (4)	+0·07	324·65 (3)	+0·03	(347·94)	—	322·39	−0·03
13	348·27 (2)	−0·21	320·78 (3)^3	−0·02	345·87 (4)	−0·02	318·64 (3)^2	+0·06
14	346·50 (2)	+0·01	316·74 (3)^2	−0·02	(344·13)	—	314·57 (3)^2	0·00
15	344·38 (3)	+0·09	312·59 (3)^3	+0·08	341·96 (3)^3	−0·06	310·28 (3)^2	−0·17
20	329·96 (1)^2	−0·08	288·03 (4)	−0·01	327·63 (2)^2	−0·07	286·10 (3)	+0·06
25	310·28 (3)^2	−0·15	258·24 (3)	+0·03	308·11 (3)^2	−0·04	(256·44)	—
30	285·27 (2)^2	−0·20	222·96 (3)	−0·12	283·53 (2)^2	+0·09	221·66 (4)	−0·16
35	(255·19)	—	182·55 (3)	−0·09	(253·41)	—	(181·24) (Zr)	—
40	(219·60)	—	136·87 (3)	−0·07	217·96 (3)^2	−0·09	—	—
45	178·90 (3)^2	+0·16	—	—	177·32 (3)	+0·15	—	—
50	(132·64)	—	—	—	—	—	—	—

Symbol u^i indicates that the line is unresolved from the corresponding line of $Zr^{90}O$; (Fe), (Zr) that the line is hidden by iron or zirconium lines respectively. Superscripts to brackets enclosing intensities, *e.g.*, $(4)^2$, indicate the number of assignments of a line. Wave numbers enclosed in brackets are calculated values. $\nu_0^* = \nu_0 +$ (terms in A and B's not coefficients of J).

This method of determining the constants is more suitable to this very complex and dense spectrum than one which requires a large number of consecutive lines, to all of which equal weight is given.

Table IV contains examples of the combination differences and the resulting values of $B'_0{}^*$ or B'_0 for the three upper substates from bands 0, 0 and 0, 1 ; Table V contains similar data for the three lower substates from bands 0, 0 and 1, 0 ; Table VI gives similar data for the upper substates from band 1, 0 and Table VII for the lower substates from band 0, 1. The data in these latter two tables seem to lack confirmation by comparison with those from a second band ; however, the combination differences [R (J) − P (J)] in band 1, 0 and [R (J − 1) − R (J + 1)] in band 0, 1 are indirectly confirmed, as the former are derived from the same branches as [R (J − 1) − P (J + 1)] in Table V and the latter from the same branches as [R (J) − P (J)] in Table IV. Table VIII contains a summary of the molecular constants for the upper and lower states.

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TABLE IV—UPPER STATE COMBINATION DIFFERENCES OF THE 0, 0 AND 0, 1 BANDS

Substate :	$^3\Pi_2$				$^3\Pi_1$				$^3\Pi_0$			
Band :	0, 0		0, 1		0, 0		0, 1		0, 0		0, 1	
	$\Delta_2 F'_3 (J)$	B'_0*	$\Delta_2 F'_3 (J)$	B'_0*	$\Delta_2 F'_2 (J)$	B'_0	$\Delta_2 F'_2 (J)$	B'_0	$\Delta_2 F'_1 (J)$	B'_0*	$\Delta_2 F'_1 (J)$	B'_0*
16	35·21	0·5335	35·16	0·5327	34·90	0·5288	34·69	0·5256	34·25	0·5191	34·16	0·5176
17	37·38	0·5340	37·14	0·5306	*u*	—	36·85	0·5264	36·25	0·5178	36·16	0·5166
18	39·48	0·5335	(Zr)	—	39·11	0·5285	38·78	0·5241	38·42	0·5192	38·34	0·5181
19	41·53	0·5324	41·76	0·5354	41·11	0·5271	40·98	0·5254	40·46	0·5187	40·43	0·5183
20	43·66	0·5317	43·68	0·5327	43·41	0·5294	Zr	—	42·48	0·5185	42·38	0·5168
21	45·82	0·5328	45·84	0·5330	45·56	0·5298	45·20	0·5256	44·68	0·5197	44·54	0·5179
22	47·85	0·5317	47·85	0·5316	47·49	0·5277	47·51	0·5279	46·60	0·5178	46·73	0·5192
23	49·99	0·5318	50·10	0·5330	*u*	—	*u*	—	48·86	0·5197	48·88	0·5192
24	52·10	0·5317	52·08	0·5315	*u*	—	Zr	—	50·87	0·5191	50·91	0·5195
25	54·23	0·5317	54·11	0·5305	53·89	0·5283	53·69	0·5264	53·06	0·5202	52·89	0·5185
26	56·33	0·5314	56·15	0·5297	55·82	0·5266	*u*	—	54·98	0·5197	(Fe)	—
27	58·38	0·5308	*u*	—					56·88	0·5171	56·90	0·5173

TABLE V—LOWER STATE COMBINATION DIFFERENCES OF THE 0, 0 AND 1, 0 BANDS

Substate :	$^3\Pi_2$				$^3\Pi_1$				$^3\Pi_0$			
Band :	0, 0		1, 0		0, 0		1, 0		0, 0		1, 0	
J	$\Delta_2 F''_3 (J)$	B''_0*			$\Delta_2 F''_2 (J)$	B''_0	$\Delta_2 F''_2 (J)$	B''_0	$\Delta_2 F''_1 (J)$	B''_0*	$\Delta_2 F''_1 (J)$	B''_0*
16	40·47	0·6132	—	—	*u*	—	40·53	0·6141	40·74	0·6173	41·02	0·6215
17	42·85	0·6121	—	—	43·20	0·6171	43·22	0·6174	43·28	0·6183	43·48	0·6211
18	45·31	0·6123	—	—	45·60	0·6162	*u*	—	45·72	0·6178	46·07	0·6226
19	47·73	0·6119	—	—	48·18	0·6177	47·92	0·6144	48·19	0·6178	48·36	0·6200
20	50·12	0·6112	—	—	50·60	0·6171	50·51	0·6160	50·63	0·6174	50·86	0·6202
21	52·50	0·6102	—	—	53·01	0·6164	*u*	—	53·06	0·6170	53·21	0·6187
22	55·00	0·6111	—	—	55·60	0·6178	55·47	0·6163	55·61	0·6179	55·57	0·6174
23	57·40	0·6106	—	—	57·91	0·6161	57·90	0·6160	57·99	0·6169	58·19	0·6190
24	59·83	0·6105	—	—	*u*	—	60·32	0·6155	60·64	0·6188	60·58	0·6182
25	62·27	0·6105	—	—	*u*	—	62·84	0·6161	62·98	0·6175	63·01	0·6178
26	64·65	0·6099	—	—	65·21	0·6152	65·51	0·6180	65·31	0·6161	65·53	0·6182
27	67·06	0·6097	—	—	67·51	0·6137	*u*	—	67·98	0·6180	67·96	0·6178

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TABLE VI—UPPER STATE COMBINATION DIFFERENCES OF THE 1, 0 BAND

Substate :	$^3\Pi_1$		$^3\Pi_0$	
J	$\Delta_2F'_2(J)$	B'_1	$\Delta_2F'_1(J)$	B'_1*
16	34·00	0·5152	33·85	0·5130
17	*u*	—	36·01	0·5144
18	38·05	0·5142	37·91	0·5123
19	40·11	0·5147	39·99	0·5127
20	Fe	—	41·93	0·5113
21	44·34	0·5156	43·99	0·5115
22	46·27	0·5141	46·08	0·5120
23	48·30	0·5138	47·97	0·5103
24	50·59	0·5162	49·93	0·5095
25	52·67	0·5164	52·04	0·5102
26	*u*	—	54·13	0·5107
27	56·91	0·5174	56·40	0·5127

TABLE VII—LOWER STATE COMBINATION DIFFERENCES OF THE 0, 1 BAND

	$^3\Pi_2$		$^3\Pi_1$		$^3\Pi_0$	
J	$\Delta_2F'_3(J)$	B'_1*	$\Delta_2F'_2(J)$	B'_1	$\Delta_2F'_1(J)$	B'_1*
16	39·93	0·6050	40·43	0·6126	40·10	0·6076
17	Zr	—	42·57	0·6081	42·54	0·6077
18	45·06	0·6089	45·16	0·6103	44·95	0·6074
19	47·33	0·6068	*u*	—	47·38	0·6074
20	49·80	0·6073	50·00	0·6098	49·82	0·6076
21	52·12	0·6060	52·67	0·6124	52·24	0·6074
22	54·57	0·6064	*u*	—	54·84	0·6093
23	56·82	0·6044	*u*	—	57·39	0·6105
24	59·22	0·6043	59·68	0·6090	59·75	0·6097
25	61·51	0·6032	62·30	0·6108	Fe	—
26	*u*	—	*u*	—	64·27	0·6063
27	66·50	0·6045	(Fe)	—	66·77	0·6070

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TABLE VIII—MOLECULAR CONSTANTS FOR $Zr^{90}O$

	Upper State				Lower State			
	Band	$^3\Pi_2$	$^3\Pi_1$	$^3\Pi_0$	Band	$^3\Pi_2$	$^3\Pi_1$	$^3\Pi_0$
B_0†	0, 0	0·53296	0·52853	0·51854	0, 0	0·61198	0·61696	0·61745
B_0	0, 1	0·53254	0·52570	0·51828	1, 0	—	0·61570	0·62078
Mean B_0	—	0·53275	0·52711	0·51841	—	—	0·61633	0·61911
B_1	1, 0	—	0·51479	0·51302	0, 1	0·60604	0·61186	0·60844
α	—	—	0·01232	0·00539	—	0·00594	0·00447	0·01067
B_e	—	—	0·53327	0·52110	—	0·61495	0·61856	0·62444
Mean $D_0 \times 10^7$	—	−9·055	−8·771	−8·346	—	−10·513	−10·754	−10·885
$D_e \times 10^7$	—	—	−9·009	−8·406	—	−10·590	−10·778	−11·088
$I_e \times 10^{40}$	—	—	51·869	53·080	—	44·979	44·717	44·296
$r_e \times 10^8$	—	—	1·521	1·539	—	1·417	1·413	1·406

† For substates $^3\Pi_2$ and $^3\Pi_0$, the B's are strictly B*.

The comparatively good agreement in the combination differences, illustrated in Tables IV and V, confirms the correctness of the analysis of bands 0, 0 and 0, 1 into three R and three P branches; that is, one R and one P branch for each substate $^3\Pi_2$, $^3\Pi_1$ and $^3\Pi_0$; also of one R and one P branch for each of the substates $^3\Pi_1$ and $^3\Pi_0$ of the 1, 0 band; as mentioned above, the analysis of substate $^3\Pi_2$ has not been accomplished.

The equations from which the wave numbers were calculated follow:

Band 0, 0,

$$\left.\begin{aligned}\Omega = 2 : R_3(J) &= 21635\cdot70 + 1\cdot1449\,(J+1) - 0\cdot07902\,(J+1)^2 \\ &\quad - 39\cdot479 \times 10^{-7}\,(J+1)^3 + 1\cdot609 \times 10^{-7}\,(J+1)^4 \ldots \\ P_3(J) &= 21635\cdot70 - 1\cdot1449\,J - 0\cdot07902\,J^2 \\ &\quad + 39\cdot156 \times 10^{-7}\,J^3 + 1\cdot448 \times 10^{-7}\,J^4 + \ldots\end{aligned}\right\}, \qquad (8\text{A})$$

$$\begin{aligned}\Omega = 1 : P_2(J) &= 21551\cdot84 - 1\cdot1455\,J - 0\cdot08843\,J^2 \\ &\quad + 39\cdot255 \times 10^{-7}\,J^3 + 1\cdot946 \times 10^{-7}\,J^4 + \quad \ldots\ldots\ldots \end{aligned} \qquad (8\text{B})$$

$$\begin{aligned}\Omega = 0 : P_1(J) &= 21539\cdot54 - 1\cdot1360\,J - 0\cdot09891\,J^2 \\ &\quad + 38\cdot3514 \times 10^{-7}\,J^3 + 2\cdot463 \times 10^{-7}\,J^4 + \quad \ldots\ldots\ldots \end{aligned} \qquad (8\text{C})$$

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Band 0, 1,

$$\left.\begin{aligned} \Omega = 2 : P_3(J) &= 20703{\cdot}82 - 1{\cdot}1386\,J - 0{\cdot}0735\,J^2 \\ &\quad + 38{\cdot}845 \times 10^{-7}\,J^3 + 1{\cdot}335 \times 10^{-7}\,J^4 \ldots \\ Q_3(J) &= 20703{\cdot}82 - 0{\cdot}0735\,(J + J^2) \\ &\quad + 1{\cdot}335 \times 10^{-7}\,(2J^3 + J^4) \ldots \end{aligned}\right\}, \qquad (9\text{A})$$

$$\Omega = 1 : P_2(J) = 20621{\cdot}06 - 1{\cdot}1414\,J - 0{\cdot}0900\,J^2 + 38{\cdot}763 \times 10^{-7}\,J^3 + 1{\cdot}980 \times 10^{-7}\,J^4 \quad \ldots\ldots \quad (9\text{B})$$

$$\Omega = 0 : P_1(J) = 20608{\cdot}73 - 1{\cdot}1391\,J - 0{\cdot}1025\,J^2 + 37{\cdot}679 \times 10^{-7}\,J^3 + 2{\cdot}166 \times 10^{-7}\,J^4 \quad \ldots\ldots \quad (9\text{C})$$

Band 1, 0,

$$\Omega = 1 : P_2(J) = 22364{\cdot}58 - 1{\cdot}1305\,J - 0{\cdot}1009\,J^2 + 38{\cdot}047 \times 10^{-7}\,J^3 + 2{\cdot}418 \times 10^{-7}\,J^4 \quad \ldots\ldots \quad (10\text{B})$$

$$\Omega = 0 : P_1(J) = 22353{\cdot}71 - 1{\cdot}1338\,J - 0{\cdot}10776\,J^2 + 39{\cdot}411 \times 10^{-7}\,J^3 + 2{\cdot}770 \times 10^{-7}\,J^4 \quad \ldots\ldots \quad (10\text{C})$$

The corresponding equations for the R branches are obvious. Columns headed (O — C) in Tables I to III contain the differences between the observed and these calculated values of the wave numbers and provide a criterion for the analysis. The calculated wave numbers for high values of J may have comparatively large errors due to small inaccuracies in the measurement of the lines used in determining the constants B and D. One effect of such errors is some uncertainty in regard to the end of some of the branches. For example, in the 0, 0 band the calculated wave number of P_1 (34) is 21387·07 ; this may contain an error of 0·24 cm^{-1} due to small inaccuracies in the constants ; the nearest observed wave number is 21387·34 cm^{-1}, giving a difference of + 0·27 ; so if an error of about 0·004 A (0·02 cm^{-1}) were made in measuring that line, it would be uncertain whether or not the wave number 21387·34 should be assigned to P^1 (34). A similar uncertainty applies to several other lines of this branch and to lines near the termination of other branches. In these ambiguous cases the *calculated* wave numbers are given in Tables I to III, and to distinguish them from the observed values are enclosed in brackets. To settle these questions by finding other assignments for the observed lines of approximately the same wave-length, would require an extensive analysis of other bands of the 0, + 1 and — 1 sequences.

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ISOTOPIC BANDS

It is well known† that the total isotopic displacement, that is, the wave number difference, $\nu^i - \nu$, of corresponding lines in corresponding bands of two isotopic molecules, such as $Zr^{90}O$ and $Zr^{94}O$ is the algebraic sum of a vibrational displacement,

$$\nu_v^i - \nu_v \doteqdot (\rho - 1)\ \nu_v;$$

and a rotational displacement,

$$\nu_r^i - \nu_r \doteqdot (\rho^2 - 1)\ \nu_r,$$

where ν_v is the interval between the system-origin and the band-origin of the more abundant molecule, in this case $Zr^{90}O$ and ν_r the interval between the band-origin and the line in question; ν_v^i and ν_r^i are the corresponding intervals for the less abundant molecule, $Zr^{94}O$; also ρ is the square root of the ratio of the reduced masses, that is $\sqrt{\mu/\mu^i}$. In the present case obtaining μ from the atomic weights, A, by means of the expression:

$$\mu = 1 \cdot 649 \times 10^{-24} \frac{A_{Zr} \times A_0}{A_{Zr} + A_0},$$

we have $\rho = 0 \cdot 99678$. Using the previously determined ‡ values of the vibrational coefficients for $Zr^{90}O$, namely,

$$\omega'_e = 820 \cdot 58 \quad ; \quad x'_e\ \omega'_e = 3 \cdot 306 \quad ,$$
$$\omega''_e = 937 \cdot 20 \quad ; \quad x''_e\ \omega''_e = 3 \cdot 346 \quad ,$$

for the calculation of ν_v, we derive $\nu_v^i - \nu_v = +3 \cdot 160$, $+0 \cdot 187$ and $-2 \cdot 410$ for the 0, 1; 0, 0; and 1, 0 bands respectively. For the rotational part ν_r of the wave number of the line in question, we have the expression following ν_0 in the appropriate equations on pp. 363 and 372 and 373. Thus for the line P_3 (J) of the 0, 1 band, we can readily calculate ν_r which is $(P_3\ (J) - \nu_0^{0,\,1})$ from the first equation in (9A) and hence derive the rotational displacement,

$$P_3\ (J)^i - P_3\ (J) \doteqdot (\rho^2 - 1)\ [P_3\ (J) - \nu_0^{0,\,1}]\ ;$$

and similarly for a line of any of the other branches, which have been analysed in the previous section.

The wave numbers of the lines of the isotopic branches were calculated by adding the algebraic sum of the vibrational and rotational displacements to the observed wave number of the corresponding line in the branch of the more abundant molecule;

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† JEVONS, "Report," p. 209 *et seq.*

‡ LOWATER, *loc. cit.*

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hence they include errors in those wave numbers. In cases where the line of $Zr^{90}O$ was not identified, its calculated wave number was used to find the corresponding line of $Zr^{94}O$. The wave numbers of R^i, Q^i and P^i branches of $Zr^{94}O$ are tabulated with the R, Q and P branches in Tables I*a* to III*c*.

UNASSIGNED LINES

In the region between the R_3 heads of the 0, 0 and 1, 1 bands there are at most nine lines which have not been assigned to a branch and only two of these, namely, ν 21546·66 (7) and ν 21533·00 (3) are at all well defined; the non-assignment of these can scarcely detract from the analysis. Between the R_3 heads of the 0, 1 and 1, 2 bands there are forty-one unassigned lines, none of which is well defined and only three of which have intensities greater than one; these three are ν 20654·05 (2), ν 20637·36 (2) and ν 20628·23 (3). These forty-one unassigned lines may probably belong to a group of bands which lie in the region between bands 3, 3 and 0, 1, but which do not belong to system α. Finally between the R_3 heads of the 1, 0 and 2, 1 bands, there are seven unassigned lines, all of which are ill defined and may belong to the unanalysed $^3\Pi_2 \rightarrow {}^3\Pi_2$ substate of the 1, 0 band.

There are numerous unassigned lines in the regions occupied by members of the sequences of higher vibrational quantum numbers, regions into which the unanalysed bands extend; it is fair to suppose that these unassigned lines belong to these unanalysed bands. In the 1, 1 band, the $^3\Pi_0 \rightarrow {}^3\Pi_0$ sub-band has been analysed and a few lines of low J-values in the other two sub-bands have been identified; in cases where these lines are blended with those of the 0, 0 band, they are included in the superscript, used in Tables I to III, which indicates the number of assignments of a line. These additional assignments from the 1, 1 band account for the abnormal intensity of some of the lines of the less abundant molecule with which they are blended.

Λ-TYPE DOUBLING

In HUND'S case *a* in a $^3\Pi \rightarrow {}^3\Pi$ band if Λ doubling were large enough to be detected, every line in $^3\Pi_1$ and $^3\Pi_0$ substates would be doubled, but the doubling would be negligibly small in the $^3\Pi_2$ substate.† The R and P branches of all the bands show no doubling that can be attributed to Λ doubling of the Π levels.

It is with much gratitude that the author acknowledges her indebtedness to the helpful suggestions and criticisms of Professor A. FOWLER, Dr. W. JEVONS and Dr. R. W. B. PEARSE.

SUMMARY

Bands 1, 0; 0, 0; and 0, 1 of system α of the spectrum of molecule $Zr^{90}O$ and its isotope of next abundance $Zr^{94}O$ have been analysed.

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† JEVONS, "Report," pp. 128 and 188.

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The 0, 0 band consists of R, R^i, P and P^i branches in each of the substates $^3\Pi_0$, $^3\Pi_1$ and $^3\Pi_2$, the presence of possible Q and Q^i branches in substate $^3\Pi_2$ being indecisive.

The 0, 1 band has the same R, R^i, P and P^i branches as the 0, 0 band; it has also Q and Q^i branches in substate $^3\Pi_2$.

The 1, 0 band has been analysed into R, R^i, P and P^i branches in each of the substates $^3\Pi_0$ and $^3\Pi_1$, but the analysis in the substate $^3\Pi_2$ has not been accomplished.

In none of the bands has Λ-type doubling been found.

The origins of the bands could not be observed directly on account of the crowding together of lines in their proximity.

For the upper and lower $^3\Pi$ states respectively the mean values of B_0 are 0·5256 and 0·6158, of α about 0·009 and 0·007 cm^{-1} and of r_e $1{\cdot}521 \times 10^{-8}$ and $1{\cdot}413 \times 10^{-8}$ cm.

Description of Plate 5

This consists of reproductions on a reduced scale of eight-fold enlargements of spectrograms taken in the third order of the 10-foot grating. Identified lines due to $Zr^{90}O$ are indicated in strips above the photographs by full vertical lines; lines for which (O — C) is large for J have their calculated locations indicated by broken lines. Dots · and double dots : indicate, with the same distinction, lines due to $Zr^{94}O$. A wave number scale is beneath each strip, also the wave-length of a line close to the ends of each strip.

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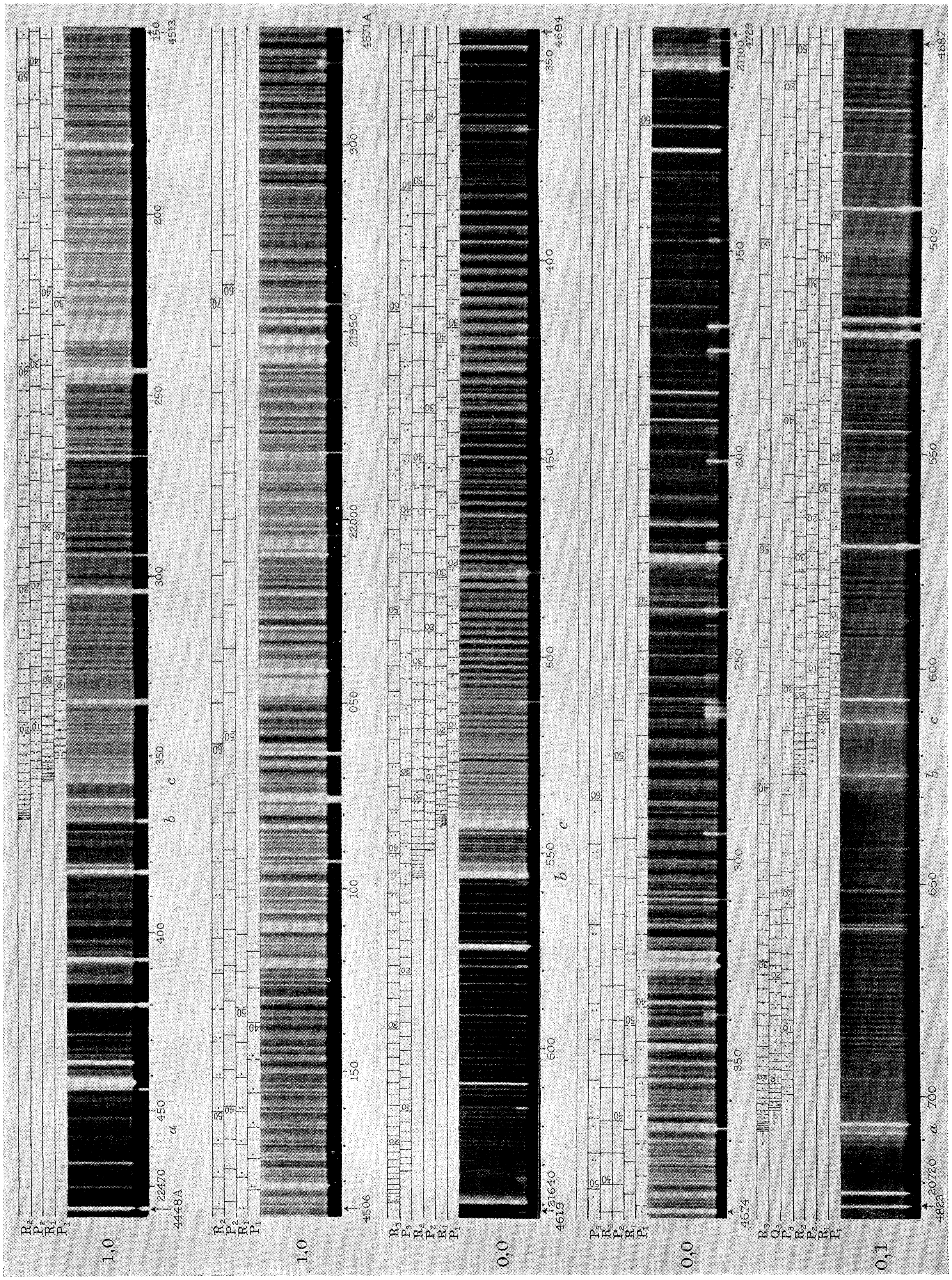

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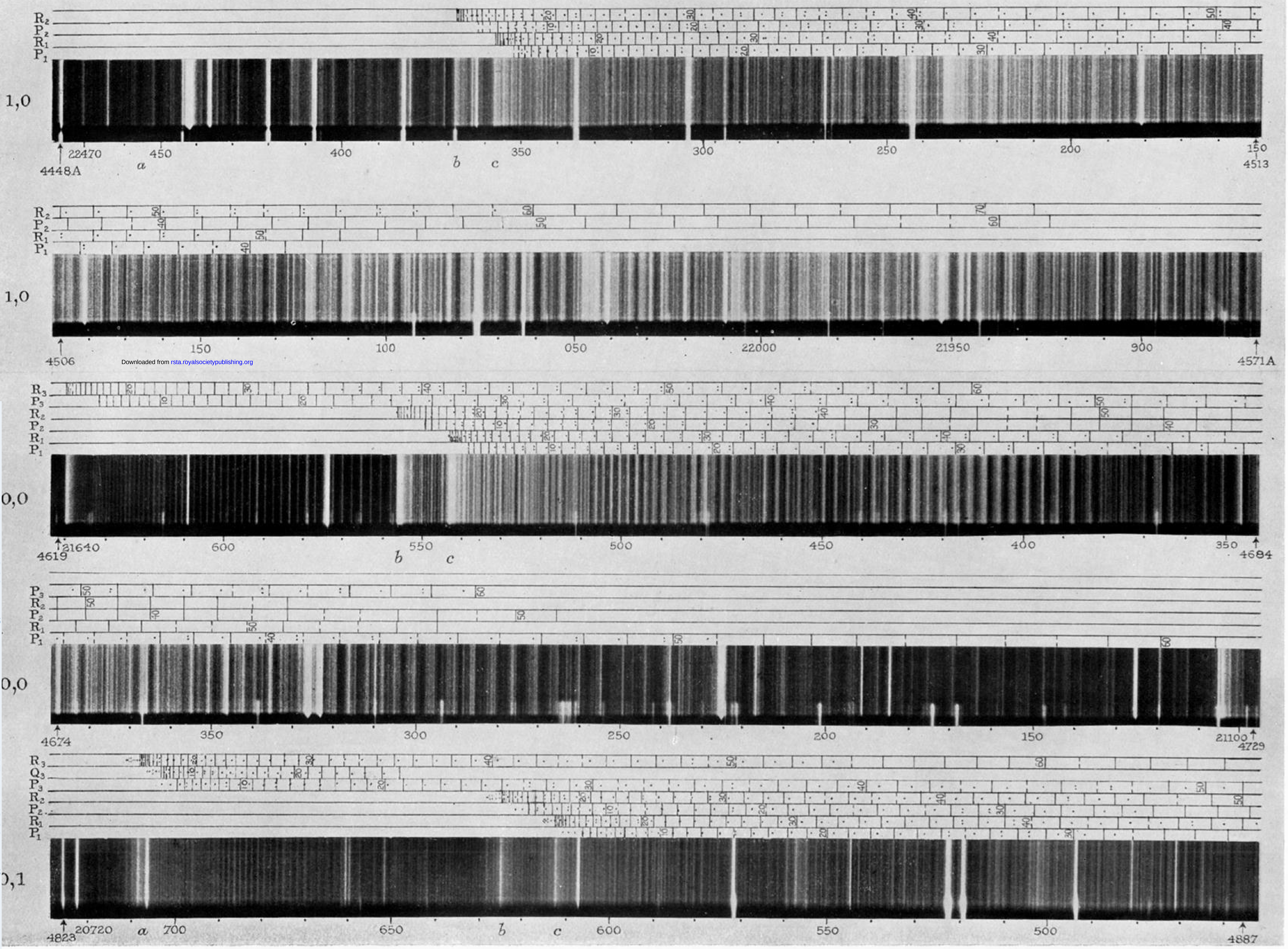

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