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QUANTUM ANALYSIS OF THE BLUE-GREEN BANDS OF TITANIUM OXIDE

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Abstract

Occurrence of the titanium oxide bands.—These bands form the most prominent characteristic of the *M* type stars, reaching their maximum intensity at the *M*8 type. They have been found by Fowler and others to be due to titanium oxide, and are usually referred to in the literature as TiO_2 bands. The spectrum of the titanium bands is made up of at least two systems, one in the blue-green region, with which this paper deals, and one in the yellow-red. As yet no quantum relations have been found between the heads in the latter region. The bands of both systems degrade to the red.

Frequency of heads and lines in the blue-green region of titanium oxide.—The spectrograms were taken by A. S. King of Mount Wilson Observatory. A table of frequencies is given for all the heads in this region, most of which have been remeasured by the writer, and also the quantum equation connecting these heads. The frequency of vibration for infinitesimal amplitude is found to be 833.31 and 1003.60 cm^{-1} for the upper (initial) and lower (final) states respectively. The heat of dissociation for the lower level, assuming a linear extrapolation, is 6.88 volts. This value is a very rough approximation. The vibrational analysis indicates that the molecule in question is titanium monoxide. Tables of frequencies of the lines and samples of their combination differences are given for the (0, 0), (0, 1) and (1, 0) bands. No perturbations have been observed. All these bands have triple heads designated *a*, *b*, and *c*, respectively.

Quantum analysis of the band spectrum of TiO.—Each band is composed of three *R* and three *P* branches. The combination principle is verified for the above three bands over a region of about 90 lines. Quantum numbers have been assigned to the lines of the various branches. No *Q* branches have been observed, indicating that we are dealing with transitions between two similar electronic levels. The necessary relations between the rotational and vibrational energy states are found to hold for the R_a and P_a branches only. Empirical formulas are given in the form of fifth degree equations for the branches of the three bands investigated.

Molecular constants of the TiO molecule.—The moments of inertia of the TiO molecule for infinitesimal rate of rotation are found to be 56.72×10^{-40} and 51.89×10^{-40} g. cm² for the initial and final states respectively. The nuclear separation for the initial (upper) state is 1.693×10^{-8} cm and for the final state 1.619×10^{-8} cm. The constants in the assumed law of force of the molecule in the form $F=K_1(r-r_0)+K_2(r-r_0)^2+K_3(r-r_0)^3+\cdots$, are evaluated.

Multiplicity of lines.—Although the triplet separation of the lines of the various branches is irregular, the relative values of the combination differences is that to be expected from a transition between two triplet electronic levels. The total quantum number *j* is found to be a half integer. This and the fact that we are dealing with triplets indicates that the emitter is neutral TiO. The transitions involved are assumed to be $^3P-{}^3P$, although the analysis is not sufficient to distinguish these from $^3D-{}^3D$ etc. The application of the Hill and Van Vleck formulas published recently, shows that these bands represent Hund's case *a*. The magnetic interaction constant *A* is found to be about 70 cm^{-1} for both the initial and final states, assuming *P* levels. If the levels are *D* or *F*, then *A* will be one half or one third as great.

INTRODUCTION

THE dominant characteristic of the spectra of the *M* type stars is the so-called Antarian group of bands, which has been shown by Fowler[1,2] to be due to an oxide of titanium. Most of the low temperature stars[3] show these bands,[4] faint in type *K*5 but steadily increasing through *M*0 to *M*8, in which they are exceedingly strong. They appear in some of the *S* type stars, but in none of the *R* or *N* type. They have been found also in sunspots.[5] According to King,[6] the temperature of the furnace at which the Antarian bands are most intense is about 2500°C, a value which checks very roughly with the stellar temperature of the *M* type stars. The first visual observations on these bands were made as early as 1884 by Vogel[7] and Duner.[8] Both gave the wave-lengths of ten heads from the spectrum of α Herculis. The most complete measurements, up to 1903, had been made by Stebbins[9] from stellar photographs of five stars, α Herculis, ρ Persei, β Pegasi, α Orionis and α Ceti, and by Sidgreaves[10] from the spectrum of o Ceti.

In 1904, A. Fowler[1] noted the similarity of the Antarian bands, both in structure and relative intensity, to those appearing in the spark spectrum of titanium oxychloride and in the arc spectrum of titanium oxide. Using either of these two sources, he was able to get all the bands listed by the above four investigators. He could not determine, however, whether those obtained in the laboratory were due to the chloride or the oxide of the metal. In 1906, Fowler passed a discharge through a vacuum tube filled with $TiCl_4$ vapor and found, at different portions of the tube, the line spectrum of the metal, and a group of bands due presumably to a chloride of titanium. These bands are composed of a complicated cluster of flutings, fading toward the violet, and are never found among the Antarian bands. When the tube was partially filled with dry N_2 or dry H_2, similar results were obtained. The same bands came out strongly in the arc spectrum of $TiCl_4$, burning in an atmosphere of dry N_2. In this last case, the Antarian bands also appeared, but since O_2 was presumably present as impurity, this cannot be taken as evidence against their oxide origin. It was found that the Antarian bands were quite intense in both the arc spectrum of metallic titanium in air, and in that of titanium oxide.

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[1] A. Fowler, Proc. Roy. Soc. **A73,** 219 (1904).

[2] A. Fowler, Proc. Roy. Soc. **A79,** 509 (1907).

[3] The stellar sequence splits at the *K* type into three branches, viz., *K-M*, *K-S*, and *K-R-N*. The first contains the titanium bands, the second both titanium and zirconium bands, the third the Swan bands.

[4] H. N. Russell, etc. "Astronomy" **2,** 520, 605, 771, 861.

[5] Hale and Adams, Astrophys. J. **25,** 75 (1907).

[6] A. S. King, Astrophys. J. **43,** 341 (1916).

[7] Vogel, "Beabachtungen zu Bothkamp" **1,** 20, etc.

[8] Duner, "Sur les Etoiles a Spectres de la Troisieme Classe." K. Sven. Vet.-Akad. Hand. **21,** No. 2 (1884).

[9] J. Stebbins, Lick Observatory Bull., No. 41 (1904).

[10] Sidgreaves, Monthly Notices, R. A. S. **58,** 344 (1898); **59,** 509 (1899).

The necessity for the presence of O_2 in the production of these bands is shown by King's[6] photographs, as well as by the plates he furnished to the writer. The line spectrum of the metal appeared, but no bands, when the electric furnace containing titanium was operated either in vacuo or with air at atmospheric pressure. When, however, oxygen was passed through the furnace, the Antarian bands appeared with intensity directly dependent upon the amount of O_2 present. The spectrum could be changed at will from a complete line to a strong band spectrum by regulating the amount of O_2 going through the furnace.

There is, moreover, astrophysical evidence[4] which indicates that the Antarian bands are due to a chemical compound of titanium and oxygen. The Swan bands, as already noted, are characteristic of the *K-R-N* stellar sequence. The concensus of opinion at present is that the Swan bands are due to some unoxidized carbon molecule such as C_2. Hence the Swan bands should appear in a reducing atmosphere, and the Antarian bands, assuming they are due to an oxide, in an oxidizing atmosphere. This would account for the remarkable fact that the two groups of bands never appear together in the same stellar spectrum.

In his later paper, Fowler[2] published photographs, obtained with a prism spectrograph, covering the region from $\lambda 4353$ to $\lambda 7198$. He measured 99 heads, subheads and maxima, maxima being regions of high intensity within a band, possibly the superposition of a number of lines. Measurements of heads obtained either in the laboratory or in stars and sunspots have been published by Fiebig, Hale, Evans, Eder and Valenta, Exner and Hascheck, and Hagenbach and Konen.[11] An inspection of the previously published spectrograms containing the titanium oxide bands, indicates immediately that these include probably at least two different systems, one lying in the blue-green and the other in the yellow-red, with a small overlapping region. The quantum analysis to be presented later confirms this, the blue-green bands forming a definite system showing all the regularities to be expected on the basis of the present theory of molecular structure. No quantum relations among the yellow-red bands have as yet been found. The bands of both systems degrade to the red.

When the present work was started, no relations, either empirical or theoretical, had been found among the various heads of the titanium oxide bands. The only work on the structure of individual bands was that of Fiebig,[12] who photographed portions of the band system in the first order of a large Rowland grating. The dispersion was sufficient to bring out the individual lines composing the bands and Fiebig accordingly attempted a fine structure analysis of the two bands $\lambda 5167$ and $\lambda 6149$. He separated a large number of lines of the former band into six series and of the latter into four series. He found that the second differences did not remain constant for any series of either band and so concluded that Deslandres' law was not satisfied.

[11] H. Kayser, Handbuch der Spectroscopie **6**, p. 706.

[12] P. Fiebig, Z. wiss. Phot. **8**, 73 (1910).

This paper[13] has two objects. The first is to obtain the vibrational quantum analysis of the bands composing the blue-green system. In order to do this more accurately, new measurements have been made of the individual band heads. The second is to use the bands λ5166.8, λ5448.2, and λ4954.6 in obtaining the fine structure analysis of this system. These three bands, as will be shown later, have the $n'-n''$ values (0,0), (0,1), and (1,0).[14] The more important constants of the molecule have thus been evaluated with a high degree of accuracy, and certain theoretical relations have been deduced.

MEASUREMENTS OF PLATES

Spectrograms in this work were taken by A. S. King at Mount Wilson Observatory in the first and second order of a 15 foot concave grating. The dispersion of the first order is 3.722A per mm. As a source of emission King used the electric furnace, the iron arc and the carbon arc. The best results were obtained by all these methods when a good supply of oxygen was present. The atomic spectrum of titanium, which has numerous lines in the region of the three bands investigated, is very weak in the furnace spectrograms. Unfortunately, second order furnace plates with good intensity could not be obtained, since the furnace burned out when it ran for a considerable period. The measurements for the fine structure analysis, therefore, had to be made from second order arc plates containing numerous intense atomic titanium lines, and these proved to be troublesome. The heads of bands for the vibrational structure analysis have been measured from first order furnace plates. All measurements were made on a 200 mm Gaertner comparator,[15] were converted to wave-numbers (cm^{-1}) and corrected to vacuum. For standards, Fe and Ti lines have been used, the latter taken from Behner's[16] work. Sixty-five heads and about 1930 lines have been measured, the latter lying between λ5539 and λ4955. It is estimated that for the most part the measured wave-numbers of the clear lines are accurate to within 0.02 cm^{-1}.

The plates just described were taken especially for this work, and the writer wishes to extend his sincere thanks to Dr. A. S. King for this material, and for the continued interest which he has shown in the investigation.

EMPIRICAL ANALYSIS OF BANDS

Fiebig[12] concluded that Deslandres' law, i.e., constant second differences, did not hold for his series. This is not surprising, for the present theory indicates that rather complex expressions are needed for the accurate representation of the individual series in a band. The main objection, however,

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[13] Preliminary results of this work are given by R. T. Birge and A. Christy, Phys. Rev. **29**, 212 (1927); A. Christy and R. T. Birge, Nature **122**, 205 (1928).

[14] The nomenclature used in this paper is that of the National Research Council Bulletin "Molecular Spectra in Gases" Vol. 11, part 3, 1926. Henceforth, this will be referred to as "Report."

[15] This comparator was purchased with a grant made to R. T. Birge from the Rumford Committee of the American Academy of Arts and Sciences.

[16] K. Behner, Zeits. wiss. Phot. **23**, 326 (1925).

to Fiebig's analysis is that the extrapolated values of the heads of his series do not agree with the observed heads. Moreover, within a given series, the second differences change abruptly in value. Hence, in this work, a completely new empirical analysis of the bands has been made. An examination of the spectrograms show that these bands seemingly have none of the distinguishing characteristics which may serve as an opening for an attempt at an empirical analysis. The origins of the bands are not at all evident. It is not even apparent whether the bands have double or triple heads. Most of the separate lines in the neighborhood of each head are themselves blends, as can be seen clearly from their structure. Moreover, numerous intense atomic titanium lines overlap not only band lines but also certain heads.

It was found, however, that at a considerable distance from the real head of a band, and before the next band of the sequence became perceptible, there are forty or fifty lines which seem to be fairly well separated. Eight or ten of these lines appeared to belong to one series. Accordingly their first differences were plotted on a large scale, and if found to vary linearly, this group of lines was taken as the working basis for a series, which was then extended in both directions. After a considerable number of lines had thus been placed in one series, there was obtained a least squares representation of the series in the form of a third degree polynomial.[17] The observed minus calculated values were plotted and were then examined to find whether any sharp break occurred which would indicate that there had been a jump from one real series to another. If no such break was evident the equation was extrapolated in an endeavor to get new observed lines. A new equation was then obtained, based upon both the old and the new lines, and the process was repeated, working mainly toward the head. The operation was continued until the various series composing one band were found to be so badly interlaced that it was thought inadvisable to proceed further. By such methods *six* series were separated in each of the three bands already mentioned. It was necessary in the case of certain series to pass as many as five least squares solutions. Usually third degree equations were sufficient to account for all the lines in a series, with an average observed minus calculated value of 0.05 cm^{-1}. In spite of this rigorous analysis, the results were not entirely correct, as was discovered when the combination principle was finally found. Owing to the close parallelism of all series in a band, and to the presence of numerous blends, it was possible to jump from one series to another without the least squares solution showing a noticeable break.

On extrapolation, the heads of the six series fell, within the experimental error, on the three apparently real heads of each band, here designated a, b, c, two series falling on each. The difference between the real heads a and b is about 2 cm^{-1}, that between a and c 10 cm^{-1}. The extrapolated heads of four of the six series were uncertain, due to the proximity of a and b, and to the great extent of the extrapolation.

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[17] R. T. Birge and J. D. Shea, "A Rapid Method for Calculating the Least Squares Solution of a Polynomial of any Degree" Univ. Calif. Pub. Math. **2**, 67 (1927).

The identification of the several series as R, P, or Q branches presented another difficulty. The bands of titanium are strikingly similar to the bands of the α group of BO,[18] and to Baldet's[19] photographs of the Comet Tail bands, both of which have been interpreted as due to a $^2S-^2P$ electronic transition. Such bands, according to present theory, should contain at least six strong branches, two R, two P and two Q. The relative distribution of intensity in the series of the titanium bands did not, however, conform to the expected theoretical distribution. As far as could be determined visually, there was no appreciable difference in the appearance of the various series within a band. Since the relative intensity of an R to a P branch or an R to a Q, is a function of the temperature as well as of j, one would anticipate that in a furnace, where the temperature is supposedly different from that of the arc, the strength of these two branches would be altered. When two such plates were compared, the intensity of the branches was found to be apparently the same in both plates. Thus the correct allocation of the series as R, P or Q branches was not possible until after the combination principle had been established.

VERIFICATION OF THE COMBINATION PRINCIPLE[20]

a. Vibrational energy levels. In 1926 King[21] extended the titanium bands from λ4353, where Fowler's spectrograms end, to λ4085. In this region the heads are not sharply defined, but using a registering microphotometer, he determined ten maxima, and gave their wave-lengths. On the basis of measurements by Fowler, Fiebig and King, Birge and Christy[13] found combinations between the bands of the blue-green region which satisfied the expected quantum equation,[22]

$$\nu_0=\nu_e+(\omega_0'n'-\omega_0'x'n'^2+\cdots)-(\omega_0''n''-\omega_0''x''n''^2+\cdots) \tag{1}$$

where ν_0 is the frequency of the origin of the band; ν_e the frequency of the origin of the (0,0) band of the system; ω_0 the frequency of vibration of the molecule for zero rotation and infinitesimal amplitude of vibration, according to the interpretation of the older quantum theory; n the vibrational quantum number; and $x=(3/2+15b/2+3c/2+15b^2/4)h/4\pi^2I_0\omega_0$, b and c are constants of the assumed law of force of the molecule. I_0 is the moment of inertia of the molecule for no vibration and infinitesimal rate of rotation. Using only data previously published, Eq. (1) was evaluated and published as[13]

$$\nu=\left.\begin{matrix}19350.0\\19340.0\end{matrix}\right\}+(833.1n'-4.5n'^2)-(1003.5n''-4.5n''^2) \tag{2}$$

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[18] F. Jenkins, Proc. Nat. Acad. Sci. **13,** 496 (1927).

[19] F. Baldet, Comp. rend. **180,** 821 (1925).

[20] Equations used in this and the following sections are taken from the Report.

[21] A. S. King, Publ. Astron. Soc. Pacific, **38,** no. 223, 1 (1926).

[22] All these equations are based on the older form of the quantum theory. In the new mechanics the energy levels necessarily remain the same, but their interpretation is slightly different.

Since then, 49 heads belonging to 26 bands have been re-measured by the writer, from King's plates, and the following equation has been obtained from these new measurements,

$$\nu = \left.\begin{matrix}19349.34\\19347.44\\19338.61\end{matrix}\right\} + (833.31n' - 4.546n'^2) - (1003.60n'' - 4.519n''^2) \tag{3}$$

TABLE I. *Blue-green system of the titanium bands.*

$n'-n''$		λ_{air} (I.A.)	ν_{vac} (cm^{-1})		$O-C$ (cm^{-1})
1–4	*b*	6159.1	16231.7	*F,f*	−0.50
2–5	*c*	6214.9	16085.9	*F,f*	+4.50
3–6	*a*	6268.0	15949.7	*F,f*	+0.20
5–8	*b*	6383.9	15660.0	*F*	−0.80
0–2	*a*	5758.55	17360.67		+0.46
1–3	*a*	5809.98	17206.95		−1.26
2–4	*a*	5861.72	17055.11		−0.62
0–1	*a*	5448.34	18349.12		−1.13
	b	48.86	347.37		−0.99
	c	51.32	339.19		−0.34
1–2	*b*	5497.07	18186.46		−0.62
3–4	*c*	5597.7	17859.4	*F,f*	+3.80
0–0	*a*	5166.86	19348.74		−0.60
	b	67.36	346.84		−0.60
	c	69.30	339.61		+1.00
3–3	*b*	5307.73	18835.22		−0.08
4–4	*c*	5358.89	18655.37		−1.65
1–0	*a*	4954.55	20177.83		−0.28
	b	55.09	176.65		+0.45
	c	56.85	168.49		+1.11
2–1	*a*	4999.47	19996.58		−2.16
	b	99.83	995.08		−1.96
	c	5002.53	984.31		−3.70
2–0	*a*	4761.17	20997.40		−0.38
	b	61.64	995.33		−0.65
	c	64.34	983.41		−3.64
3–1	*a*	4804.34	20809.71		+0.43
	b	04.70	807.11		−0.27
	c	07.28	795.97		−2.58
4–2	*a*	4847.47	20623.57		+2.84
	c	50.39	611.14		+1.14
5–3	*a*	4892.75	20432.72		+0.60
	b	93.21	430.80		+0.58
	c	95.12	422.81		+1.42
3–0	*a*	4584.06	21808.61		+0.25
	b	84.43	806.87		+0.41
	c	86.91	795.05		−2.58
4–1	*a*	4626.11	21610.38		−0.39
	b	26.40	609.04		+0.17
5–2	*a*	4668.64	21413.54		+0.41
	b	69.01	411.84		+0.61
	c	71.11	402.23		−0.17
6–3	*c*	4713.92	21207.84		+0.98
7–4	*a*	4756.09	21019.73		+2.12
	b	56.65	017.36		+1.58
	c	58.76	008.02		+1.08
4–0	*a*	4421.58	22610.03		+0.19
	c	23.88	598.26		−0.86
5–1	*a*	4462.53	22402.52		−0.64
6–2	*c*	4505.90	22186.93		+1.23
7–3	*c*	4548.11	21981.00		+2.09
8–4	*a*	4589.34	21783.32		+0.52
5–0		4270	23412.6	*K*	+10.40
6–1		4315	23168.5	*K*	−7.20
7–2	*c*	4351.79	22962.59		+2.68
8–3	*c*	4395.26	22745.40		+1.37
9–4	*b*	4436.3	22534.9	*F*	+0.77
6–0		4135	24177.0	*K*	+3.80
7–1		4174	23951.1	*K*	+1.40
8–2		4224	23723.8	*K*	−1.20
9–3		4254	23500.7	*K*	+0.60
9–2		4085.3	24471.1	*K*	−10.00

Notes:
F = Fowler's measurements (converted to I.A.)
f = Fiebig's measurements (converted to I.A.)
K = King's measurements in I.A.

This differs from the preceding mainly in assuming a triple, instead of a double head for each band. The former equation omitted the middle head. Columns 1, 2 and 3 of Table I give the quantum assignations, the wavelength and the frequency of the heads of all bands which have been measured up to the present time. Those measured by Fowler, Fiebig or King, and not by the writer, are followed by the letters *F*, *f* or *K* respectively. The measurements given by the first two investigators are in Rowland units and have been converted to I.A. Column 4 gives the observed minus calculated values obtained from Eq. (3). The average *O-C* of the bands measured by the writer is 1.00 cm^{-1}. The large deviations shown by some bands are due primarily to two causes. First, because of the proximity of the heads in a band, the measurements could not be made very accurately. Second, the above equation refers to the heads of bands, while, theoretically, the origins should be used; this alone would introduce certain discrepancies. The wavelengths of the heads, or rather, of the maxima in the photometric curve given by King, are expected to be only approximate. An excellent low dispersion photograph of practically the entire spectrum of the titanium oxide molecule has been published by A. Fowler.[2]

Since the bands of this system thus show the usual relations for a diatomic molecule, and since we have already seen that the emitter must be some oxide of titanium, it follows that the molecule must be TiO or TiO^+. To decide between these two alternatives, we need the fine structure analysis of individual bands.

n' \ n''	0	1	2	3	4	5	6	7	8
0	7	7	4						
1	6		5	4	10′				
2	5	3			4	8′			
3	3	5		3	10?		4′		
4	1-	4	3		7				
5		1	3	2					3′
6			1	2					
7			1=	1	1				
8				1=	1				
9					1=				

Fig. 1. Intensities of bands of the blue-green system of titanium oxide. The intensity of (3, 4) band is doubtful as it is overlapped by a band head of the yellow-red system.

The titanium monoxide system of the blue-green region consists of eleven sequences, containing 39 bands, the intensity of which follows roughly Condon's[23] theoretical distribution, shown in Fig. 1. The intensities given therein are estimated from visual observations made by the writer from the plates measured, and from a comparison with those given by Fowler. The prime (′) indicates that the estimate is based upon Fowler's observations alone.[24]

One of the most interesting deductions that can be made from a set of vibrational energy data concerns the heat of dissociation of the molecule. In the present case the coefficients of n'^2 and n''^2, in Eq. (3), are quite uncertain. Hence the extrapolation of the $\omega_n:n$ curve, by the method of Birge and Sponer,[25] is very doubtful. It cannot even be said definitely that this curve is linear over the region covered by the data. If, however, we assume Eq. (3) the linear extrapolation for the *lower* level gives 6.88

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[23] E. Condon, Phys. Rev. **28**, 1182 (1926).

[24] King does not give the intensity of the heads he has measured.

[25] Birge and Sponer, Phys. Rev. **28**, 259 (1926).

volts as the heat of dissociation. We do not wish to place any emphasis on this result.

There is a marked difference in appearance between the bands of the above system and those of the yellow-red region. The former have three heads, all apparently of the same intensity, when the overlapping of series is considered. Those of the yellow-red region appear to have double heads, the outermost head having the greater intensity. The separation of the heads is about 19 cm^{-1}. As has been remarked before, we have been unable to find any quantum relations among these latter bands.

b. Rotational energy levels. When the combination principle was sought, the main obstacle encountered was that it was not possible, at first, to identify with any certainty the several series of each band as R, P, or Q branches. Moreover, the validity of assignation of the lines into their respective series was questionable, especially in the region toward the heads. It became necessary, therefore, to form all possible combinations of two series from the six of the (0,0) band, and compare the frequency differences thus obtained with those gotten from all possible combinations of some two series in the (1,0) band. Only such lines were used as were thought to belong unquestionably to the particular series assigned. This condition made the working portion of the series fairly short. No perturbations were found in any of the series as far as could be ascertained from the observed minus calculated values of their least squares equations. The spacing, as well as the overlapping of lines, is such that even if a perturbation existed its observation would be doubtful.

The lines of the R and P branches are given theoretically by

$$R(j)=\nu_0+F'(j+1)-F''(j) \tag{4}$$

$$P(j)=\nu_0+F'(j-1)-F''(j). \tag{5}$$

From Eqs. (4) and (5), it follows

$$R(j)-P(j)=F'(j+1)-F'(j-1)=2\Delta F'(j) \tag{6}$$

$$R(j-1)-P(j+1)=F''(j+1)-F''(j-1)=2\Delta F''(j). \tag{7}$$

Eqs. (6) and (7) may be taken as definitions of $2\Delta F'(j)$ and $2\Delta F''(j)$. Since $2\Delta F'(j)$ is a function of the initial state only, two bands having the same initial vibrational energy level should have identical values of $2\Delta F'$. Two bands having the same final level should have identical values of $2\Delta F''$. The molecular energy due to vibration and rotation of a simple molecule is assumed to be

$$E/hc=(E_n+E_m)/hc=E_n/hc+B_nm^2+D_nm^4+F_nm^6+H_nm^8+\cdots \tag{8}$$

For a non-vibrating molecule, one may write

$$F_m=E_m/hc=B_0m^2+D_0m^4+F_0m^6+H_0m^8+\cdots \tag{9}$$

Hence it follows that

$$2dF/dm=4B_0m+8D_0m^3+12F_0m^5+16H_0m^7. \tag{10}$$

Because of the necessary relations between the vibrational and rotational energy, it is known that[26]

$$D_0=-4B_0{}^3/\omega_0{}^2. \tag{11}$$

Each of the two pairs of series used in a given attempt to satisfy the combination principle were assumed to consist of an R and a P branch.[27] The following criterion was assumed in connection with the probable values of the expected $2\Delta F$. Mecke[28] has plotted the nuclear separation (r_0) of all known hydrides of various elements against the respective atomic number of the element. He found that the r_0 of the hydrides of the elements lying between He and Ne, Ne and A, A and Kr, fell respectively on three widely spaced lines, the lines of each group having somewhat different slopes. The nuclear separation for titanium hydride, according to this graph, should be 1.92×10^{-8} cm. The value of r_0 for titanium monoxide was estimated by comparing the value of the nuclear separation of the hydrides with that of the oxides. It was estimated to lie between 1.90 and 2.50×10^{-8} cm. Since $B_0=27.70\times10^{-40}/r_0{}^2\mu$, where μ is the reduced mass of the molecule, B_0 could be calculated, and thus finally the expected values of $2\Delta F$.

With these values in mind, the frequency differences obtained from any two series of the (0,0) band were compared with those from any two series of the (1,0) band. When two sets of values of $2\Delta F$ were obtained, one from each band, which were at least approximately equal, they were plotted on a large scale and from each graph B_0 and D_0 were evaluated. As has been remarked above, the working portions of the series were short, consequently many different frequency differences of the (0,0) band seemed to be the same as those of the (1,0) band. If, in addition, the D_0 obtained from the plot of any of the above sets agreed in sign and roughly in magnitude with the theoretical D_0 calculated from Eq. (11), then such a set of values was deemed a possibly correct $2\Delta F$. A number of the above frequency differences satisfied this additional condition. The pairs of series from which these sets of $2\Delta F$ were obtained were composed evidently of an R and a P branch and were in apparent agreement with Eq. (7). Such a pair of series of the (0,0) band were then shifted by two units with respect to each other in order to give the relation shown in Eq. (6), and were compared with an arbitrary pair of series of the (0,1) band. Here, however, no combination relations could be obtained. This failure indicated either that the above frequency differences were not the true $2\Delta F$ or that the lines of the (0,1) band had been incorrectly assigned to their respective series.[29] All attempts, however, to

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[26] Report p. 172.

[27] $R-Q$ and $Q-P$ combinations also were tried, but without any success.

[28] R. Mecke, Zeits. f. Physik **42**, 390 (1927).

[29] It was shown afterward that the original assignment of the lines in the (0, 1) band was correct.

TABLE II. *Frequencies of the lines of the (0, 0) band.*

$k-1/2$	$R_a(k)$	$P_a(k)$	$R_b(k+1)$	$P_b(k+1)$	$R_c(k-1)$	$P_c(k-1)$
14.		19320.39″				
15.	19348.43″	318.01″		19313.95		
16.	347.36″	315.56″		311.49	19338.83″	19308.32
17.	347.11″	312.99″	19344.63″	308.93	338.83″	305.89
18.	346.34″	310.28″	343.78″	306.24	338.01	303.42″
19.	345.50″	307.69″	343.00″	303.42″	337.42″	300.63″
20.	344.63″	304.78″	342.14″	300.63″	335.96″	298.05
21.	343.78″	301.90″	341.04″	297.66″	335.96″	295.68″
22.	342.58″	298.89″	339.85″	294.65	334.65″	292.45″
23.	341.49″	295.68″	338.83″	291.48	333.67	289.24″
24.	340.13″	292.45″	337.42″	288.29	332.58	286.26
25.	338.83″	289.24″	335.96″	284.87″	331.38″	283.05
26.	337.42″	285.84″	334.65″	281.54″	330.08″	279.85
27.	335.96″	281.41″	333.02	278.14″	328.87″	276.46
28.	334.26″	278.88″	331.38″	274.66″	326.99″	273.06
29.	332.58″	275.26″	329.59	270.84	325.76″	269.52
30.	330.78″	271.52″	327.76	267.00′	324.00′	265.89
31.	328.87″	267.62′	325.76″	263.20	322.26′	262.17
32.	326.99″	263.69″	323.77′	259.30	320.39″	258.35
33.	324.79″	259.63″	321.71	255.44″	318.51″	254.46
34.	322.67′	255.44″	319.50	251.04′	316.41″	250.45′
35.	320.39″	251.36′	317.19″	246.95″	314.30″	246.36′
36.	318.01″	246.95″	314.80	242.55″	312.26″	242.55″
37.	315.56″	242.55″	312.26″	238.11″	309.74″	238.11″
38.	312.99″	238.11″	309.74″	233.60″	307.40	233.60″
39.	310.28″	233.60″	307.12	299.08″	304.78″	229.08″
40.	307.69″	229.08″	304.32	224.38′	302.18	224.61′
41.	304.78″	224.23′	301.48	219.66	299.59	219.96″
42.	301.90″	219.33	298.53	214.79″	296.80	215.28″
43.	298.89″	214.41	295.68″	209.94″	293.94	210.43
44.	295.68″	209.38	292.45″	204.87″	290.96	205.53
45.	292.45″	204.27	289.24″	199.66″	287.88	200.54
46.	289.24″	199.07	285.84″	194.42″	284.87″	195.44
47.	285.84″	193.73	282.41″	189.06″	281.54″	190.20
48.	282.41″	188.36	278.88″	183.54″	278.14″	185.01
49.	278.88″	182.88	275.26″	178.25	274.66″	179.64
50.	275.26″	177.39	271.52″	172.68	271.52″	174.26″
51.	271.52″	171.64	267.79′	166.98	267.54′	168.65
52.	267.60′	165.86	263.91′	161.21	263.82′	163.00
53.	263.69″	160.00	260.01″	155.32	260.01″	157.26
54.	259.63″	154.04	256.03″	149.33	256.03″	151.46
55.	255.44″	148.03	251.71′	143.44	252.11′	145.51
56.	251.23′	141.88′	247.46″	137.19	248.03	139.51
57.	246.95″	135.63′	243.11	130.98	243.86	133.43′
58.	242.55″	129.33	238.66	124.63	239.56	127.20
59.	238.11″	122.91	234.14	118.20″	235.17	121.00″
60.	233.60″	116.40	229.48	111.63	230.67	114.51″
61.	228.66	109.80	224.76′	105.06	226.10	107.95″
62.	223.85	103.11	219.96″	098.44	221.46′	101.47
63.	218.95	096.46″	215.28″	091.66	216.68	094.81
64.	213.95	089.52″	209.94″	084.69	211.84	088.04
65.	208.86	082.53″	204.87″	077.70	206.86	081.20
66.	203.67	075.42″	199.66″	070.61	201.82	074.27
67.	198.43	068.26″	194.42″	063.51	196.70′	067.25″
68.	193.04	060.95″	189.06″	056.26′	191.44	060.08
69.	187.59′	053.67	183.54″	048.79	186.12′	052.85
70.	182.02	046.23	177.93	041.44	180.65	045.55
71.	176.36	038.72	172.27	033.89	175.15	038.15″
72.	170.63	031.06	166.50	026.22	169.53	030.55″
73.	164.76	023.35	160.62	018.51	163.77	022.99
74.	158.80	015.43″	154.66	010.68	158.00	015.43″
75.	152.79′	007.57″	148.60	002.74	152.10	007.57″
76.	146.66	18999.65″	142.42	18994.76	146.03	18999.65″
77.	140.41	991.61″	136.12′	986.79″	139.94	991.61″

TABLE II (*Continued*)

$k-1/2$	$R_a(k)$	$P_a(k)$	$R_b(k+1)$	$P_b(k+1)$	$R_c(k-1)$	$P_c(k-1)$
78.	19134.08′	18983.49″	19129.80	18978.45″	19133.74′	18983.49″
79.	127.65′	975.05	123.33	970.09″	127.43′	975.39
80.	121.00″	966.68	116.78	961.73″	121.00″	967.15
81.	114.51″	958.27	110.14	953.48″	114.51″	958.83
82.	107.95″	949.62	103.37	944.70	107.95″	950.37
83.	101.23″	941.00	096.46″	936.06	101.23″	941.79
84.	094.03	932.26	089.52″	927.22	094.40	933.15
85.	087.04	923.35	082.53″	918.36′	087.54	924.40
86.	079.91	914.46	075.42″	909.33	080.54	915.55
87.	072.70	905.40	068.26″	900.33	073.50	906.64
88.	065.37	896.29	060.95″	891.17	066.22	897.61
89.	057.95	887.06	053.42	881.92	059.12	888.47
90.	050.49	877.73′	045.85	872.56′	051.58	879.29″
91.	042.89	868.31′	038.15″	863.11	044.10	869.91″
92.	035.08	858.80	030.55″	853.74″	036.47	860.56
93.	027.29	849.15	022.65	843.99″	028.93″	851.05
94.	019.46	839.46	014.81	834.18″	021.04′	841.36
95.	011.45	829.68″	006.69	824.38	013.28	831.70
96.	003.44	819.72	18998.49	814.65″	005.22	821.90
97.	18995.12	809.73″		804.44″	18997.10	812.00″
98.	986.79″	799.77″	982.10	794.31″	988.88	802.00
99.	978.45″	789.41″		784.08	980.54	791.93
100.	970.09″	779.16	965.01	773.76	972.17	781.73
101.		768.69	965.50	763.30′	963.68	771.42
102.	952.78	758.21	947.72	752.85	995.10	761.01
103.	943.93	747.61	938.88	742.15	946.40	750.55
104.	935.00	737.00	929.91	731.50	937.66	740.03
105.	926.01′	726.17	920.95	720.84	928.71	729.26
106.	916.84	715.31	911.81	709.77	919.74	718.52
107.	907.68	704.36	902.53′	698.78	910.65	707.69
108.	898.38	693.31	893.21	687.73	901.43	696.70
109.	888.96		883.73		892.10	685.64
110.	879.29″		874.11		882.83	
111.	869.91″		864.54			
112.	860.10		854.70			
113.	850.34		844.95			
114.	840.50		834.93			
115.			824.85			
116.	820.26		814.65″			
117.	809.73″		804.44″			
118.	799.77″		794.31″			
119.	789.41″		783.60			
120.	778.67		772.98			
121.	768.08					
122.	757.26		751.48			
123.	746.38					
124.	735.49					

Notes.

(′) Calculated value; real line is overlapped by atomic titanium line.

(″) Blended line.

reassign the lines of this band in order to get combinations proved futile. It was thus found impossible to obtain within the limits of the assumed values of $2\Delta F$ any pair of series in the (0,0) band which simultaneously gave the proper combinations with both the (1,0) and (0,1) bands.

It was thought advisable, then, to drop the above criterion, and to determine whether it was at all possible to get any combination between the three bands, irrespective of the values of $2\Delta F$ obtained. Such combinations were finally found, after many trials and repeated correction of the series. It was now comparatively easy to extend the series almost up to the head. After the first two pairs of R and P branches in each band had been identi-

TABLE III. *Frequencies of the lines of the (0, 1) band.*

$k-1/2$	$R_a(k)$	$P_a(k)$	$R_b(k+1)$	$P_b(k+1)$	$R_c(k-1)$	$P_c(k-1)$
8.		18332.60				
9.		330.81″				
10.		328.98″				
11.		327.15″				18319.40
12.		325.15″				317.51″
13.		323.14″				315.53
14.		320.81				313.80″
15.	18348.78	318.53				311.26″
16.	348.36″	316.18				309.00
17.	348.36″	313.80″	18345.56	18310.02″	18339.50″	306.56″
18.	347.22″	311.26″	345.00″	307.39″	338.75	304.18″
19.	346.46′	308.59	344.22″	304.65″	338.17	301.82″
20.	345.85	305.92	343.41	302.07″	337.60	299.13″
21.	345.00″	303.15	342.54	299.13″	336.88′	296.44
22.	344.22″	300.26	341.53	296.24	336.11	293.71
23.	343.09	297.28	340.50	293.23	335.31″	290.54″
24.	342.02	294.28	339.50″	290.19	334.25″	288.02″
25.	340.79″	291.12″	338.17″	287.03	333.26	285.16″
26.	339.50″	288.02″	336.81′	283.79	331.98″	281.96″
27.	338.17″	284.62″	335.31″	280.43	330.81″	278.69″
28.	336.74′	281.27	333.95	277.08	329.56	275.43″
29.	335.31″	277.81	332.40″	273.53	328.17″	272.00″
30.	333.59	274.18	330.81″	269.99	326.66	268.55′
31.	331.98″	270.58	328.98″	266.32	325.15″	265.02′
32.	330.10	266.87	327.15″	262.57′	323.55″	261.33″
33.	328.17″	263.00	325.15″	258.76	321.67	257.66″
34.	326.25	259.14	323.14″	254.81	319.85″	253.83″
35.	324.20	255.10	321.18	250.83′	317.92	250.11
36.	322.11	251.08′	318.97	246.82″	315.99	246.07
37.	319.85″	246.82″	316.67	242.56″	313.80″	242.00
38.	317.51″	242.56″	314.42	238.37′	311.65	237.93
39.	315.10	238.35′	311.93	233.92″	309.42	235.92″
40.	312.65	233.92″	309.42″	229.54′	307.08″	229.40′
41.	310.02″	229.43′	306.56″	225.02′	304.65″	225.01′
42.	307.39″	224.84′	304.18″	220.48″	302.07″	220.48″
43.	304.65″	220.13	301.35	215.74′	299.50	216.00′
44.	301.82″	215.40	298.48	210.94	296.77	211.32
45.	298.91	210.44″	295.56	206.10	294.02	206.63
46.	295.87	205.59″	292.53	201.17	291.12″	201.83
47.	292.78	200.61″	289.66″	196.11	288.02″	197.08″
48.	289.66″	195.54″	286.28″	191.01	285.16″	191.94′
49.	286.28″	190.30	282.93″	185.82	281.96″	186.85
50.	282.93″	185.00	279.51″	180.53	278.69″	181.74
51.	279.51″	179.65	276.00″	175.18	275.43″	176.51
52.	276.00″	174.21	272.46′	169.70	272.00″	171.17
53.	272.37″	168.66	268.81	164.17′	268.58′	165.74
54.	268.67′	163.09	265.07′	158.71″	265.00′	160.46″
55.	264.86′	157.37″	261.33″	152.86″	261.33″	156.67″
56.	260.97	151.76″	257.33	146.97″	257.66″	148.90″
57.	257.01	145.71	253.33	141.08″	253.83″	143.26
58.	252.89	139.77	249.25	135.17′	249.82	137.41
59.	248.77	137.71	245.07	129.11′	245.77	131.49
60.	244.51	127.59″	240.76	123.03	241.63	125.51
61.	240.16	121.36	236.45	116.73′	237.46	119.39
62.	235.75	115.03	232.00	110.43	233.19	113.22
63.	231.26	108.67	227.49	104.07	228.78	106.91
64.	226.67	102.22″	222.82	097.56	224.32	100.55″
65.	221.93	095.61	218.10	090.96	219.74	094.16
66.	217.14	088.88	213.35	084.32	215.17	087.62
67.	212.31	082.17	208.51	077.51	210.44″	080.88″
68.	207.39	075.29	203.50	070.68	205.59″	074.22
69.	202.29	068.39′	198.38	063.73	200.61″	067.48
70.	197.08″	061.38	193.24	056.74	195.54″	
71.	191.95′	054.29′	188.01	049.64	190.53	

TABLE III (*Continued*)

$k-1/2$	$R_a(k)$	$P_a(k)$	$R_b(k+1)$	$P_b(k+1)$	$R_c(k-1)$	$P_c(k-1)$
72.	18186.66		18182.68		18185.31	
73.	181.23		177.29″		180.08	
74.	175.72		171.80		174.72	
75.	170.18		166.12		169.27	
76.	164.53		160.46″		163.70	
77.	158.71		154.67″		158.10	
78.	152.86		148.90		152.37	
79.	146.97		142.80		146.57	
80.	141.08		136.74		140.70	
81.	134.82		130.59		134.60	
82.	128.60		124.38		127.59	
83.	122.36″		118.04		122.36″	
84.	115.95″		111.62		115.95″	
85.	109.45		105.09		109.73	
86.	102.85		098.48″		103.29	
87.	096.19		091.80		096.73	
88.	089.35		085.05		090.11	
89.	082.69″		078.09″		083.37	
90.	075.60		071.13		076.51′	
91.	068.62′				069.55	
92.					062.58	
93.					055.46	

(′) Calculated value; real line is overlapped by atomic tiatnium line.
(″) Blended line.

fied, the wave-lengths of lines composing two theoretical Q branches were calculated. No lines could be found, at least in the clear portion of the bands, at the calculated positions. The remaining lines were finally shown to form an additional R and P branch. It was thus established that each band is composed of three R and three P branches, and these will be designated R_a, P_a, R_b, P_b, R_c, P_c. The three heads, a, b, c, are formed respectively by the three R branches. From a total of about 1930 lines measured in the three bands, 1235 have been assigned to the above branches, many of them being allocated to more than one branch. Of the remaining lines, a large number are due to other overlapping bands, a smaller number to atomic titanium. In addition, there are 34 lines still unassigned. Many of the latter are of such low intensity as to make their presence questionable, and some are due to impurities as shown by a comparison with the furnace spectrograms.

The values of $2\Delta F$ thus obtained were plotted as a function of a parameter k, so chosen that it is essentially zero when $2\Delta F$ is zero. In all cases k was found to be a half integer. The relation of k to the theoretical j is discussed in a later part of the paper. The frequency of the various lines of the (0,0), (0,1) and (1,0) bands is given in Tables II, III, and IV, Columns 2–7. The double prime (″) over the number indicates that this line is blended. The (′) indicates that it is overlapped by an atomic titanium line, the frequency listed being a calculated value. Column 1 gives the true k for the R_a and P_a branches. The true k for R_b and P_b is one unit greater, while that of R_c and P_c is one unit less. The reason for such numbering appears later. Fig. 2 shows enlargements of the (0,0) band made from one of the second

TABLE IV. *Frequencies of the lines of the (1, 0) band.*

$k-1/2$	$R_a(k)$	$P_a(k)$	$R_b(k+1)$	$P_b(k+1)$	$R_c(k-1)$	$P_c(k-1)$
14.	20176.85″	20148.90″	20174.17″	20144.41		20141.00″
15.	176.27″	146.53″	173.64″	141.90		138.90″
16.	175.62″	144.11″	173.06″	139.43		136.16′
17.	175.03″	141.00″	172.20″	136.60′	20165.92″	133.72″
18.	174.17″	138.46″	171.22″	133.72″	165.37′	131.09″
19.	173.06″	135.53	170.31	131.09″	164.49″	128.14″
20.	172.20″	132.52	169.24″	128.14″	163.57	125.37″
21.	171.22″	129.41	167.89″	124.89″	162.58″	122.49″
22.	169.87″	126.42	166.89″	121.61″	161.56	119.47″
23.	168.55	123.08	165.64′	118.48	160.53″	116.29″
24.	167.47″	119.73	164.06″	115.08	159.11″	113.06″
25.	165.92″	116.29″	162.58″	111.63	157.77	109.72″
26.	164.06″	112.82	160.82″	108.08	156.30′	106.29″
27.	162.58″	109.11	159.11″	104.43	154.68″	102.82′
28.	160.53″	105.41	157.28″	100.69	153.21″	099.17″
29.	158.67	101.58″	155.34	096.80	151.21″	095.40″
30.	156.68	097.63	153.21″	092.91	149.40″	091.65″
31.	154.68″	093.61′	151.21″	088.85	147.63″	087.59″
32.	152.37	089.50	148.90″	084.67	145.34″	083.80′
33.	150.06	085.25	146.53″	080.51	143.32″	079.69
34.	147.63″	080.96	144.11″	076.13	141.00″	075.51
35.	145.34″	076.53	141.56	071.68	138.90″	071.16
36.	142.56	071.98	138.90″	067.11′	136.25′	066.84′
37.	139.86	067.38′	136.23′	062.54″	133.72″	062.54″
38.	137.08	062.54″	133.44	057.84″	131.09″	057.84″
39.	134.17	057.84″	130.47	052.98″	128.14″	052.98″
40.	131.09″	052.98″	127.47	048.03″	125.37″	048.27
41.	128.14″	048.03″	124.32	042.93″	122.49″	043.45
42.	124.89″	042.93″	121.11′	037.90′	119.47″	038.47′
43.	121.61″	037.61′	117.87	032.66	116.29″	033.37
44.	118.13	032.27″	114.37	027.39	113.06″	028.23
45.	114.68	026.96″	110.93″	021.97	109.72″	022.94
46.	110.93″	021.53″	107.33″	016.46	106.29″	017.55
47.	107.33″	015.90	103.55″	010.90	102.66′	012.25″
48.	103.55″	010.11	099.70″	005.21	099.17″	006.55″
49.	099.70″	004.32	095.74″	19999.35	095.40″	000.73″
50.	095.74″	19998.39	091.65″	993.48	091.65″	19995.13′
51.	091.65″	992.43	087.59″	987.47	087.59″	989.32
52.	087.59″	986.41	083.44′	981.34″	083.55′	983.37
53.	083.12	980.20	079.24″	975.22″	079.24″	977.23
54.	078.73	973.93	074.69	968.85″	075.07	971.12
55.	074.22	967.44	070.18	962.42″	070.68	964.84′
56.	069.60	961.06	065.59	956.02′	066.26′	958.52″
57.	064.93	954.47	060.84	949.57″	061.78″	951.99″
58.	060.11	947.73	056.01	942.75″	057.08	945.34″
59.	055.23	940.96′	051.13	935.96′	052.31	938.83
60.	050.31	934.10	046.09	929.24″	047.44	932.04
61.	045.10	927.08″	040.97	922.06	042.50	925.23
62.	039.96	920.03	035.74	915.01′	037.43′	918.22
63.	034.61	912.83	030.42′	907.81	032.27″	911.25
64.	029.19′	905.48	024.99	900.55	026.96″	904.03′
65.	023.68	898.17	019.44	893.14′	021.53″	896.77
66.	018.05	890.69	013.87	885.65	016.13	889.45
67.	012.25″	883.11	008.08	878.04	010.54	882.01
68.	006.55″	875.42	002.24	870.46″	004.86	874.45
69.	000.73″	867.65	19996.33′	862.61	19999.11	866.78
70.	19994.59	859.82	990.30′	854.70	993.19	859.02
71.	998.46	851.78′	984.14	846.77	987.25	851.13′
72.	982.32	843.65	977.88	838.63″	981.34″	843.16
73.	975.94	835.50′	971.55	830.46	975.22″	835.12′
74.	969.56″	827.23″	965.11′	822.03	968.85″	827.23″
75.	963.04″	818.82′	958.52″	813.77	962.42″	818.69′
76.	956.42	818.40″	951.99″	805.28	955.79′	810.40″
77.	949.57″	801.83″	945.34″	796.70″	949.22	801.83″

TABLE IV (*Continued*)

$k-1/2$	$R_a(k)$	$P_a(k)$	$R_b(k+1)$	$P_b(k+1)$	$R_c(k-1)$	$P_c(k-1)$
78.	19942.75″	19793.19″	19938.29′	19787.94″	19942.75″	19793.19″
79.	935.85′	784.27	931.32	779.11″	935.65′	784.60
80.	928.75″	775.38	924.27	770.22	928.75″	775.82
81.	921.67″	766.43	917.08	761.20″	921.67″	766.91
82.	914.40′	757.28″	909.78	752.14″	914.57′	758.01
83.	907.18″	748.19	902.46	742.89″	907.18″	748.92′
84.	899.53	738.86′	894.92′	733.60′	899.99	739.74′
85.	892.00′	729.54″	887.43	724.23	892.54′	730.45
86.	884.21″	719.99	879.63	714.73	884.89	721.08′
87.	876.54	710.36″	871.81	705.07	877.28	711.58″
88.	868.63	700.64	863.95″	695.34	869.52	702.06
89.	860.69	690.88″	855.90	685.51	861.72	692.36
90.	852.57′	680.99	847.81	675.62	853.63	682.52
91.	844.35	670.99	839.56	665.44	845.59	672.68
92.	836.07′	660.84	831.22	655.46	837.46	662.73″
93.	827.65	650.67	822.69	645.27	829.14	652.52′
94.	819.14′	640.40″	814.20′	634.90	820.81	642.35
95.	810.40″	629.92″	805.52	624.46	812.27	632.06
96.	801.83″	619.40″	796.70″	613.92	803.46″	621.64
97.	793.19″	608.69″	787.94″	603.27″	794.84	611.19
98.	784.00	598.05	779.11″	592.52	785.97	600.47
99.	774.87	587.18	769.83	581.63	777.30	589.78″
100.	765.75	576.27	760.68″	570.79	768.02	578.94
101.	756.57	565.26		559.71″	758.90	567.93
102.	747.10	554.10	741.92′	548.41″	749.64′	556.93
103.	737.83	542.84	732.56	537.22″	740.27′	545.81
104.	727.96	531.49	722.77	525.82	730.79	534.53
105.	718.38	520.00	713.04′	514.32	721.20′	523.21
106.	708.52	508.46	703.25	502.71	711.58″	511.71
107.	698.72	496.77	693.25	491.05′	701.75	500.15
108.	688.61	485.05	683.25	479.23	691.78	488.53
109.	678.53	473.11	673.03	467.30	681.75	476.74′
110.	668.32	461.10	662.73″		671.66	464.83″
111.	657.90	448.99	652.33′		661.39	452.75
112.	647.43	436.86	641.98		651.01	440.76
113.	636.90		631.22″		640.40″	
114.	626.15		620.53		629.92″	
115.	615.39		609.72		619.40″	
116.	604.46		598.82		608.69″	
117.	593.50		587.75		597.59	
118.	582.36		576.64″		586.56	
119.	571.09				575.49	
120.	559.71″				564.18	

(′) Calculated value; real line is overlapped by atomic titanium line.
(″) Blended line.

order arc plates furnished by Dr. King. The measurements listed in the above tables were made from this plate. The heads of the band, as well as the lines of the various branches, are indicated. Every tenth line is numbered, the value given being equal to the value of $k-\frac{1}{2}$ listed in Table II The broken line in Fig. 3 is the plot of the difference between the two sets of $2\Delta F'$ obtained from the (0,0) and (0,1) bands, and the solid line is a similar plot of the difference in $2\Delta F''$. The rather large discrepancies shown by certain pairs of $2\Delta F$ are due to the fact that the lines of the R and P branches from which they are taken are blended, as indicated in Tables 2 to 4. Aside from the above irregular discrepancies, the combination principle is completely fulfilled.

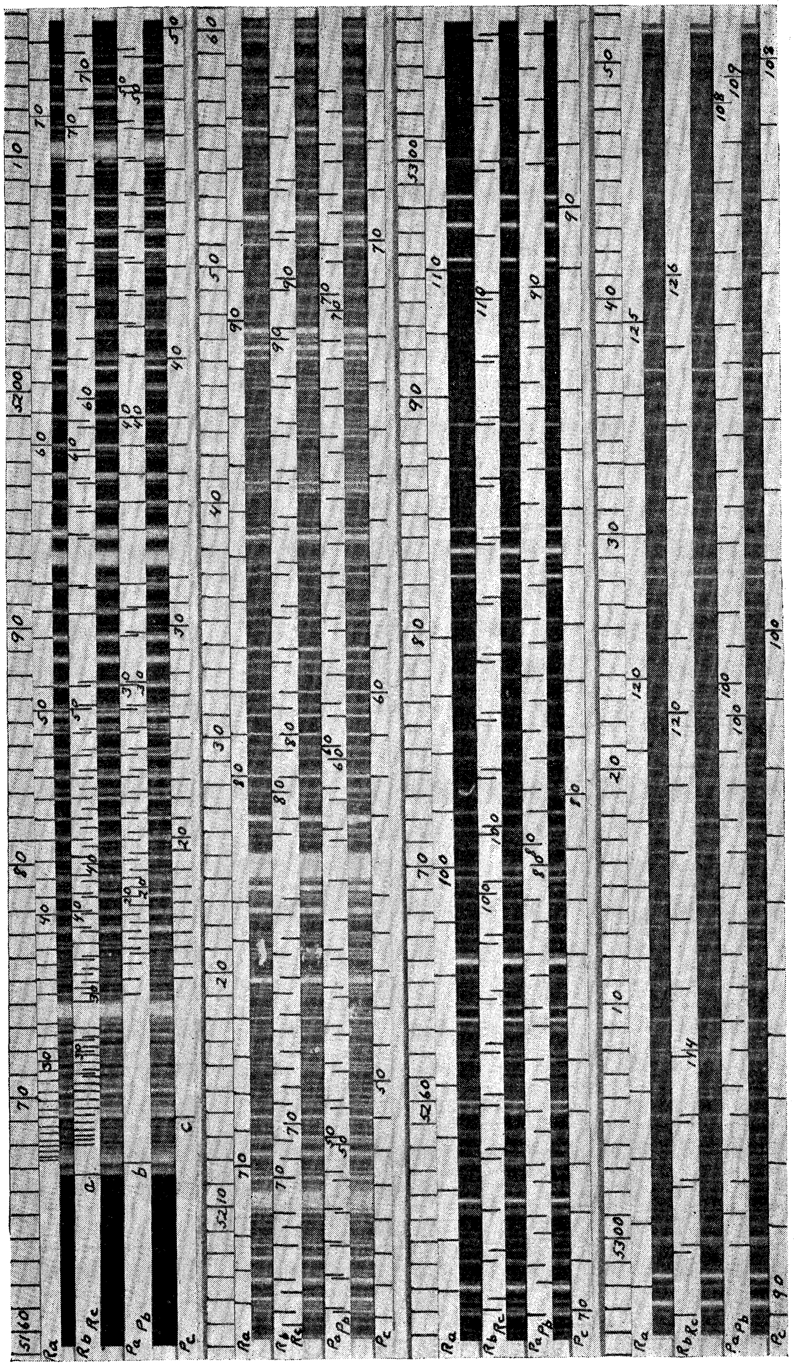

Fig. 2. (0, 0) band, λ5166.9, of TiO.

MOLECULAR CONSTANTS AND THEORETICAL CONCLUSIONS

Setting $m=k-\alpha$ in Eq. (10) and transferring from differentials into finite differences,[30] we get

$$2\Delta F=(4B_0+8D_0)(k-\alpha)+8D_0k^3+12F_0k^5+16H_0k^7 \tag{12}$$

We can neglect all powers of α higher than the first, since its value is usually found to be very small. From Eq. (12) we have

$$2\Delta F/k=(4B_0+8D_0)(1-\alpha/k)+8D_0k^2+12F_0k^4+16H_0k^6. \tag{13}$$

Plotting the value of $2\Delta F/k$ against k, and extrapolating the curve to $k=0$, we get the value of $(4B_0+8D_0)$. In doing this it is essential to start from a region where α/k is not effective. We can solve for D_0 by taking two points on the curve and hence get B_0. This is method two, or the graphical method of the Report.[31]

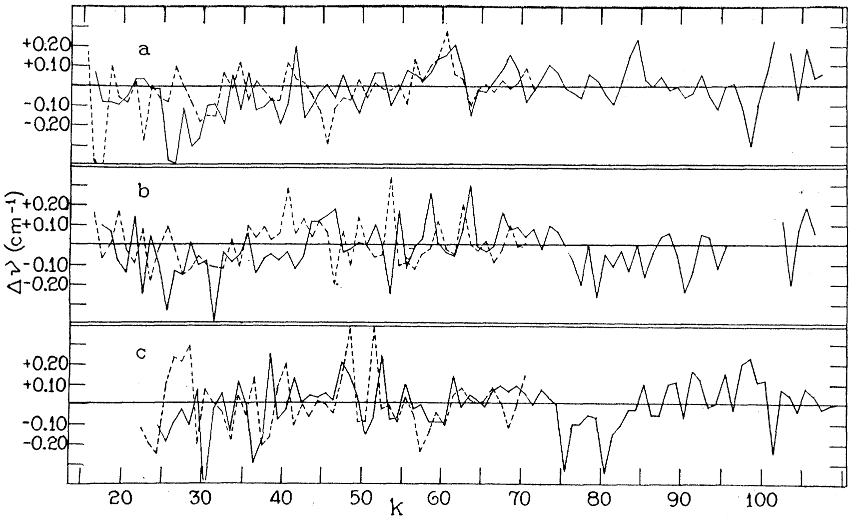

Fig. 3. Combination principle residuals for $2\Delta F$. Solid lines: $2\Delta F''$ (0, 0) $-2\Delta F''$ (1, 0), broken lines: $2\Delta F'(0, 0)-2\Delta F'(0, 1)$, for each of the three components a, b, and c.

Substituting B_0, as found above, into Eq. (11), we can solve for D_0 and compare this value with that found from the graph of $2\Delta F/k$. If the two values of D_0 agree, we can conclude that Eq. (13) and hence Eq. (12) will give us the true B_0 and the true moment of inertia of the molecule. If there is no such agreement, we may assume that the B_0 given by Eq. (12) involves, besides the true moment of inertia, other undetermined quantities. It was found in our case that of the six sets of $2\Delta F$ only $2\Delta F_a'$ and $2\Delta F_a''$ gave such an agreement. For the $2\Delta F_b$, the value of D_0 as obtained from Eq. (13) was 11 percent lower, and for the $2\Delta F_c$, 9 percent higher than that evaluated

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[30] Report, pp. 174 and 124.

[31] Report, p. 172.

from Eq. (11). The moment of inertia published previously[32] was calculated from the $2\Delta F_a/k$ curves.

A more accurate way of obtaining the constants involved in Eq. (12) is the analytical, or method three of the Report.[33] A quantity $2\Delta F^*$ is defined as:

$$2\Delta F^* = 2\Delta F - 8D_0k^3 - 12F_0k^5 - 16H_0k^7 = (4B_0 + 8D_0)(k - \alpha) \tag{14}$$

where $2\Delta F$ is the frequency difference as obtained from the actual R and P branches. This $2\Delta F^*$, as shown by Eq. (14), should be a linear function of k, unless α happens itself to be a function of k. A tentative value of B_0 can be obtained by the graphical method, and from Eq. (11), D_0 can be calculated. The value of F_0 is

$$F_0 = D_0^2(2 - \bar{\alpha}\omega_0/6B_0^2)/B_0 \tag{15}$$

where $\bar{\alpha}$ is defined by

$$\bar{\alpha} = (B_0 - B_n)/n \tag{16}$$

B_1 is necessary for the evaluation of $\bar{\alpha}$. However, Birge[34] has found, from a study of a large number of molecules, that

$$2B_0x/\bar{\alpha} = 1.4 \pm 0.2$$

thus giving a means of evaluating $\bar{\alpha}$ from other known constants. Substituting this value of $\bar{\alpha}$ in Eq. (15), we can calculate F_0. Its order of magnitude is 10^{-13}, affecting the value of $2\Delta F^*$ only for very large values of k. H_0 may be neglected. Performing the operations indicated in Eq. (14), values of $2\Delta F^*$ were calculated. It was found in every case that the resulting $2\Delta F^*$ could be satisfactorily represented as a linear function of k, thus proving that α in Eq. (14) is constant. The situation is thus similar to that found by Pomeroy[35] in the case of AlO bands. B_0 and α were then evaluated, using the method of least squares. The new B_0 was inserted into Eq. (11) and a new D_0 calculated. This value was found to differ from the older one by only 0.2 percent. Therefore, if the new value of D_0, and hence F_0, were substituted in Eq. (14) it would not appreciably alter the values of $2\Delta F^*$.

For $2\Delta F_1$, an equation similar to (12) was assumed to hold. D_1 was evaluated from the expression given by Kemble,[36]

$$D_n = D_0 + \bar{\beta}n \tag{18}$$

the value of $\bar{\beta}$ in the form given by Pomeroy[35] being:

$$\bar{\beta} = (2 - 4H_0B_0^2/D_0^3 + 9B_0^2F_0^2/2D_0^4)12B_0^4/\omega_0^3 \tag{19}$$

B_1 was initially calculated, as before, from the $2\Delta F_1/k$ curve. F_1 was assumed to be the same as F_0. The error involved in this assumption is considerably

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[32] A. Christy and R. T. Birge, Nature **122,** 205 (1928).

[33] Report, p. 173.

[34] R. T. Birge, Phys. Rev. **31,** 919 (1927).

[35] W. C. Pomeroy, Phys. Rev. **29,** 59 (1927).

[36] E. C. Kemble, J. Optical Soc. Am. **12,** 1 (1926).

below the experimental error. B_1 differs from B_0 by 0.7 percent and D_1 from D_0 by 0.2 percent. F_1, therefore, differs from F_0 by an amount presumably less than 0.2 percent but even if the difference were considerably larger, the error involved in $2\Delta F^*$ would be negligible. By the methods described in the above paragraphs, B_1, α_1, and D_1 were calculated.

The values of $2\Delta F_a$ from which all constants have been calculated were obtained from smoothed R_a and P_a branches. Generally fifth degree polynomials were required to represent all the lines of these branches from about $k=20.5$ to 108.5. The average observed minus calculated value is 0.04 cm^{-1}. Therefore, the uncertainty in the values of $2\Delta F$ should be $0.04\sqrt{2}=0.06$ cm^{-1}. The equations are:

$$(0,0)\quad R_a\,\nu=19{,}344.052-96.998\times10^{-2}k-459.292\times10^{-4}k^2+4.499\times10^{-6}k^3-0.481\times10^{-8}k^4+2.528\times10^{-10}k^5 \tag{20}$$

$$P_a\,\nu=19{,}345.628+113.314\times10^{-2}k-404.574\times10^{-4}k^2+93.675\times10^{-6}k^3+77.254\times10^{-8}k^4+26.993\times10^{-10}k^5 \tag{21}$$

$$(1,0)\quad R_a\,\nu=20{,}172.066-107.414\times10^{-2}k-532.950\times10^{-4}k^2-65.141\times10^{-6}k^3-53.572\times10^{-8}k^4-12.257\times10^{-10}k^5 \tag{22}$$

$$P_a\,\nu=20{,}174.380+108.560\times10^{-2}k-455.647\times10^{-4}k^2-56.100\times10^{-6}k^3+43.980\times10^{-8}k^4+16.287\times10^{-10}k^5 \tag{23}$$

$$(0,1)\quad R_a\,\nu=18{,}345.337-79.862\times10^{-2}k-435.242\times10^{-4}k^2+3.729\times10^{-6}k^3 \tag{24}$$

$$P_a\,\nu=18{,}342.771+85.916\times10^{-2}k-469.246\times10^{-4}k^2-45.565\times10^{-6}k^3+4.600\times10^{-8}k^4+25.660\times10^{-10}k^5. \tag{25}$$

These equations are purely empirical and no theoretical significance should be attached to them. They are not expected to hold, and undoubtedly do not hold, for values of k less than 20.5. The final values of the constants follow:

$B_0'=0.488361$ cm^{-1} $\qquad$ $B_0''=0.533775$ cm^{-1}

$D_0'=-6.7092\times10^{-7}$ cm^{-1} $\qquad$ $D_0''=-6.0397\times10^{-7}$ cm^{-1}

$F_0'=8.612\times10^{-14}$ cm^{-1} $\qquad$ $F_0''=2.575\times10^{-13}$ cm^{-1}

$H_0'=-1.512\times10^{-18}$ cm^{-1} $\qquad$ $H_0''=-4.624\times10^{-18}$ cm^{-1}

$\alpha_0'=+0.0225$ $\qquad$ $\alpha_0''=-0.0220$

$B_1'=0.485088$ cm^{-1} $\qquad$ $B_1''=0.531020$ cm^{-1}

$D_1'=-6.7126\times10^{-7}$ cm^{-1} $\qquad$ $D_1''=-6.1636\times10^{-7}$ cm^{-1}

$\alpha_1'=+0.0209$ $\qquad$ $\alpha_1''=+0.0070$

$\bar{\alpha}_1'=B_0'-B'_1=+0.003723$ cm^{-1} $\qquad$ $\bar{\alpha}_1''=B_0''-B_1''=+0.002755$ cm^{-1}

$\bar{\beta}'=-0.0034\times10^{-7}$ cm^{-1} $\qquad$ $\bar{\beta}''=-0.1239\times10^{-7}$ cm^{-1}

$I_0'=(56.72\pm0.03)\times10^{-40}$ g.cm^2 $\qquad$ $I_0''=(51.89\pm0.03)\times10^{-40}$ g.cm^2

$r_0'=1.693\times10^{-8}$ cm $\qquad$ $r_0''=1.619\times10^{-8}$ cm.

It is estimated that the values of B and hence I are correct to 0.06 percent, and D to 0.30 percent. The values of α, however, are questionable, and it is quite possible that the true value of α' and α'' is zero. In fact this assumption may be made without altering the resulting values of B and D.

In the development of the quantum theory it has been assumed that the law of force of a molecule may be represented by:

$$F=K_1(r-r_0)+K_2(r-r_0)^2+K_3(r-r_0)^3+\cdots \tag{26}$$

where K_1, K_2, and K_3 are known functions of ω_0, x, B_0, and $\bar{\alpha}$. These functions may be found in the Report.[37] The values of K resulting from the use of these equations are

$K_1'=4.877\times10^5$ dyne.cm^{-1} $\quad$ $K_1''=7.074\times10^5$ dyne.cm^{-1}

$K_2'=-1.256\times10^{14}$ dyne.cm^{-2} $\quad$ $K_2''=-1.719\times10^{14}$ dyne.cm^{-2}

$K_3'=1.480\times10^{22}$ dyne.cm^{-3} $\quad$ $K_3''=1.596\times10^{22}$ dyne.cm^{-3}.

The values of $2\Delta F$ obtained from both the initial and final levels make it evident that we are dealing with triple electronic levels in both the initial and final states. These, in turn, according to the views of Mulliken,[38] Birge,[39] Hund,[40] and others, indicate that the molecule has an even number of electrons. If these bands had been found to have double electronic levels, it would have indicated TiO^+ as the probable emitter. Under the circumstances the only possible conclusion is that the actual emitter is *neutral* TiO.

It should be noted that the nuclear separation of TiO ($r_0''=1.619\times10^{-8}$ cm) is surprisingly small,[41] and is in fact much less than the minimum predicted value, 1.90×10^{-8} cm. The value of r_0 for titanium hydride as obtained from Mecke's graph is 1.92. Thus r_0'' for TiO is 11 percent less than that of the hydride, a difference much greater than that shown by the few elements whose oxides and hydrides have been investigated. We may conclude, therefore, that TiO is a firmly bound molecule, and we shall expect it to have a comparatively high heat of dissociation.

MULTIPLICITY OF LINES

A band which corresponds to an electronic transition from a single to a triple electronic level will have three R and three P branches. The lines of these three R or P branches normally occur in such a way as to give clearly defined triplets. These are called natural triplets.[42] Such triplets also normally occur as a result of transitions between two triple electronic levels, the second positive group of nitrogen being a well-known example of such a band system. In this case, however, certain complications may

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[37] Report p. 235.

[38] R. S. Mulliken, Phys. Rev. **26**, 561 (1925), and subsequent papers.

[39] R. T. Birge, Nature **117**, 300 (1926).

[40] F. Hund, Zeits. f. Physik **36**, 657 (1926), and subsequent papers.

[41] Compare HO, 0.979; BO, 1.207; CO, 1.15; NO, 1.15; AlO, 1.618. These values are taken from Birge, Int. Crit. Tables, Vol. V, pp. 409-.

[42] Report, Chap. IV, Sect. 5D.

enter, due to the complexity of both levels. According to the theory of complex diatomic molecules advanced by Hund,[40,43,44,45] and developed by Mulliken,[46,47,48,49] Kemble,[50] and others, the total spin vector s may be quantized either with respect to σ_k, Hund's case a, or with respect to j_k, case b. σ_k is the component of the electronic orbital momentum K, along the internuclear axis about which K precesses, while j_k is the vector sum of the rotational momentum of the nuclei m, and of σ_k. In case a, the quantized component of s along σ_k is designated σ_s, while in case b, the quantized component of s along j_k is simply s. Such a type of multiplicity of the electronic levels arises from the fact that s can set itself in various ways with respect to σ_k or to j_k. In atoms, it will be recalled, the multiple character of the level is due to the quantization of a vector s, representing the resulting spin of all the electrons with respect to a vector l, representing the resultant orbital momentum of the atom. The vector sum of s and l, denoted by j, represents the total momentum of the atom (all quantities being in Bohr units of momentum, $h/2\pi$). For a doublet level, j has two possible values, for a triplet, three, etc. The character of a level, S, P, D, $\cdots$, depends upon the value of l, being 0 for S, 1 for P, 2 for D, etc. In molecules the character of the level depends upon the value of σ_k, $\sigma_k=0$ for S, 1 for P, 2 for D, etc. For a triplet level such as ^3P, we have $s=1$, and σ_s or $s=\pm 1$ or 0. The various levels therefore are given by j_k+1, j_k-1, j_k+0, or σ_k+1, σ_k-1, σ_k+0. Kemble[50] has shown that case a corresponds to a small B/A and small m, while case b corresponds to a large B/A or large m, or both where B has its usual meaning $h/8\pi^2 I$, and A is the magnetic interaction constant defined as follows. If the angle between s and σ_k is θ, then the magnetic energy of s and σ_k is given by $U(\theta)=Ah\cos\theta$. It is clear therefore that for any given molecule, whether we are dealing with case a or case b will depend upon the moment of inertia of the molecule and also upon its magnetic interaction constant.

Heretofore the custom has been to plot the natural triplet separation of the R and P branches as a function of k. However, since the separation between the three R or P branches is a function of both the initial and final levels, if both are triplets a more or less complicated graph may result. This is the situation in TiO, the bands showing no clear-cut triplets, and when an attempt is made to plot this separation a very irregular graph is obtained. In fact, R_a, which is the central R branch for moderate and high values of k, becomes the violet branch as it nears the origin and thus forms the outermost head. On the other hand, an examination of the $2\Delta F$ values, samples of which are given in Tables V and VI, shows that for both initial and final

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[43] F. Hund, Zeit. f. Physik **40**, 742 (1927).

[44] F. Hund, Zeits. f. Physik **42**, 93 (1927).

[45] F. Hund, Zeits. f. Physik **43**, 805 (1927).

[46] R. S. Mulliken, Phys. Rev. **29**, 637 (1927).

[47] R. S. Mulliken, Phys. Rev. **30**, 138 (1927).

[48] R. S. Mulliken, Phys. Rev. **30**, 785 (1927).

[49] R. S. Mulliken, Phys. Rev. **32**, 388 (1928).

[50] E. C. Kemble, Phys. Rev. **30**, 387 (1927).

states $2\Delta F_b(k+1)$, $2\Delta F_a(k)$, and $2\Delta F_c(k-1)$ form close regular triplets. The Swan bands and those of the second positive group of nitrogen show the same regularities. This triplet separation is plotted for both the initial and final states of the (0,0) band of TiO, in Figs. 4 and 5. For comparison the same type of graph is given for the (0,0) band of the second positive

TABLE V. *Combination differences of the (0, 0) and (0, 1) bands, for small, medium and large values of k.*

$k-1/2$	(0, 0) $2\Delta F_a'(k)$	(0, 1) $2\Delta F_a'(k)$	(0, 0) $2\Delta F_b'(k+1)$	(0, 1) $2\Delta F_b'(k+1)$	(0, 0) $2\Delta F_c'(k-1)$	(0,1) $2\Delta F_c'(k-1)$
17	34.12	34.56	35.70	35.54	32.94	32.94
18	36.06	35.96	37.54	37.61	34.59	34.57
19	37.81	37.87	39.58	39.57	36.79	36.35
20	39.85	39.93	41.51	41.34	37.91	38.47
21	41.88	41.85	43.38	43.41	40.28	40.44
44	86.30	86.42	87.58	87.54	85.43	85.45
45	88.18	88.47	89.58	89.46	87.34	87.39
46	90.17	90.28	91.42	91.36	89.42	89.29
47	92.11	92.17	93.35	93.55	91.34	90.94
48	94.05	94.12	95.34	95.27	93.13	93.22
66	128.25	128.28	129.05	129.03	127.55	127.55
67	130.17	130.14	130.91	131.00	129.44	129.56
68	132.09	132.10	132.80	132.82	131.36	131.37
69	133.92	133.90	134.75	134.65	133.27	133.13
70	135.79	135.70	136.49	136.50		

TABLE VI. *Combination difference of the (0, 0) and (1, 0) bands, for small, medium and large values of k.*

$k-1/2$	(0, 0) $2\Delta F_a''(k)$	(1, 0) $2\Delta F_a''(k)$	(0, 0) $2\Delta F_b''(k+1)$	(1, 0) $2\Delta F_b''(k+1)$	(0, 0) $2\Delta F_c''(k-1)$	(1, 0) $2\Delta F_c''(k-1)$
18	39.42	39.50	41.21	41.11	38.20	37.78
19	41.56	41.65	43.15	43.08	39.96	40.00
20	43.60	43.65	45.34	45.42	41.74	42.00
21	45.74	45.78	47.49	47.63	43.51	44.10
22	48.10	48.14	49.56	49.41	46.72	46.29
45	96.61	96.60	98.03	97.91	95.52	95.51
46	98.72	98.78	100.18	100.03	97.68	97.47
47	100.88	100.82	102.30	102.12	99.86	99.74
48	102.96	103.01	104.16	104.20	101.90	101.93
49	105.02	105.16	106.20	106.22	103.88	104.04
73	155.20	155.09	155.82	155.85	154.10	154.11
74	157.19	157.12	157.88	157.78	156.20	156.53
75	159.15	159.16	159.90	159.83	158.35	158.45
76	161.18	161.21	161.81	161.82	160.49	160.59
77	163.17	163.23	163.97	164.05	162.54	162.60
103	215.78	215.71	216.22	216.10	215.07	215.11
104	217.76	217.83	218.04	218.24	217.14	217.06
105	219.69	219.50	220.14	220.06	219.14	219.08
106	221.65	221.61	222.17	221.99	221.02	221.05
107	223.53	223.47	224.08	224.02	223.04	223.05

group of nitrogen, using the data of Hulthén and Johansson,[51] and for the (0,0) Swan band (due probably to C_2), using Johnson's[52] data. These plots have the advantage of being functions of one state only, and as will be shown later certain theoretical relations can be deduced from them. The series of points labelled S, plotted near each vertical axis, are obtained from the expression $S=2\Delta F_a(k)-\{2\Delta F_b(k+1)+2\Delta F_c(k-1)\}/2$, while the other series of points, T, are obtained from $T=\{2\Delta F_b(k+1)-2\Delta F_c(k-1)\}/2$. For convenience these graphs will be referred to as S and T, respectively. As will be observed from the above expressions, S represents the amount by which the central $2\Delta F$ deviates from the mean of the two outer $2\Delta F$ with which it forms a natural triplet, while T represents half the difference of the two outer $2\Delta F$. For the (0,0) band of TiO, the writer has attempted unsuccessfully to express T as a function of $1/k$ or $1/k^2$. The resulting deviations are very large. Finally a least squares solution in the form of a polynomial was passed through T, and the following empirical equations were obtained for the initial and final states, respectively,

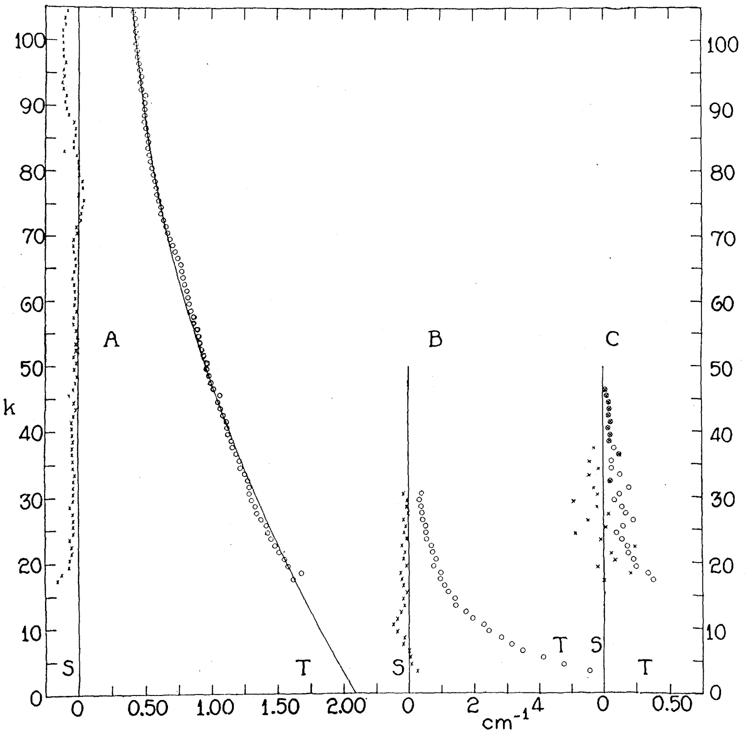

Fig. 4. Initial states. Difference between the various components of $2\Delta F'$ for (A) TiO, (B) N_2, (C) C_2.

$$T'=2.10-0.0290k+0.000123k^2 \tag{27}$$

$$T''=2.46-0.0282k+0.000110k^2. \tag{28}$$

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[51] Hulthén and Johansson, Zeits. f. Physik **26**, 308 (1924).

[52] R. C. Johnson, Trans. Roy. Soc. London, **A226**, 157 (1926).

In the bands of the three molecules, TiO, N_2, and C_2, $2\Delta F_a$ is the central $2\Delta F$, while $2\Delta F_b$ and $2\Delta F_c$ are the two outermost ones.

The problem now is to determine what theoretical significance may be attached to the graphs designated S and T. According to Kemble,[50] the energy of any level is made up of two parts, a kinetic energy which is proportional to m^2, and a magnetic energy, due to the orientation of s, which is proportional to $A \cos \theta$. Mulliken[48,49] in two recent papers discusses at some length the spacing of doublet electronic states for both case a and case b. Using F_1 and F_2 to represent the two members of each double level, he shows that in case b (A small) the energy of two corresponding levels $F_1(j+1)$ and $F_2(j)$ is the same. (The magnetic energy of two such levels is almost zero, and the kinetic energy is the same since both have the same value of j_k, and hence m. See reference 48.) For low values of j, on the other hand, the energy difference of these two levels may be comparatively large. In case a (A large) even at high values of j the energy difference between the two corresponding levels just mentioned is considerable. The same results may be obtained for the corresponding cases of triplet electronic states, the three corresponding levels being $F_1(j+1)$, $F_2(j)$, and $F_3(j-1)$. The nomenclature here adopted for triplets is analogous to that used by Mulliken[48] for doublets, in that F_1 refers to the parallel position of s and j_k in case b,

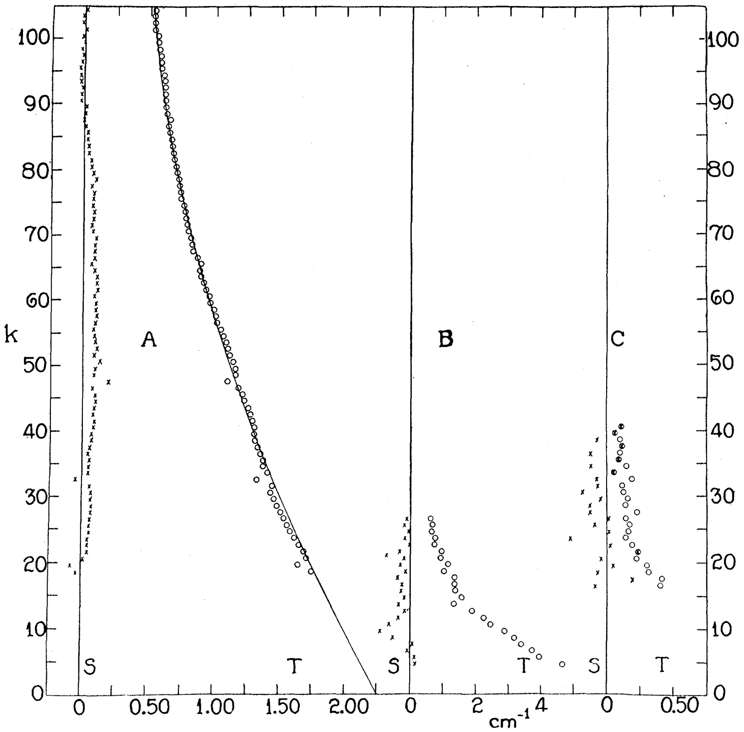

Fig. 5. Final states. Difference between the various components of $2\Delta F''$ for (A) TiO, (B) N_2, (C) C_2.

while F_3 refers to the anti-parallel position. As one passes from case *b* to case *a*, the parallel position of *s* and j_k changes to a parallel or anti-parallel position of *s* and σ_k, according to whether one has, in case *a*, inverted or normal triplets, but such a level will be called F_1, whether one has case *b*, case *a*, or an intermediate case. The relations found above for the *energies* will obviously apply also to the *energy differences* $2\Delta F_1(j+1)$, $2\Delta F_2(j)$, and $2\Delta F_3(j-1)$. The rate of approach of $2\Delta F_3(j-1)$ to $2\Delta F_1(j+1)$ as j increases and one approaches case *b* will be fairly rapid for small A and, conversely, fairly slow for large A. From Figs. 4 and 5, we see that the slope, dk/dT, is inversely proportional to the rate of approach of $2\Delta F_c$ to $2\Delta F_b$. Assuming for the moment that the empirically designated $2\Delta F_b(k+1)$ corresponds to $2\Delta F_1(j+1)$ and $2\Delta F_c(j-1)$ to $2\Delta F_3(j-1)$,[53] it follows that dk/dT should be large when A is large conversely.

A comparison of the three plots shows that the value of T, for the same k, is least for C_2, greater for N_2, and greatest for TiO. As k increases from zero, T becomes zero in both the former molecules for only moderate values of k, while in TiO, even at $k=104.5$, the separation is still 0.45 cm^{-1}, a quantity greater than the experimental uncertainty. The slope dk/dT is less for N_2 and greater for TiO.[54] The fact that $T=\{2\Delta F_b(k+1)-2\Delta F_c(k-1)\}/2=0$, need not indicate that case *b* (defined by $F_b(k+1)=F_c(k-1)$) has been reached. The data obtained from the spectra give directly *differences* of terms and not the actual terms. It may well happen then that $T=0$, within experimental error, but $F_b(k+1)\neq F_c(k-1)$. However, as already mentioned, dk/dT increases with A. With this as a criterion, we may conclude that the TiO bands, having a relatively large dk/dT, represent a good case *a*, and the second positive group of N_2, with a small dk/dT, a good case *b* at least for large values of k.

In a recent article, Hill and Van Vleck[55] have derived, on the new quantum mechanics, formulas applicable to case *a* for triplet electronic levels. They also suggested a method by which case *b* can be derived. They found it impossible because of algebraic difficulties, to obtain formulas representing the gradual transition from case *a* to case *b*. Fortunately, the TiO bands represent a good case *a*, for which formulas have been derived. The equations as given by the above writers corresponding to the levels for which $\sigma_s=1,\ 0,\ -1$, are as follows:

$$\sigma_s=-1,\quad F_1(j)=-A\sigma_k+B\{j(j+1)-\sigma_k^2+2\sigma_k\} -2B^2\{j(j+1)-\sigma_k(\sigma_k-1)\}/\sigma_k A \tag{29}$$

$$\sigma_s=0,\quad F_2(j)=B\{j(j+1)-\sigma_k^2+2\}+4B^2/A \tag{30}$$

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[53] This statement anticipates the proof of the correspondence given in a later part of this section.

[54] Unfortunately the data on the Swan bands for low values of j are poor, hence the slope cannot be safely determined. It should also be noted that the scale of T for nitrogen is four times as small as for the other two molecules, so that the relations between the two values of dk/dT, as just stated, are not so evident from the graph.

[55] Hill and Van Vleck, Phys. Rev. **32**, 261 (1928).

$$\sigma_s=1, \quad F_3(j)=+A\sigma_k+B\{j(j+1)-\sigma_k^2-2\sigma_k\}$$
$$+2B^2\{j(j+1)-\sigma_k(\sigma_k+1)\}/\sigma_k A. \tag{31}$$

By the definitions of F_1, F_2, F_3, previously given, the nomenclature of the above equations refers to normal case *a*. For inverted case *a*, A is negative, and F_3 refers to $\sigma_s=-1$, while F_1 refers to $\sigma_s=+1$. All other symbols are the same as those used previously, except that j is the new quantum j, and is half a unit less than the old. We have seen that the natural triplets are given by $F_1(j+1)$, $F_2(j)$, and $F_3(j-1)$.

From the above equations, we get

$$2dF_1(j+1)/dj=2\Delta F_1(j+1)=2B(2j+3)-4B^2(2j+3)/\sigma_k A \tag{32}$$
$$2dF_2(j)/dj=2\Delta F_2(j) \quad =2B(2j+1) \tag{33}$$
$$2dF_3(j-1)/dj=2\Delta F_3(j-1)=2B(2j-1)+4B^2(2j-1)/\sigma_k A \tag{34}$$

and

$$\{2\Delta F_1(j+1)-2\Delta F_3(j-1)\}/2=T=4B(1-B/\sigma_k A)-(8B^2/\sigma_k A)j \tag{35}$$

The slope of the curve is

$$dj/dT=-\sigma_k A/8B^2 \tag{36}$$

If we are dealing with case *a* and normal triplets, A is a fairly large positive quantity. The term $B/\sigma_k A$ is negligible in comparison with unity, and $8B^2/\sigma_k A$ must be very small, especially in our case where $B^2=0.2385$. Eq. (35) thus shows that T should be a positive quantity, and the slope dj/dT a large negative quantity.

A comparison of Eq. (35) with our graphs of $\{2\Delta F_b(k+1)-2\Delta F_c(k-1)\}/2$ for TiO shows that $\{\Delta F_1'(j+1)-\Delta F_3'(j-1)\}$ corresponds to $\{\Delta F_b'(k+1)-\Delta F_c'(k-1)\}$ and $\{\Delta F_1''(j+1)-\Delta F_3''(j-1)\}$ corresponds to $\{\Delta F_b''(k+1)-\Delta F_c''(k-1)\}$. It follows then, that irrespective of the relation of k to j,

$$\sigma_s'=\sigma_s''=-1 \text{ for } \Delta F_b$$
$$\sigma_s'=\sigma_s''=+1 \text{ for } \Delta F_c$$
$$\sigma_s'=\sigma_s''= \ \ 0 \text{ for } \Delta F_a$$

and the triplet levels in T*iO* represent therefore case *a*. By a graphical method $\sigma_k A$, of Eq. (35) was found to be about 70 cm^{-1} for for both the initial and final states. This value is only approximate and for the initial state may be somewhat less. A schematic representation of the energy levels, assuming $^3P-{}^3P$ transitions, and of the first lines of the R and P branches, is given in Fig. 6. Each rotational level, as will be shown later,should be an unresolved doublet.

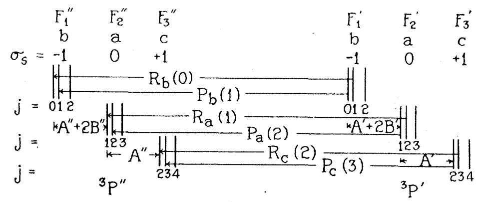

Fig. 6. Schematic representation of the energy levels of TiO, for a $^3P-{}^3P$ transition.

Equations (32), (33) and (34) may be rewritten as

$$2\Delta F_1(j+1)=4B(1-2B/\sigma_kA)j+6B-12B^2/\sigma_kA=4B_1j+\text{const.} \qquad (37)$$

$$2\Delta F_2(j)=4Bj+2B=4B_2j+\text{const.} \qquad (38)$$

$$2\Delta F_3(j-1)=4B(1+2B/\sigma_kA)j-2B-4B^2/\sigma_kA=4B_3j+\text{const.} \qquad (39)$$

defining B_1, B_2, and B_3. The value of B as found from Eq. (39), for the TiO bands, should be about 1.5 percent greater than the true B $(=B_2)$ calculated from Eq. (38); that of Eq. (37) should be 1.5 percent less. It is found that the calculated value of B from the $2\Delta F_c$ curves is 1.0 percent too high, that from the $2\Delta F_b$ curves is 1.2 percent too low. This seems to be additional evidence that the interpretation given above is correct.[56]

The only apparently contradictory feature in these results develops when we consider the graph of $S=2\Delta F_a(k)-\{2\Delta F_b(k+1)+2\Delta F_c(k-1)\}/2$ which should correspond to $2\Delta F_2(j)-\{2\Delta F_1(j+1)+2\Delta F_3(j-1)\}/2$. This quantity as calculated from the formulas of Hill and Van Vleck is

$$S=8B^2/\sigma_kA\,. \qquad (40)$$

Substituting the values of B^2 and $A\sigma_k$, we get $8\times 0.2385/70=0.03$ cm^{-1}, a value well within the experimental error of the work. S' and S'' as shown by the graph are not constant. This may be explained by the fact that for high values of j we do not have a strict case a, to which the theoretical formulas apply. Nevertheless, S' is definitely negative and considerably less than S'' which in turn is definitely positive, apparently a rather serious discrepancy. In the derivation of their formulas, however, Hill and Van Vleck did not consider any powers of j greater than the second. The omission of higher terms of j and the fact that we are dealing with a slow transition from case a to case b, may explain the differences between the observed and the calculated S.

CHARACTERISTICS OF THE LEVELS

On the basis of Hund's theory, the normal state of TiO may be any of the following,[57] ^3S, ^3P, ^3D, ^3F, ^3G. In order to identify the character of the electronic level associated with a band system, it is necessary to determine just what lines are missing, in the vicinity of the origin. In the case of the TiO bands, as well as in the case of the Swan and N_2 bands already discussed, it is quite impossible to do this, due to the blending of all lines in the vicinity of the origin. In the previous section, the value of the product of σ_kA was found and not the value of either σ_k of A singly. However, if we cannot determine σ_k, we can determing $\Delta\sigma_k$.

It has been shown definitely that no long Q branches exist. If there are any so near the origin as not to be separable, they must be extremely short. Mulliken[58] has shown that for case a and $\Delta\sigma_k=0$, the relative intensity of an R to a Q branch is proportional to j^2. In our case, considering the intensities of the R branches, those of the Q should be practically zero. This seems to

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[56] It has been remarked previously that D_c was found to be greater than, and D_b less than, D_a. However, the theoretical equations are not sufficiently developed to make possible comparisons between the various values of D.

[57] The writer is indebted to Prof. R. S. Mulliken for information on this point.

[58] R. S. Mulliken, Phys. Rev. **29**, 391 (1927).

indicate that for the TiO bands $\Delta\sigma_k = 0$. Furthermore, for S states case b occurs even for low values of j, regardless of the magnitude of A. Since we are dealing obviously with case a, at least when j is small, σ_k must be greater than zero, and the possible transitions are ${}^3P - {}^3P$, ${}^3D - {}^3D$, etc. The same situation holds in the case of the Swan and N_2 bands, which are commonly designated as ${}^3P - {}^3P$ transitions. In a previous publication[32] the bands of TiO were tentatively designated as ${}^3P - {}^3P$. Until other data are found proving that this is incorrect the designation may be retained. Eq. (12) which, as has been shown before, holds for both the initial and final $2\Delta F_a$, may be written as

$$2\Delta F = 4B_0 k + 8D_0 k + 8D_0 k^3 + \cdots - 4B_0\alpha - 8D_0\alpha. \tag{61}$$

We have found that α may be put equal to zero without affecting the results obtained, and at any rate, α is a very small quantity, about 0.02. Comparing Eq. (41) with Eq. (33) and recalling that k was found to be a half integer, we see that $k = j + 1/2$, or $j = k - 1/2$. j is in terms of the new quantum mechanics. For TiO, the new j should be an integer, and half a unit less than the j (or k) of the old quantum mechanics. The above relation, $j = k - 1/2$, is in harmony with these conclusions.

The previous analysis thus shows that the bands of TiO are made up of branches involving transitions ${}^3P_0 - {}^3P_0$, ${}^3P_1 - {}^3P_1$, ${}^3P_2 - {}^3P_2$. This is in complete agreement with Hund's[40] prediction that the strong branches should be those for which $\Delta\sigma_s = 0$. We would expect, however, six additional branches in each band, due to σ-type doubling. This doubling occurs whenever $\sigma_k > 0$, and is caused by the splitting of each rotational level into two. Hund,[44] Hulthén,[59] and Kronig[60] have shown that two such levels have for "eigenfunktionen" two Ψ's, one of which is symmetrical and the other antisymmetrical, and that they alternate in relative position in each pair of levels. Both Hund and Kronig have found that for $\Delta\sigma_k = 0$, we may have transitions only between a symmetrical (s) and an antisymmetrical (a) level. Therefore the lines of each of the R and of the P branches should be close doublets, the components of each doublet corresponding to $s - a$ and $a - s$ transitions, respectively. The value of $R_{sa}(j) - R_{as}(j)$ would be the difference between the rotational doublets in the initial and final states. If these doublets are approximately the same the two components will coincide. This may explain the apparent lack of doubling in the six strong branches found in the TiO bands.

In conclusion, I desire to express to Prof. R. T. Birge, under whose guidance this work has been done, my deep appreciation of his ready cooperation and many helpful suggestions. Also, I wish to thank Dr. F. Lowater for photographs of the spectrum of TiO, and Dr. King for the plates without which this investigation would have been impossible.

UNIVERSITY OF CALIFORNIA,
BERKELEY, CALIFORNIA,
February 14, 1929.

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[59] Hulthen, Zeits. Physik **46**, 349 (1927).

[60] Kronig, Zeits. f. Physik **46**, 814 (1927).

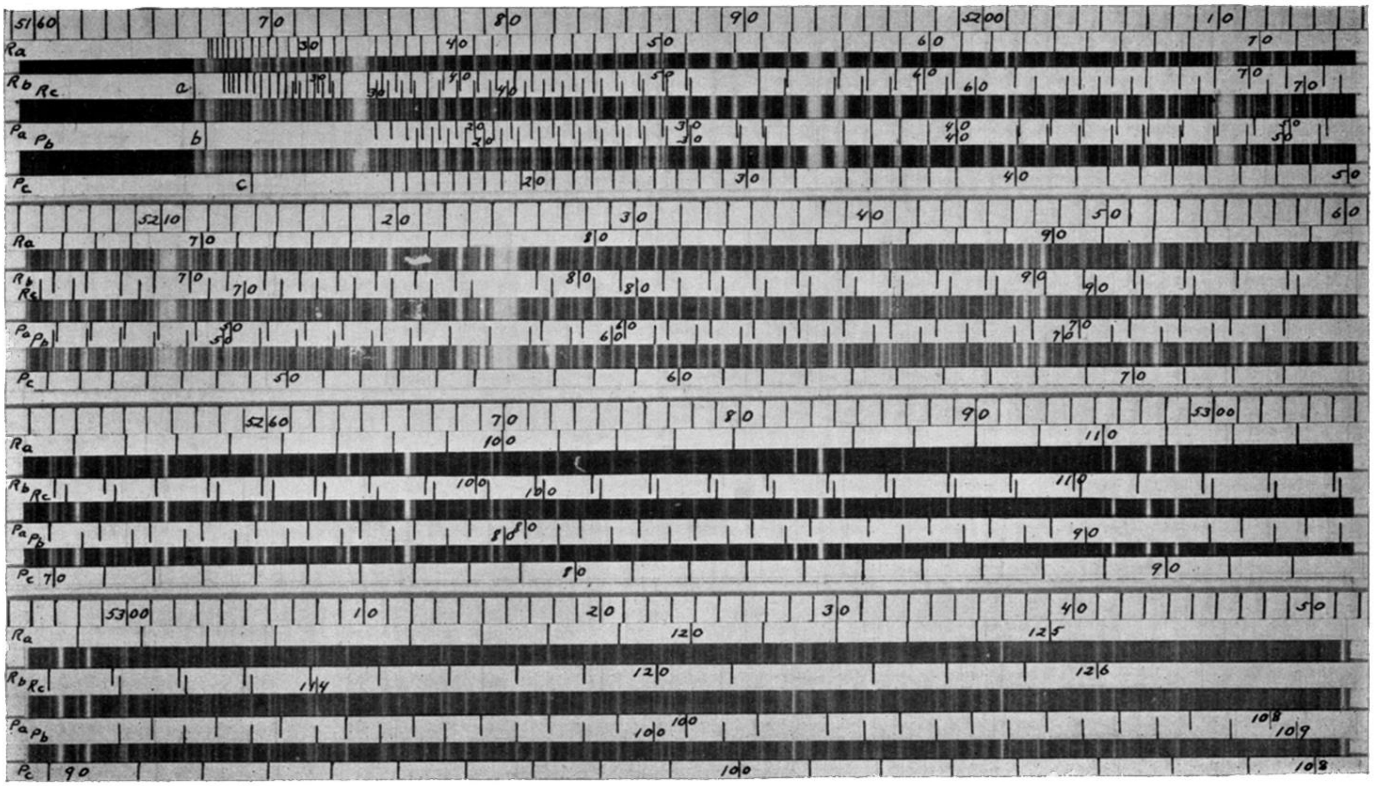

Fig. 2. (0, 0) band, λ5166.9, of TiO.