

## THE BETA BANDS OF NITRIC OXIDE. I. MEASUREMENTS AND QUANTUM ANALYSIS

BY FRANCIS A. JENKINS,<sup>1</sup> HENRY A. BARTON,<sup>1</sup> AND ROBERT S. MULLIKEN.

### ABSTRACT

**Band structure and wave-number data for band lines.** Using an active nitrogen source, the  $\beta$  bands of NO included in the region of 2300 to 5300A have been photographed in the second order of a 21-ft. Rowland concave grating. Each complete band consists of two sub-bands with a  $P$  and an  $R$  branch of the ordinary type and also a very weak  $Q$  branch. The latter is relatively more intense in the lower frequency sub-band. Here there are four missing lines in the otherwise continuous  $P-R$  series, while there are two in the higher frequency sub-band. The lines of the latter are narrow doublets superficially resembling those of the violet CN bands. The six branches for each of eighteen bands have been measured, and wave-numbers are tabulated for 20 to 30 lines in the  $P$  and  $R$  branches, and for the few visible members of the  $Q$  branches. The bands measured include nine of the strong  $n'=0$  progression ( $n''=4$  to 12), three of  $n'=1$  ( $n''=6, 11, 13$ ), four of  $n'=2$  ( $n''=9, 13, 14, 15$ ), and two of  $n'=3$  ( $n''=8, 16$ ).

**Isolation and representation of spectral terms.** Combinations involving the  $P$  and  $R$  branches are found to hold, and show the existence of four different sets of rotational terms, two (one for each sub-band) in the initial electronic state and similarly two in the final state. For low values of  $j$  the rotational terms in all four cases are representable by  $F(j) = B(j^2 - \sigma^2)$ . From a consideration of the missing lines, the observed transitions are classified as  ${}^2P_1 \rightarrow {}^2P_1$ , with  $\sigma' = \sigma'' = \frac{1}{2}$ , for the higher frequency system, and  ${}^2P_2 \rightarrow {}^2P_2$ ,  $\sigma' = \sigma'' = 3/2$ , for the lower frequency system. A table is given of the weighted mean values of  $\Delta_2 F$  in the observed vibrational states of the initial and final electronic levels, and another of the empirical coefficients in analytical expressions for  $\Delta_2 F(j)$  and  $F(j)$ . Certain anomalies in the form of the latter in particular the appreciable difference in  $B$  for the components of a doublet, are shown to be a necessary consequence of Hund's theory of molecular electronic states as applied quantitatively to doublet states by E. C. Kemble. These effects are found to be larger in the initial state, thus showing, according to the theory, that the doublet separation must be smaller here than in the final state. Equations for the band origins are obtained (Eqs. 8 of the text) which permit a representation of the vibrational energy levels; in these, cubic and biquadratic terms are both definitely required, and when they are included the observed values are reproduced with a mean error of  $0.03 \text{ cm}^{-1}$ .

**Constants of the nitric oxide molecule.** The moment of inertia  $I_0$  and the inter-nuclear distance  $r_0$  for the vibrationless molecules are evaluated as  $I_0' = (24.80 \pm 0.02) \times 10^{-40} \text{ gr cm}^2$ ,  $I_0'' = (16.30 \pm 0.02) \times 10^{-40}$ ,  $r_0' = 1.418 \times 10^{-8} \text{ cm}$ ,  $r_0'' = 1.150 \times 10^{-8}$ .  $B$ , the coefficient of  $j^2$  in  $F(j)$ , is represented within experimental error by the linear relation  $B = B_0 - \alpha n$ , where for the  ${}^2P_1$  bands  $B_0' = 1.0704$ ,  $B_0'' = 1.6754$ ,  $\alpha' = 0.01162$ ,  $\alpha'' = 0.01783$ , and for the  ${}^2P_2$  bands  $B_0' = 1.1678$ ,  $B_0'' = 1.7239$ ,  $\alpha' = 0.01892$ ,  $\alpha'' = 0.01866$ . The  $\beta$  bands exhibit a longer series of  $n''$  values than any system yet investigated in respect to the variation of  $B$  with  $n$ . Equations are given which permit a quantitative representation of the frequencies of all observed lines (Eqs. (2), (8), and (6) in conjunction with Table IV). From the equations for band-origins, the following quantities are obtained for the vibration frequency  $\omega_0$  for infinitesimal

<sup>1</sup> National Research Fellow.

amplitudes,  ${}^2P_1$  bands,  $\omega_0' = 1029.43 \text{ cm}^{-1}$ ,  $\omega_0'' = 1892.12$ ,  $x'\omega_0' = 7.460$ ,  $x''\omega_0'' = 14.424$ ;  ${}^2P_2$  bands  $\omega_0' = 1030.88$ ,  $\omega_0'' = 1891.98$ ,  $x'\omega_0' = 7.455$ ,  $x''\omega_0'' = 14.454$ . The change of  $\omega_0$  (and also of  $r_0$  and  $I_0$ ) during the emission is exceptionally great. Since the final state of the NO  $\beta$  bands is the normal state of nitric oxide, the above values of  $I_0''$ ,  $r_0''$ ,  $\omega_0''$ , etc., apply to this state. An integration of the vibration frequency curve for the final state to the point of dissociation is carried out to determine the *heat of dissociation*.

**Electronic states and relation to other bands.** The doublet separation (for the rotationless molecule) in the initial  ${}^2P$  state is  $32.9 \text{ cm}^{-1}$ , if that in the final  ${}^2P$  state is taken as 124.4 in accordance with Fr. Guillery's data on the  $\gamma$  ("third positive nitrogen") bands of NO. Only the *difference* between these ( $91.54 \text{ cm}^{-1}$ ) can be accurately found from the  $\beta$  bands. (See Fig. 1). The  $\gamma$  bands have the final doublet level in common with the  $\beta$  bands; hence all constants derived for the final state of the  $\beta$  bands apply equally well to that of the  $\gamma$  bands. The ultra-violet  $\text{O}_2^+$  bands and certain SiN bands, whose structure is like that of the  $\text{NO}\beta$  bands, are probably also  ${}^2P \rightarrow {}^2P$  transitions.

#### INTRODUCTION

ONE of the most unusual and interesting of band spectra is the  $\beta$  system<sup>2</sup> of nitric oxide, discovered and photographed by E. P. Lewis<sup>3</sup> in 1904. These bands appear with considerable intensity only when excited in active nitrogen. In his original work on the spectrum of the nitrogen afterglow, Lewis stated that traces of oxygen are necessary for the production of this system, and that therefore an oxide of nitrogen is the probable emitter. Later, in connection with the work of Lord Rayleigh<sup>4</sup> on the properties and chemical reactions of active nitrogen, Fowler and Lord Rayleigh<sup>2</sup> remeasured the principal band edges of the  $\beta$  system with sufficient accuracy to permit their arrangement in the usual Deslandres' progressions. These authors were then of the opinion that the bands could be obtained in pure nitrogen. Subsequent work by Lewis,<sup>5</sup> and also by Lord Rayleigh,<sup>6</sup> has supported the original idea that oxygen must be present.

Let us now consider briefly the evidence which has led to the conclusion that these bands are due to the nitric oxide (NO) molecule. We know<sup>5,6</sup> that the  $\beta$  bands are probably given out by the same molecule as the  $\gamma$  bands<sup>2</sup> (also called third positive nitrogen bands), since the two systems always occur together. In active nitrogen the relative intensity of the  $\beta$  and  $\gamma$  bands is practically constant, although in other sources, such as the uncondensed discharge through air, nitric oxide, or impure nitrogen, the  $\beta$  system is relatively very weak. The  $\gamma$  bands require the presence of traces of oxygen or oxygen compounds for their production,<sup>5,6</sup> as Deslandres<sup>7</sup> first pointed out. These bands are certainly not due to oxygen alone, so that we are limited to a compound of N and O as the emitter of both the  $\beta$  and  $\gamma$

<sup>2</sup> Following the designation used by A. Fowler and R. Strutt, Proc. Roy. Soc. **85A**, 377 (1911).

<sup>3</sup> E. P. Lewis, Phys. Rev. (I) **18**, 125 (1904), Astrophys. Jour. **20**, 49 (1904).

<sup>4</sup> R. Strutt, Proc. Roy. Soc. **85A**, 227 (1911) and later papers.

<sup>5</sup> E. P. Lewis, Phil Mag. **25**, 826 (1913).

<sup>6</sup> R. Strutt, Proc. Roy. Soc. **93A**, 254 (1917).

<sup>7</sup> H. Deslandres, Compt. rend. **101**, 1256 (1885).

systems. The bands are obtained more efficiently by introducing NO (*not* any *other* oxide of nitrogen) into pure active nitrogen than by introducing oxygen.<sup>6</sup> More recently it has been concluded by Mulliken<sup>8</sup> and by Birge<sup>9</sup> that the vibrational constants in the final state are the same for the  $\beta$  and  $\gamma$  systems. This was only true with the somewhat arbitrary assumption that no  $\beta$  bands are observed with a final vibrational quantum number less than 2.<sup>10</sup> There can now be no doubt as to the correctness of this interpretation, for Spomer and Hopfield<sup>11</sup> have found that the  $\beta$  and  $\gamma$  systems both appear in the ultra-violet absorption spectrum of nitric oxide, as photographed by Leifson.<sup>12</sup> The  $\gamma$  bands had previously been identified on these plates by Spomer,<sup>13</sup> proving that the final electronic state (in emission) of these bands is the normal state of the NO molecule. Combining this with the results of Spomer and Hopfield, we have definite proof that both systems result from transitions to a common final state in nitric oxide, which is its normal state. At present these two band systems constitute the entire known spectrum of nitric oxide.<sup>14</sup>

In connection with work on the electronic states of molecules, one of the writers has given an interpretation of the levels in nitric oxide,<sup>15</sup> based partially on the results to be reported here. The complete evidence for this interpretation will be postponed until the experimental material has been presented, but we may note at this point that the normal state is a doublet  $P$  ( $^2P$ ) state, and that the  $\gamma$  bands result from a transition from a single upper level ( $^2S$ ) to the double normal level. The doublet interval of the latter is therefore measured by the electronic frequency difference at the (0, 0) band<sup>16</sup> of the (double)  $\gamma$  system, which is  $124.4 \text{ cm}^{-1}$ ; this value is based on Frl. Guillery's recent analysis<sup>17</sup> of the  $\gamma$  bands. Since the  $\beta$  bands also have double heads, with a *different* electronic separation at the system-origin ( $91.54 \text{ cm}^{-1}$ ) we conclude that their initial state is also double, with a separation of  $32.9 \text{ cm}^{-1}$ .<sup>18</sup> Our results show that this is also a  $^2P$  state, and that the observed transitions are  $^2P_1 \rightarrow ^2P_1$  and  $^2P_2 \rightarrow ^2P_2$ . These relations are shown in Fig. 1.

<sup>8</sup> R. S. Mulliken, *Nature* **114**, 349 (1924).

<sup>9</sup> R. T. Birge, *Nature* **114**, 642 (1924).

<sup>10</sup> As shown in Part II of this paper, this is exactly the condition that we should expect in the light of recent theories of the intensity distribution in band systems.

<sup>11</sup> H. Spomer and J. J. Hopfield, *Phys. Rev.* **27**, 640 (1926) Abstract.

<sup>12</sup> S. W. Leifson, *Astrophys. Jour.* **63**, 73 (1926).

<sup>13</sup> H. Spomer, *Nature* **117**, 81 (1926).

<sup>14</sup> The system of bands in the extreme ultra-violet measured by R. T. Birge and J. J. Hopfield, *Phys. Rev.* **26**, 283 (1925) Abstract, and attributed to NO by Spomer (Ref. 13) and Birge and Spomer (Ref. 21), has been found by Birge and Hopfield, *Phys. Rev.* **29**, 356 (1927) Abstract, to be due to  $\text{N}_2$ .

<sup>15</sup> R. S. Mulliken, *Phys. Rev.* **28**, 493 (1926), Fig. 1.

<sup>16</sup> The notation used here conforms essentially with that of the recent Report of the National Research Council on "Molecular Spectra in Gases." In one or two cases the symbols are as defined by Mulliken (Ref. 23). As usual, the ( $n'$ ,  $n''$ ) band denotes that band which has the initial vibrational quantum number  $n'$  and final  $n''$ .

Since the work of Fowler and Lord Rayleigh, additional  $\beta$  bands in the blue and violet have been found by Lewis<sup>5</sup> and by Lord Rayleigh.<sup>6</sup> Birge<sup>19</sup> has assigned vibrational quantum numbers to the bands, including several additional ones identified on Lewis' spectrograms. New wave-lengths of all the known  $\beta$  bands are given in a recent description of this system by Johnson and Jenkins;<sup>20</sup> vibrational quantum numbers are also given. As stated above, the assigned values for these quantum numbers in the final state of the bands were chosen so as to harmonize with the well-established assignment<sup>13</sup> in the  $\gamma$  system. The intensity distribution among the bands of the system, discussed by Johnson and Jenkins, and also by Birge, is considered in Part II of the present paper. Birge and Sponer<sup>21</sup> give equations and a diagram for the vibrational levels in the various electronic states of nitric oxide, and have calculated from these the heat of dissociation.

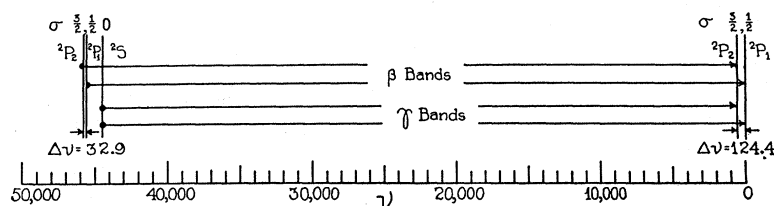


Fig. 1. Electronic states of the nitric oxide molecule. The  $2P$  doublet separations are magnified five times.

The present article<sup>22</sup> is concerned with a detailed description of the  $\beta$  bands, which have been photographed with sufficient dispersion to resolve them completely. Our analysis has brought out several new features, because the type of electron transition involved is different from that of any other band system hitherto studied. These features are well explained by the present quantum theory of band spectra, and in particular they support the postulates recently advanced by one of the writers<sup>23</sup> concerning the relations between band-spectrum structure and electronic states in molecules.

#### EXPERIMENTAL PROCEDURE

The usual stream method for obtaining active nitrogen spectra was used in photographing the bands. Nitrogen from a commercial cylinder (stated to

<sup>17</sup> M. Guillery, *Zeits. f. Physik*, **42**, 121 (1927); analysis of  $\text{NO}\gamma$  bands. See also reference 38 below. The authors are indebted to Frl. Guillery and Dr. Mecke for the opportunity of examining this paper in proof.

<sup>18</sup> In regard to the alternative possibility that the initial  $\Delta\nu$  equals  $91.54 + 124.4$ , see p. 171, below.

<sup>19</sup> R. T. Birge, *Report on Molecular Spectra*, p. 138.

<sup>20</sup> R. C. Johnson and H. G. Jenkins, *Phil. Mag.* (7) **2**, 621 (1926).

<sup>21</sup> R. T. Birge and H. Sponer, *Phys. Rev.* **28**, 277 (1926). See Figs. 3 and 4.

<sup>22</sup> Preliminary reports of this work will be found in *Nature* **119**, 118 (1927) and *Phys. Rev.* **29**, 211 (1927) Abstract.

<sup>23</sup> R. S. Mulliken, *Phys. Rev.* **28**, 481 (1926) (general); *idem*, **28**, 1202 (1926) ( $\sigma$ -type doubling, etc.); *Proc. Nat. Acad. Sci.* **12**, 151 (1926) ( $\text{ZnH}$ ,  $\text{CdH}$ ,  $\text{HgH}$  bands).

be 99.5 percent pure) was pumped at a pressure of 13 mm through a tube in which was passed a strong condensed discharge from a transformer, with a spark gap in series; the electrode nearest the after-glow tube was earthed. The nitrogen passed through a short Z-shaped piece of blackened tubing and into a wider perpendicular tube fitted with a quartz window.<sup>24</sup> The after-glow in the latter was lemon yellow under these conditions, showing chiefly the characteristic active nitrogen bands ( $\alpha$  bands) in the visible. In order to obtain the NO bands, air was admitted from a stopcock placed before the exciting discharge, causing the yellow color of the after-glow to fade into the faint bluish color characteristic of the NO spectrum.<sup>25</sup> The spectrum then showed only the  $\beta$  and  $\gamma$  bands, with a practical absence of nitrogen and other band or line spectra. Only a slight advantage as regards intensity is obtained if nitric oxide itself is introduced into the nitrogen before its activation, and the spectrum is somewhat *weaker* if either air or NO is admitted into pure active nitrogen in the after-glow tube. To obtain the bands with the best intensity, it is necessary to use a large-capacity pump, and to introduce just enough air to quench completely the  $\alpha$  bands. Since the afterglow extended throughout the 20 cm length of the after-glow tube, it was found best to place the latter directly in front of the slit, without the use of a condensing lens.

The 21-foot Rowland concave grating, having a ruled space of 6 inches with 20,000 lines to the inch, was employed. In the second order this gives a dispersion of about 0.97Å per mm. The mounting is of the Paschen type, so that the complete spectrum in the first and second orders could be photographed at once. Since the exposures were necessarily long, (the best set of plates was obtained in a 10-hr. exposure), it was essential to maintain constant temperature. This was accomplished by a sensitive thermostatic device mounted in the insulated room containing the grating and plate-holder. The temperature was thus held constant within a few hundredths of a degree. With this precaution it was found possible to resolve doublets in the second order spectrum with a separation of 0.03Å.

In determining the wave-lengths, the lines of the international iron arc<sup>26</sup> were used throughout. Two comparison spectra, one exposed before the bands and one after, were always used, in order to detect slight accidental displacements. When these were found, they were always less than 0.02Å, and the correct placing of the comparison spectrum in the region concerned was determined from other plates where the two iron spectra showed no displacement relative to each other. It is thus hoped that the wave-lengths are correct to within 0.005Å, and the relative accuracy within any band

<sup>24</sup> The arrangement was similar to that shown by Mulliken, *Phys. Rev.* **26**, 7 (1925) Fig. 1, except that the bulb *B* was omitted.

<sup>25</sup> If still more air is admitted, the blue is suddenly replaced by a dull, yellowish-green glow<sup>6,20</sup> having a continuous spectrum in the visible, beginning at  $\lambda 4300$ . This coincides closely with the region of the visible absorption of NO<sub>2</sub>, and as suggested by Lord Rayleigh (*Proc. Roy. Soc.* **86A**, 57 (1911)), probably represents the emission spectrum of this compound.

<sup>26</sup> W. F. Meggers, C. C. Kiess, and K. Burns, "Redetermination of the Secondary Standards of Wave-Length from the New International Arc," *Bull. Bur. Stan.* **19**, 263 (1924).

should be greater. In reducing the wave-lengths to vacuum and converting to wave-numbers, Kayser's tables<sup>27</sup> were used. A comparator made by Wolz, having 300 divisions to the mm, and also a Hilger instrument reading directly to 0.001 mm, served for the measurements. Two settings were usually made on each line.

#### ANALYSIS OF BAND STRUCTURE

*Description of bands.* The  $\beta$  bands have double heads degraded toward the red, and extend from  $\lambda 2300$  to  $\lambda 5300$ , with a maximum intensity at about  $\lambda 3400$ . On our most intense exposure, the first band sufficiently strong for measurement was the (0, 4) band at  $\lambda 2620$ . Sixteen bands from this to the (2, 14) band at  $\lambda 4200$  were completely measured in the second order, and two more of longer wave-length,  $\lambda 4479$  (2, 15) and  $\lambda 4572$  (3, 16), in the first order.

As will be seen on referring to Plate I, each complete band consists of two sub-bands of similar general appearance and intensity. In accordance with our interpretation of the electronic transitions responsible for these, the first higher frequency band will be called the  ${}^2P_1$  band, and the second, the  ${}^2P_2$  band. Each of these consists of a *P* and *R* branch of the usual type, forming a continuous series except for the missing lines near the origin. In addition, a very weak *Q* branch occurs in each, with an intensity falling off sharply from the first line. The *Q* branch is much stronger in the  ${}^2P_2$  bands than in the  ${}^2P_1$ . The intensity of the *P* and *R* branches is approximately symmetrical in both. These intensity relations are in good agreement with the theory, as shown in Part II of this paper, where quantitative measurements and a more complete discussion are given.

The lines of the  ${}^2P_1$  bands are probably all very close doublets, but with an undetectable separation near the origin. The doublets begin to be resolved at about the 15th line in each branch, their separation here being about 0.03Å. The components are of equal intensity. The lines soon become too weak for good measurements of the doublet separation, so that only 7 to 10 reliable values could be obtained in any one branch. Within this range a linear increase was found. The quantitative results are given in Eq. (7). The lines of the  ${}^2P_2$  bands, as far as can be observed, are strictly single throughout.

In agreement with theoretical considerations (see below), we find that the number of missing lines is different for the two sub-bands, there being two missing lines in the *P-R* series near the  ${}^2P_1$  head and four in that near the  ${}^2P_2$  head. Because of the theoretical significance of these missing lines, we have made a particular effort to establish that they are actually absent and not merely of low intensity. Active nitrogen spectra are especially favorable for this purpose, since the intensity maximum in any branch is nearer the band origin than in the case of ordinary high-temperature sources, so that the first lines are relatively strong. Furthermore, a 40-hour exposure

<sup>27</sup> H. Kayser, "Tabelle der Schwingungszahlen," S. Hirzel, Leipzig (1925).

Plate I. This plate shows three of the strongest  $\beta$  bands, together with greatly enlarged details from these and two others.

*Enlargements of complete bands.* The upper three strips show nearly the entire (0, 10), (0, 9), and (0, 8) bands, enlarged about four times from our plates. The double character of each band is evident from the sudden confusion of the regular sequence of  $P_1$  and  $R_1$  lines by the lines of the second head. The latter, when sorted out from the lines of the first head, form two other series ( $P_2$  and  $R_2$ ) very similar in appearance to the  $P_1$  and  $R_1$  series. With the exception of lines belonging to a weak  $Q$  branch near each head, these four series include all the lines found in a band. The  $P$  and  $R$  series are marked out for the (0, 10) band, the length of the marks showing qualitatively the rise and fall of intensity in each branch. Each  $R$  branch returns upon itself, forming the head. The origins are, however, very close to the heads; they lie about half-way between the points at which the  $P$  and  $R$  branches begin, in each band. Near the higher frequency ( ${}^2P_1$ ) head there are two missing lines in the otherwise continuous series formed by the  $P$  and  $R$  branches, and four near the lower frequency ( ${}^2P_2$ ) head. The variation in the relative position of the  $P$  and  $R$  branches in the  ${}^2P_1$  bands with the  $n''$  (and hence with the value of  $C$ ) is well shown in these three bands. In the (0, 9) band the two series are closely superimposed for the lower values of  $j$ .

*Details with greater enlargement.* The smaller cuts, Nos. 1 to 6, show interesting parts of certain bands, enlarged 10 times.

*No. 1*, from the head of the (0, 12) band, exhibits to advantage the two missing lines near the origin in the  ${}^2P_1$  sub-band. Here the first lines of the  $R$  and  $P$  branches ( $R_1(1)$  and  $P_1(2)$ ) are marked by a short line below, and the dots indicate the calculated positions of the missing lines. The first lines of the two branches were practically equal in intensity on the original plate. The first two lines of the  $Q$  branch,  $Q_1(1)$  and  $Q_1(2)$ , are marked above by lines indicating their relative intensity.

*No. 2* shows a portion of the (0, 10) band where the higher members of the  ${}^2P_1$  band become resolved into doublets. The three lines marked are  $P_1(17)$ ,  $P_1(18)$  and  $P_1(19)$ , which were clearly resolved on the plate with doublet separations of about 0.032Å.

*No. 3* shows the  ${}^2P_2$  head in the (0, 9) band. Four lines of the  $Q$  branch are visible, marked above. The first of these,  $Q_2(2)$ , is stronger than the first line of the  $P$  branch, marked by a line below, at the right. The dots and lines drawn below have the same significance as in *No. 1*, but here a double dot means that the position of a missing line is occupied by a known line of another series.

*No. 4* is taken from the  ${}^2P_1$  head of the (0, 8) band, which shows the first three lines of the weak  $Q$  branch in this head. They are more distinct here than in *No. 1*, the first line  $Q_1(1)$  being shown to better advantage. The presence of  $R_1(1)$  between the first two strong lines on the left is fairly obvious, while  $P_1(2)$  is well separated.

*No. 5.* This cut and *No. 6* were taken from a heavy exposure of the (0, 7) band on one of the set of plates which was used to establish definitely the absence of the apparently missing lines. Here we can say with certainty that the lines  $R_2(0)$  and  $P_2(2)$  do not occur. Owing to frequent superposition of  $Q$  lines and lines of the higher frequency band, it was only by considering the evidence from a large number of bands on these plates that we were finally able to conclude with certainty that all four lines near the  ${}^2P_2$  head are missing.

*No. 6.* This shows the  ${}^2P_1$  head of the (0, 7) head, and affords most convincing evidence of the absence of (at least) two lines near the origin of this band.

The difficulties involved in preserving faint lines during enlargement and reproduction of course render the evidence of Plate I in respect to the missing lines and  $Q$  branches less convincing than that obtained by an examination of the original plates. The photometric records described in Part II of this paper are more satisfactory in this respect.

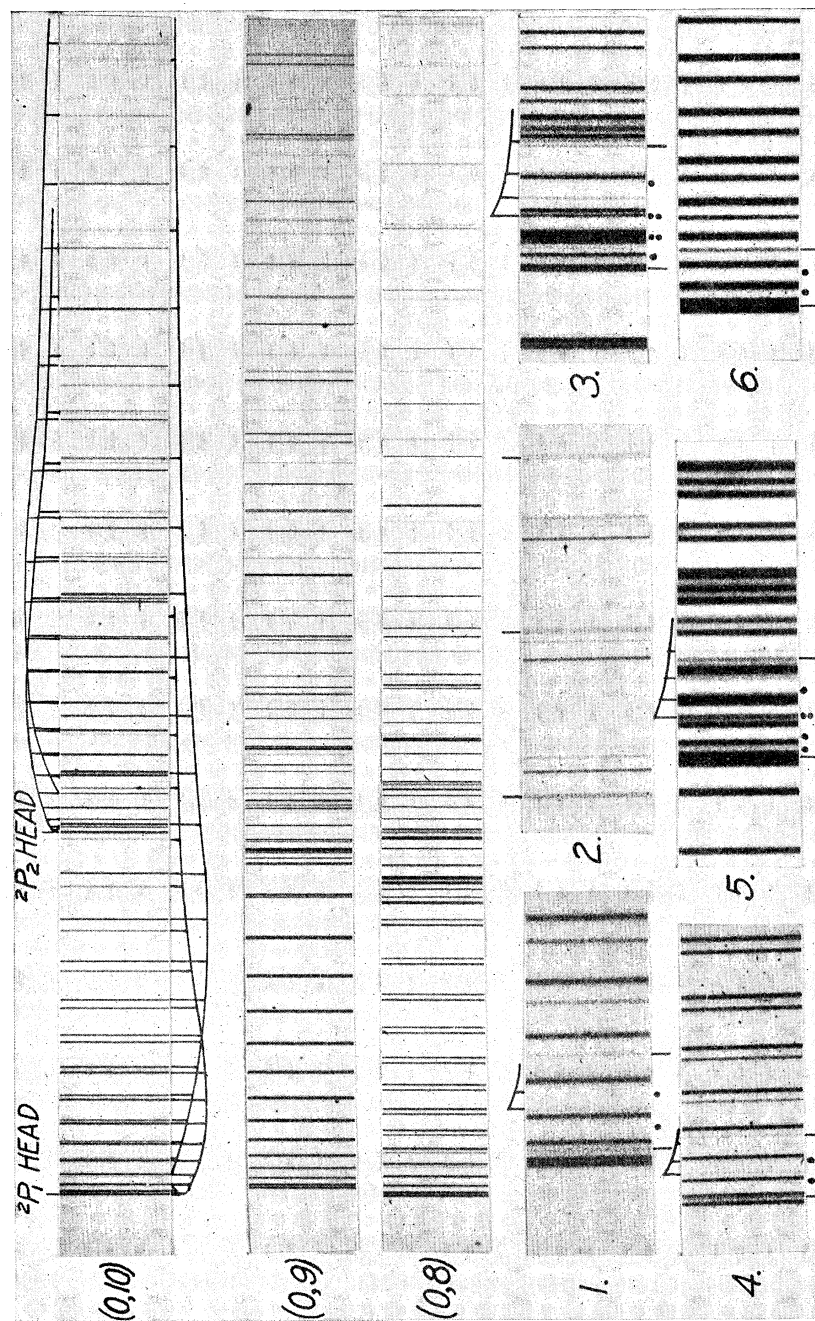




TABLE I

Frequencies of band lines in NO  $\beta$  system.

Of the letters following certain wave-numbers, *d* indicates a line which is caused by the coincidence of two lines of the band, *l* of three, and *q* of four. Lines marked in this way therefore show the use of the same wave-number in two or more places. This procedure was in all cases justified by an anomalous intensity of the line, or by a slight dissymmetry. The wave-length given at the top of each double column is that of the *R* line forming the head.

Each frequency given for the  $^2P_1$  band represents the mean value obtained by measuring the center of a doublet. The doublet widths are given by Eqs. (7) of the text.

The following bands were measured by one of us on the comparator at the Palmer Physical Laboratory, Princeton University: (0, 7), (0, 8), (0, 12), (1, 6), (2, 9), (2, 13), and (3, 8). Before using the Princeton instrument, checks were made to be sure that its screw gave no systematic errors as compared with the one used at this Laboratory, on which the remaining bands were measured.

Lines above  $j=24$  in the stronger bands were measured on a heavy exposure where the resolution was inferior to that of the best plates. Hence the accuracy is of a lower order than for the lines of smaller  $j$ , being comparable with that for some of the fainter bands. The relative intensities of the bands and band-lines are given in Part II.

(0, 4)					(0, 5)			
$j''$	$\lambda 2620.511$ $R_1(j)$	$P_1(j)$	$\lambda 2626.628$ $R_2(j)$	$P_2(j)$	$\lambda 2747.557$ $R_1(j)$	$P_1(j)$	$\lambda 2754.252$ $R_2(j)$	$P_2(j)$
1	38,149.14 <i>l</i>				36,385.06 <i>d</i>			
2	149.14 <i>l</i>	38,141.23 <i>d</i>	38,060.30 <i>l</i>		385.23	36,377.06	36,296.79 <i>d</i>	
3	149.14 <i>l</i>	136.58 <i>d</i>	060.30 <i>l</i>	38,046.05 <i>d</i>	385.06 <i>d</i>	371.99	296.79 <i>d</i>	36,282.83
4	147.38	130.35	059.44		383.63	366.37	295.77	277.17
5	144.94 <i>d</i>	123.65	057.24	034.12 <i>d</i>	381.26 <i>d</i>	359.67	293.81	270.60
6	141.23 <i>d</i>	115.41	054.39	026.41	377.74	351.82	290.92 <i>d</i>	263.11
7	136.58 <i>d</i>	106.40	050.10	017.73	373.34	343.09	287.08	254.68
8	130.94	096.34	044.99		367.88	333.32	282.26	245.18
9	124.29	085.42	038.85	37,997.37 <i>d</i>	361.44	322.55	276.44	234.87
10	116.47	073.28	031.63	985.58	354.11	310.74	269.56 <i>d</i>	223.50
11	107.84	060.30 <i>d</i>	023.57	972.97	345.75	298.02	261.88	211.27
12	098.14	046.05 <i>d</i>	014.51 <i>d</i>	959.36	336.43	284.28	253.17	197.97
13	087.51	031.09	004.21	944.56	326.11	269.56 <i>d</i>	243.51 <i>d</i>	183.70
14	075.59	014.52 <i>d</i>	37,993.01	928.78	314.86	254.03	232.77	168.48
15	062.83	37,997.37 <i>d</i>	980.57	912.10	302.55	237.29	220.95	152.26
16	049.07	979.36	967.49	894.41	289.29	219.60	208.32 <i>d</i>	135.01
17	034.12 <i>d</i>	959.96	953.03	875.49	275.21	200.98	194.48	116.84 <i>d</i>
18	018.15	940.00	937.97	855.67	259.98	181.51	179.80	097.62
19	001.69	918.91	921.30	834.81	243.79 <i>d</i>	160.94	163.99	077.46
20	37,984.11	896.58	903.89	812.98	226.81	139.41	147.34	056.31
21		873.61		789.97	208.66 <i>d</i>	116.84 <i>d</i>	129.67	034.12
22		849.38		766.42	189.58	093.64	110.86	011.02
23					169.77	069.21		35,986.80
24						038.84		
25						017.55		
1	38,144.94 <i>d</i>	$Q_1(j)$	$Q_2(j)$		$Q_1(j)$		$Q_2(j)$	
2			38,055.44		36,381.26 <i>d</i>		36,290.92 <i>d</i>	
3			052.61				288.85	
4							285.07	
(0, 6)					(0, 7)			
$j''$	$\lambda 2885.245$ $R_1(j)$	$P_1(j)$	$\lambda 2892.590$ $R_2(j)$	$P_2(j)$	$\lambda 3034.853$ $R_1(j)$	$P_1(j)$	$\lambda 3042.973$ $R_2(j)$	$P_2(j)$
1	34,648.53				32,940.30			
2	648.96 <i>d</i>	34,640.56	34,560.98 <i>d</i>		940.96 <i>d</i>	32,932.39	32,853.07 <i>d</i>	
3	648.96 <i>d</i>	636.01	560.98 <i>d</i>	34,547.47 <i>d</i>	940.96 <i>d</i>	927.91	853.07 <i>d</i>	33,839.19
4	647.60	630.36	560.21	541.90 <i>d</i>	939.71	922.46	852.49	833.88
5	645.36	623.81	558.32	535.48 <i>d</i>	937.60	916.09	850.88	827.71 <i>d</i>
6	642.11	616.25	555.69	528.04 <i>d</i>	934.54	908.64	848.39	820.58
7	637.97	607.69	552.07	519.75 <i>d</i>	930.62	900.33	844.94 <i>l</i>	812.63
8	632.76	598.22	547.47 <i>d</i>	510.55 <i>d</i>	925.73	891.11	840.75 <i>d</i>	803.81
9	626.69	587.75	541.90 <i>d</i>	500.41 <i>d</i>	919.89	880.94	835.47	794.02
10	619.64	576.34	535.48 <i>d</i>	489.40 <i>d</i>	913.22	869.84	829.43	783.34
11	611.66	563.96	528.04 <i>d</i>	477.56	905.56	32,857.82	822.43	32,771.82
12	602.76	550.65	519.75 <i>d</i>	464.75	896.96	844.94 <i>l</i>	814.54	759.42
13	592.86	536.34	510.55 <i>d</i>	450.95 <i>d</i>	887.63	831.08	805.65	746.08
14	582.04	521.18	500.41 <i>d</i>	436.23	877.27	816.35	795.98	731.82
15	570.35	505.05	489.40 <i>d</i>	420.54	866.00	800.69	785.26	716.68
16	557.64	488.02	477.23	403.89	853.94	784.20	773.70	700.59
17	544.02	469.96	464.00	386.31	840.75 <i>d</i>	766.77	761.13	683.60
18	529.53	450.95 <i>d</i>	449.87	367.77	826.93	748.40	747.73	665.74
19	514.13	431.16	434.88	348.34	811.99	729.24	733.44	646.92
20	497.68	410.32	418.93	327.74	796.47	709.09	718.15	627.16
21	480.38	388.67	401.82 <i>d</i>	306.47	779.76	688.15	701.96	606.55
22	462.18	366.01			762.35	666.48 <i>d</i>	684.80	585.02
23	442.94	342.40			743.86	643.45	666.61 <i>d</i>	562.50
24	422.74	317.93			724.49	619.75	647.71	539.06
25	401.82 <i>d</i>	292.51			704.37	595.16	627.74	514.76
26					683.53	569.74	606.96	489.49
27					661.31	543.42	585.02	463.28
28					638.46	516.27	562.50	436.32
29						488.11		408.31
30						459.12		379.35

TABLE I (continued)

j	$Q_1(j)$		$Q_2(j)$		$Q_1(j)$		$Q_2(j)$		
	34,644.10		34,555.23		32,937.01		32,847.25		
2			552.87				844.97 <i>t</i>		
3			549.85				842.04		
4			545.59				838.10		
5			540.72				833.26		
6							827.65 <i>d</i>		
7									
(0, 8)					(0, 9)				
j''	$\lambda 3197.973$		$\lambda 3206.937$		$\lambda 3376.428$		$\lambda 3386.379$		
	$R_1(j)$	$P_1(j)$	$R_2(j)$	$P_2(j)$	$R_1(j)$	$P_1(j)$	$R_2(j)$	$P_2(j)$	
1	31,260.20				29,607.75 <i>d</i>				
2	260.80 <i>d</i>	31,252.31	31,173.43 <i>d</i>		608.62 <i>d</i>	29,599.77 <i>d</i>	29,521.21 <i>d</i>		
3	260.80 <i>d</i>	247.81	173.43 <i>d</i>	31,159.54	608.62 <i>d</i>	595.49 <i>d</i>	521.62	29,507.76	
4	259.70	242.47	172.86	154.35 <i>d</i>	607.75 <i>d</i>	590.28 <i>d</i>	521.21 <i>d</i>	502.68 <i>d</i>	
5	257.78	236.21	171.41	148.28	605.91	584.22 <i>d</i>	519.91	496.77	
6	254.90	229.05	169.15	141.38	29,603.26 <i>d</i>	29,577.30 <i>d</i>	29,517.79	29,490.09	
7	251.24	220.93	166.02	133.65	599.77 <i>d</i>	569.51 <i>d</i>	514.91	482.56	
8	246.60	211.95	161.97	125.06	595.49 <i>d</i>	560.87	511.19	474.27	
9	241.06	202.10	157.12	115.61	590.28 <i>d</i>	551.28	506.61	465.15	
10	234.73	191.35	151.39	105.36	584.22 <i>d</i>	540.85	501.25	455.20	
11	227.49	179.71	144.75	094.16	577.30 <i>d</i>	529.56	495.03	444.42 <i>d</i>	
12	219.33	167.28 <i>d</i>	137.23	082.18	569.51 <i>d</i>	517.46	487.97	432.84	
13	210.31	153.79	128.90	069.27	561.01	504.49	480.05	420.42	
14	200.44	139.55	119.64	055.54 <i>d</i>	551.56	490.72	471.30	407.17	
15	189.75	124.42	109.53	040.86	541.36	476.11	461.70	393.03	
16	178.15	108.47	098.47	025.38	530.28	460.67	451.24	378.12	
17	165.55 <i>d</i>	091.67	086.63	009.02	518.40	444.42 <i>d</i>	439.96	362.35	
18	152.34	073.85 <i>d</i>	073.85 <i>d</i>	30,991.75	505.75	427.28	427.71	345.71	
19	138.07	055.38 <i>d</i>	060.17	973.61	492.23	409.42	414.80	328.27	
20	123.12	035.84	045.55	954.56	477.92	390.65	400.92	309.96	
21	107.21	015.55	030.04	934.62	462.79	370.97	386.23	290.79	
22	090.51	30,994.43	013.75	913.88	446.71	350.74	370.67	270.81	
23	072.92	972.44 <i>d</i>	30,996.48	892.20	429.92	329.51	354.22	249.97	
24	054.60	949.63 <i>d</i>	978.33	869.67	412.11	307.54	336.97	228.36	
25	035.16	925.90 <i>d</i>	959.33	846.25	393.75	284.70	318.85	205.76	
26	015.23	901.36	939.34	821.93	374.63	261.02	299.91	182.39	
27	30,994.08	875.98	918.60	796.73	354.98	236.61	280.11	158.20 <i>d</i>	
28	972.44 <i>d</i>	849.71	896.91	770.63	333.63	211.31	259.42	133.15	
29	949.63 <i>d</i>	822.50	874.40	743.70	311.81	185.38	237.87	107.24	
30	925.90 <i>d</i>	794.69	850.84	715.87	289.27	158.20 <i>d</i>	215.45	080.48	
31		765.89		687.24		130.62		052.89	
32		736.20		657.58		102.18		024.54	
(0, 10)					(0, 11)				
j''	$\lambda 3572.392$		$\lambda 3583.484$		$\lambda 3788.483$		$\lambda 3800.914$		
	$R_1(j)$	$P_1(j)$	$R_2(j)$	$P_2(j)$	$R_1(j)$	$P_1(j)$	$R_2(j)$	$P_2(j)$	
1	27,983.71 <i>d</i>				26,387.29				
2	984.49 <i>d</i>	27,976.13	27,897.51 <i>d</i>		388.32 <i>d</i>	26,379.61	26,302.02 <i>q</i>		
3	984.49 <i>d</i>	971.60	897.87	27,884.15 <i>d</i>	388.32 <i>d</i>	375.48	302.02 <i>q</i>	26,288.27	
4	983.71 <i>d</i>	966.47	897.51 <i>d</i>	879.11 <i>d</i>	387.71	370.51	302.02 <i>q</i>	283.47	
5	982.09	960.53	896.45	873.29 <i>d</i>	386.24	364.71	301.04	277.84	
6	979.64	953.72	894.56	866.69 <i>d</i>	383.98 <i>d</i>	358.09	299.34	271.63 <i>d</i>	
7	976.36	946.12	891.84 <i>d</i>	859.51	380.94	350.72	296.89 <i>d</i>	264.58	
8	972.23	937.66	888.45	851.47	377.15	342.57	293.76	256.81	
9	967.35	928.41	884.15 <i>d</i>	842.71	372.53	333.56	289.86 <i>d</i>	248.32	
10	961.65	918.32	879.11 <i>d</i>	833.12	367.14	323.81	285.12	239.00	
11	955.09	907.40	873.29 <i>d</i>	822.72	361.02	313.28	279.68	229.06	
12	947.79	895.72	866.69 <i>d</i>	811.56	354.10	302.02 <i>q</i>	273.44	218.34 <i>d</i>	
13	939.68	883.21	859.23	799.58	346.40	289.86 <i>d</i>	266.43	206.85	
14	930.79	869.89	850.98	786.84	337.93	277.09	258.69	194.56	
15	921.11	855.79	841.89	773.28	328.80	265.53	250.16	181.55	
16	910.59	840.91	832.03	758.92	318.80	249.18	240.85	167.79	
17	899.24	825.22	821.32	743.77	308.15	234.06	230.81	153.23	
18	887.18 <i>d</i>	808.76	809.83	727.81	296.89 <i>d</i>	218.34 <i>d</i>	219.93	137.89	
19	874.31	791.45	797.57	710.99	284.54 <i>d</i>	201.64	208.30	121.80 <i>d</i>	
20	860.68	773.41	784.38	693.41	271.59 <i>d</i>	184.27	195.80	104.96 <i>d</i>	
21	846.22	754.70	770.41	675.01	257.81	166.19	182.72	087.30 <i>d</i>	
22	831.08	734.96	755.64	655.80	243.48	147.35	168.73	068.90	
23	815.00	714.59	740.02	635.79	228.26	127.73	153.93	049.71	
24	798.23	693.39	723.76	614.96	212.24	107.44	138.46	029.78	
25	780.64	671.47	706.47	593.32	195.22	086.38	121.98 <i>d</i>	009.07	
26	762.26	648.73	688.39	570.89	178.03	064.53	104.97 <i>d</i>	25,987.56	
27	743.64	625.21	669.57	547.61	159.99	041.97	087.30 <i>d</i>	965.35	
28	723.48	600.89	649.88	523.60	140.80	018.66	068.56	942.35	
29	702.41	575.78	629.40	498.74	121.85	25,994.64	049.12		
30	681.15	549.92	608.03	473.06		969.81	028.99		
31		523.46		446.60		944.33			
32		495.97		419.38					

TABLE I (continued)

	$Q_1(j)$	$Q_2(j)$	$Q_1(j)$	$Q_2(j)$
1	27,980.36		26,383.98d	
2	979.15	27,891.85d	382.72	26,295.90
3	977.64	889.79		294.04
4		887.20d		291.55
5		884.22d		288.02
6		880.79		284.54d
7		876.29		280.03

$j''$	(0, 12)				(1, 6)			
	$\lambda 4027.812$ $R_1(j)$	$P_1(j)$	$\lambda 4041.784$ $R_2(j)$	$P_2(j)$	$\lambda 2802.593$ $R_1(j)$	$P_1(j)$	$\lambda 2809.399$ $R_2(j)$	$P_2(j)$
1	24,819.22				35,670.69t			
2	820.39d	24,811.59			670.69t		35,584.34d	
3	820.39d	807.48	24,734.59d	24,720.71d	670.69t		584.34d	35,570.36
4	819.92	802.67	734.59d	715.98	669.22	35,652.30	583.14	564.72
5	818.58	797.01	733.81d	710.68	666.89d	645.50	581.11	558.38
6	816.50	790.62	732.31	704.53	663.57	637.90	578.31d	550.88
7	813.69	783.45	730.11	697.74	659.08	629.24	574.40	542.47
8	810.11	775.55	727.22	690.30	653.82	619.59	569.65	533.13
9	805.85	766.82	723.60	682.12	647.50	608.99	563.82	522.91
10	800.82	757.44	719.27	673.23	640.23	597.34	556.88d	511.60
11	794.98	747.34	714.21	663.63	631.92	584.79	549.41	499.56
12	788.62	736.48	708.40	653.33	622.70	571.24	540.99d	486.26
13	781.31	724.84	701.89	642.28	612.58	556.88d	531.11	472.36
14	773.35	712.50	694.62	630.50	601.40	540.99d	520.31	457.03
15	764.67	699.45	686.63	618.03	589.17	524.74	508.64	440.94
16	755.31	685.63	677.89	604.80	576.11d	507.34	496.28	423.96
17	745.15	671.10	668.44	590.80	562.22	488.98	482.71	406.01
18	733.81d	655.88	658.22	576.18	547.21	469.59	468.06	386.97
19		639.99	647.30	560.75		449.34	452.44	367.07
20		623.24d	635.56	544.59		427.94		346.11
21			623.24d	527.75				
22			610.00	510.12				
23				491.89				

	$Q_1(j)$	$Q_2(j)$	$Q_1(j)$	$Q_2(j)$
1	24,816.03		35,666.89d	
2		24,728.26		35,578.31d
3		726.52		576.11d
4		724.10		573.05
5		720.95d		
6		717.22		

$j''$	(1, 11)				(1, 13)			
	$\lambda 3647.236$ $R_1(j)$	$P_1(j)$	$\lambda 3658.544$ $R_2(j)$	$P_2(j)$	$\lambda 4113.628$ $R_1(j)$	$P_1(j)$	$\lambda 4127.887$ $R_2(j)$	$P_2(j)$
1	27,409.56d				24,301.49			
2	410.24d	27,401.75	27,325.12d		302.20d	24,293.82	24,218.11	
3	410.24d	397.60	325.52	27,311.76d	302.62	289.93	218.67d	24,205.03
4	409.56d	392.57	325.12d	306.76d	302.20d	285.14	218.67d	200.34
5	407.98	386.67	324.09	301.07d	300.92	279.59	217.91	194.99
6	405.53	379.94	322.11	294.70	29.87	273.31	216.38	188.97
7	402.33	372.42	319.38d	287.51	2. .	266.24	214.22	182.25
8	398.37	364.07	315.99	279.54	292.6	258.47	211.34	174.87
9	393.48	354.95	311.76d	270.85	288.46	249.92	207.77	166.79
10	387.83	345.03	306.76d	261.31	283.50	240.6	203.48	158.01
11	381.42	334.30	301.07d	251.09	277.85	230.69	198.47	148.54
12	374.23	322.71	294.51	239.99	271.45	219.96	192.75	138.34
13	366.24	310.45	287.12	228.13	264.37	208.48	186.31	127.46
14	357.52	297.29	278.99	215.55	256.64	196.38	179.14	115.81
15	347.95	283.48	269.97	202.08d	248.05	183.53	171.25	103.51
16	337.56	268.67	260.23	187.95	238.80	169.89	162.63	090.45
17	326.42	253.19	249.57	172.93	228.89	155.57	153.33	076.68
18	314.76d	237.04	238.15	157.18	217.98	140.65	143.24	062.21
19	301.73	220.02	226.11	140.60	206.83	124.95	132.41	046.96
20	288.13	202.15d	213.09	123.21d	194.33	108.65d	121.01	031.07
21	274.07	183.50	199.35	104.99	182.01	091.43	108.65	014.37
22	259.07	164.21	184.66	086.08		073.57	095.65d	23,997.04
23	243.22	144.17	169.36	066.32		055.05		978.95
24		123.21d		045.66				960.11
25		101.61		024.32				

	$Q_1(j)$	$Q_2(j)$	$Q_1(j)$	$Q_2(j)$
1	27,406.11		Not visible	
2		27,319.43d		24,212.42
3		317.41		210.78
4		314.63d		
5		310.95		

TABLE I (continued)

$j''$	(2, 9)				(2, 13)				
	$\lambda 3159.825$		$\lambda 3168.301$		$\lambda 3949.850$		$\lambda 3962.834$		
	$R_1(j)$	$P_1(j)$	$R_2(j)$	$P_2(j)$	$R_1(j)$	$P_1(j)$	$R_2(j)$	$P_2(j)$	
1	31,636.98d								
2	638.19d		31,553.56d		25,310.27d	25,301.71	25,227.34t		
3	638.19d	31,625.42	553.56d	31,540.53d	310.27d	297.67	227.34t	25,214.00	
4	636.98d	619.99	552.96	534.92	309.68	292.83	227.34t	209.25	
5	634.92	613.80	551.39	528.80	308.31	287.17	226.37d	203.83	
6	631.98	606.61	548.82	521.92	306.10d	280.80	224.74	197.63	
7	628.20	598.54	545.51d	513.98	303.23	273.62	222.32	190.79	
8	623.38	589.52	541.23	505.30	299.50	265.70	219.18	183.20	
9	617.70	579.65	536.14	495.70	295.10	257.02	215.32	175.01d	
10	611.20	568.79	530.15	485.30d	289.98	247.59	210.71	165.87	
11	603.86	557.07	523.13	473.89	284.01	237.29	205.41	156.11	
12	595.49	544.52	515.47	461.76	277.33	226.37d	199.29	145.63	
13	586.19	531.02	506.80	448.63	269.91	214.66	192.51	134.39	
14	576.10	516.65	497.26d	434.66	261.73	202.22	184.94	122.41	
15	565.23	501.38	486.68	419.76	252.83	189.01	176.64	109.67	
16	553.40	485.30d	475.35	404.07	243.16	175.01d	167.49	096.24	
17	540.53d	468.15	463.01	387.43	232.85	160.43	157.62	082.05	
18	527.06	450.20	449.97	369.84d	221.77d	145.03	147.08	067.06	
19	512.56	431.56	435.77	351.37		128.88	135.77	051.33	
20	497.26d	411.76	420.79	332.11		111.99	123.65	034.92	
21	480.96	391.37	404.78	311.79			110.94	017.74	
22		369.84d		290.73					
23		347.68							
$Q_1(j)$					$Q_2(j)$				
1	Not visible				25,306.10d				
2					25,221.81d				
3					219.74				
4					217.17				
(2, 14)					(2, 15)				
$j''$	$\lambda 4200.677$		$\lambda 4215.243$		$\lambda 4479.783$		$\lambda 4496.197$		
	$R_1(j)$	$P_1(j)$	$R_2(j)$	$P_2(j)$	$R_1(j)$	$P_1(j)$	$R_2(j)$	$P_2(j)$	
1	23,797.86				22,316.27q				
2	798.71d	23,790.31	23,716.27d		316.27q	22,307.79d	22,234.24d		
3	799.01	786.44	716.77d	23,703.32	316.27q	303.95d	234.80d	22,221.44d	
4	798.71d	781.74	716.77d	698.66	316.27q	299.38d	234.80d	216.87d	
5	797.41	776.28	715.96	693.39d	315.13	294.21d	234.24d	211.68d	
6	795.44	770.08	714.49	687.53	313.40	288.28d	232.95	205.89t	
7	792.75	763.14	712.37	680.84d	310.92	281.34	231.08	199.45d	
8	789.36	755.47	709.51	673.57	307.79d	273.93	228.53d	192.51	
9	785.26	747.09	705.85	665.59	303.95d	265.84	225.33	184.86	
10	780.41	738.01	701.76	656.91	299.38d	257.09	221.44d	176.67d	
11	774.85	728.15	696.81	647.54	294.21d	247.61	216.87d	167.63	
12	768.58	717.63	691.17	637.44	288.28d	237.51	211.68d	158.00	
13	761.57	706.42	684.82	626.69	281.89	226.73d	205.89t	147.77d	
14	753.97	694.41	677.77	615.25	274.74	215.28	199.45d	136.74	
15	745.54	681.77	670.02	603.06	266.88	203.12	192.16	125.14	
16	736.48	668.33	661.52	590.20	258.37	190.33	184.25	112.85	
17	726.71	654.33	652.21	576.62	249.23	176.67d	175.57	099.86d	
18	716.27d	639.56	642.37	562.33	239.39	162.71	166.37	086.30	
19	704.99	624.08	631.74	547.28	228.70	147.77d	156.38	071.99	
20	693.39d	608.10	620.32	531.57	217.68	132.54	145.78	057.05	
21	680.84d	591.12		515.17	205.89t	116.41	134.59	041.41	
22		573.59		498.06		099.86d	122.46	025.16	
23						082.44	109.85	008.25	
24								21,990.43	
25								972.11	
$Q_1(j)$					$Q_2(j)$				
1	Not visible				22,312.12				
2					22,228.53d				
3					226.73d				
4					224.77				

TABLE I (continued)

$j''$	(3, 8)				(3, 16)			
	$\lambda_{2915.949}$	$P_1(j)$	$\lambda_{2923.099}$	$P_2(j)$	$\lambda_{4574.018}$	$P_1(j)$	$\lambda_{4590.776}$	$P_2(j)$
1	34,284.14 $f$				21,856.51 $q$			
2	284.14 $f$		34,200.31 $t$		856.51 $q$	21,848.26 $d$	21,776.18 $d$	
3	284.14 $f$	34,271.55	200.31 $t$		856.51 $q$	844.51 $d$	776.73 $d$	21,763.68 $d$
4	282.69	266.08	199.75		856.51 $q$	839.82	776.73 $d$	759.15 $d$
5	280.34	259.57	197.65	34,175.35	855.38	834.57	776.18 $d$	754.04 $d$
6	277.11	252.06	194.80 $d$	168.07	853.73	828.65	774.96	748.31 $t$
7	272.88	243.58	190.90	159.85	851.32	822.06	773.11	741.92 $d$
8	267.64	234.17	186.17	150.64	848.26 $d$	814.76	770.58 $d$	734.99 $d$
9	261.44	223.77	180.50	140.62	844.51 $d$	806.85	767.47	727.47
10	254.36	212.46	173.86	129.71	840.14	798.26	763.68 $d$	719.44 $d$
11	246.38	200.28 $t$	166.32	117.58	835.14	788.97	759.15 $d$	710.49
12	237.41	186.96	157.75 $d$	104.65	829.44	779.02	754.04 $d$	701.05
13	227.39	172.74	148.18 $d$	090.82	823.08	768.39	748.31 $t$	690.98 $d$
14	216.53	157.71 $d$	137.81	076.03	816.08	757.20	741.92 $d$	680.16
15	204.66	141.48	126.31	060.26	808.36	745.27	734.99 $d$	668.70
16	191.77	124.47	113.98 $d$	043.51	800.10	732.72	727.16	656.66
17	178.07	106.44	100.80	025.66 $d$	791.10	719.44 $d$	718.76	643.88 $d$
18	163.45	087.69	086.41	007.30	781.46	705.68	709.83	630.53
19	148.06 $d$	067.88	071.86	33,987.67	771.01	690.98 $d$	700.01	616.53
20	131.19	046.99	055.01	967.12	760.33	676.11	689.58	601.89
21	113.96 $d$	025.56 $d$	037.67	945.70	748.31 $t$	660.17	678.39	586.55
22		002.73	019.49	923.16	736.33	643.88 $d$	666.64	570.54
23		33,979.04				626.75	654.35	554.02
24						608.73		536.50
25								518.49
	$Q_1(j)$		$Q_2(j)$		$Q_1(j)$		$Q_2(j)$	
1	Not visible				21,852.25			
2			34,194.83 $d$				21,770.58 $d$	
3			192.43				769.26	
4			189.65				766.80	

was made under favorable conditions, by which the brighter bands were considerably over-exposed, but no trace of the lines in question was found.

*Measurements.* Table I gives the wave-number data for all of the bands measured. The six branches,  $R_1$ ,  $Q_1$ ,  $P_1$ ,  $R_2$ ,  $Q_2$ ,  $P_2$ , of the complete band are given in each case. The first three branches mentioned constitute the  ${}^2P_1$  band, and the other three the  ${}^2P_2$  band. The wave-length of the line forming the head is given for these two sub-bands in each case. The precision is greater for the stronger bands ( $n' = 0$  progression,  $n'' = 6$  to 11) than for the others. For the former, as the combination relations show, the relative errors of measurement within a band appear to be about  $0.02 \text{ cm}^{-1}$ . For the sake of uniformity, however, wave-numbers are given to two places even for the weaker bands. The measurements given here include all the stronger bands of the system.<sup>28</sup> Several fainter bands could also have been measured, but would probably have contributed little to the value of the data here included.

*Application of the combination principle.* According to the quantum theory of band spectra,<sup>16</sup> the rotational energy levels<sup>29</sup> of a molecule may in general be assumed to be given<sup>30</sup> for low speeds of rotation by the familiar Kramers and Pauli expression

$$F(j) = Bm^2 = B[(j^2 - \sigma^2)^{1/2} - \rho]^2 \quad (1)$$

The lines of the  $P$ ,  $Q$ , and  $R$  branches are conveniently designated by their

<sup>28</sup> For a diagram of all bands which occur, and their relative intensities, see Part II, p. 185.

<sup>29</sup> The actual energies are obtained on multiplying  $F(j)$  by  $hc$ .

<sup>30</sup> Cf. R. S. Mulliken, Phys. Rev. **28**, 490-3 (1926).

$j$  in the final state. That is (neglecting fine-scale rotational doubling, which will be considered in a later section).

$$\begin{aligned} R(j) &= \nu^0 + F'(j+1) - F''(j) \\ Q(j) &= \nu^0 + F'(j) - F''(j) \\ P(j) &= \nu^0 + F'(j-1) - F''(j) \end{aligned} \quad (2)$$

The spacing of the rotational levels in the initial or final states can be investigated by certain combination relations. Thus

$$R(j) - P(j) = F'(j+1) - F'(j-1) = \Delta_2 F'(j) \quad (3a)$$

gives a series of quantities, each representing the sum of two adjacent intervals between the levels in the initial state, while

$$R(j-1) - P(j+1) = F''(j+1) - F''(j-1) = \Delta_2 F''(j) \quad (3b)$$

gives a similar series for the final state. Further information may often be obtained from combinations involving the  $Q$  branch, but in the present case the latter is too weak to be of use for this purpose. Since all bands having the same value of  $n'$  must have identically the same set of initial rotational levels, it should be possible to obtain from all such bands a set of initial-state combination differences  $\Delta_2 F'(j)$  which are identical for all. An analogous statement holds with regard to  $n''$  and  $\Delta_2 F''(j)$ .

Choosing two bands with the same value of  $n'$ , for instance the (0, 10) and (0, 11)  ${}^2P_1$  bands, it was found after a few trials that one (and only one) set of  $R-P$  differences can be obtained which is identical within experimental error for both bands. These differences should represent  $\Delta_2 F_1'$  values, and from Eqs. (2) and (3a) the members of each  $P-R$  pair should have a common value of  $j''$ . For the correct absolute assignment of  $j$  values, we depend on the fact that the  $\Delta_2 F'$  quantities should in this case (see below under *Term formulation*) be approximately equal to  $4B'j$ . The designation of every line in these two bands by an appropriate  $j'$  and  $j''$  is now possible.

Considering next the final state, differences were taken in the (1, 11) band between lines suspected of being  $R_1(j-1)$  and  $P_1(j+1)$ , and compared with the corresponding  $\Delta_2 F_1''$  values from the (0, 11) band. The numbering of the lines in the (1, 11) band to give the desired equalities was easily found, and the proper assignment of  $j$  values was established by the relations  $\Delta_2 F_1''(j) = 4B''j$ , and Eq. (3b). The same procedure could be carried throughout the band system, but was not needed for the assignment of  $j$  values, since the regular variation in the relative positions of the  $P$  and  $R$  lines in any progression (or sequence) of bands was obvious. For the  ${}^2P_2$  bands, an analogous procedure to the above yielded the values of  $\Delta_2 F_2'$  and  $\Delta_2 F_2''$  and established the correct  $j$  numbering.

The combination differences in the (0, 10), (0, 11), and (1, 11) bands are given in Table II. The combination relations were tested for all the

eighteen bands here measured, and agreements similar to the above were found. The identities found in the  $\Delta_2 F$  quantities for both initial and final states render it certain that the  $F(j)$  levels concerned differ by two units in  $j$ .

As far as could be determined, the required combinations with the  $Q$  branch are also fulfilled. In general this would permit one to obtain sets of  $\Delta_1 F$  values, but in the present case the  $Q$  lines are obviously too few and weak. In regard to possible  $Q$  branch doubling, "crossing over," etc., cf. p. 169, below.

TABLE II

*Example of combination differences.*

For the values marked by asterisks one (or both) of the lines entering into the combination was superimposed on, or incompletely resolved from, another line of sufficient intensity to render the measurement of the former less reliable.

The  $\Delta_2 F_1''(j)$  values were obtained from the  ${}^2P_1$  bands by taking the wave-number differences between the lines  $R_1(j-1) - P_1(j+1)$ , while  $\Delta_2 F_2''(j)$  represents the corresponding differences  $R_2(j-1) - P_2(j+1)$  in the  ${}^2P_2$  bands. For the initial state,  $\Delta_2 F_1'(j)$  and  $\Delta_2 F_2'(j)$  give the differences  $R_1(j) - P_1(j)$  and  $R_2(j) - P_2(j)$ , respectively.

$j''$	(1, 11)		(0, 11)				(0, 10)	
	$\Delta_2 F_1''(j)$	$\Delta_2 F_2''(j)$	$\Delta_2 F_1''(j)$	$\Delta_2 F_2''(j)$	$\Delta_2 F_1'(j)$	$\Delta_2 F_2'(j)$	$\Delta_2 F_1'(j)$	$\Delta_2 F_2'(j)$
2	11.96*		11.81*		8.71*		8.36*	
3	17.67*	18.36*	17.81*	18.55*	12.84*	13.75*	12.89*	13.72*
4	23.57*	24.45*	23.61*	24.18*	17.20*	18.55*	17.24*	18.40*
5	29.62*	30.42*	29.62*	30.39*	21.53	23.20	21.56	23.16*
6	35.56	36.58	35.52	36.46	25.89*	27.71*	25.92	27.87*
7	41.46	42.57	41.41*	42.53	30.22	32.31*	30.24	32.33*
8	47.38	48.53	47.38	48.57*	34.58	36.95	34.57*	36.98*
9	53.34	54.68	53.34	54.76	38.97	41.54*	38.94	41.44*
10	59.18	60.67*	59.25	60.80*	43.33	46.12	43.33*	45.99*
11	65.12	66.77*	65.12*	66.78*	47.74	50.62	47.69	50.57*
12	70.97	72.94*	71.16*	72.83	52.08*	55.10*	52.07	55.13*
13	76.94	78.96*	77.01	78.88	56.54*	59.58	56.47	59.65*
14	82.76	85.04*	82.87	84.88	60.84	64.13	60.90	64.14
15	88.85	91.04	88.75	90.90	65.27	68.61	65.32*	68.61
16	94.76	97.04	94.74	96.93	69.62	73.06	69.68*	73.11
17	100.52	103.05	100.46*	102.96	74.09	77.58	74.02	77.55
18	106.40	108.97	106.51	109.01*	78.55*	82.04	78.42*	82.02
19	112.68*	114.99*	112.65*	115.00*	82.90	86.50*	82.86	86.58
20	118.23	121.07	118.22	121.02*	87.32*	90.84*	87.27*	90.97*
21	123.92	127.01	124.24*	126.90	91.62*	95.43*	91.52	95.40
22	129.90	133.03	130.08*	133.01	96.13	99.83	96.12	99.84
23	135.86*	139.00	136.04	138.95	100.53	104.22	100.41	104.23
24	141.61	145.04	141.88	144.86	104.80	108.68	104.84*	108.80*

*Term formulation.* It is at once evident that the combinations give four different sets of  $\Delta_2 F$  values, two in the initial state and two in the final, thus confirming the supposition that the bands are due to a transition between two doublet electronic states. As has been said, we are here concerned with a final state which is probably  ${}^2P_{1,2}$  from analogy with aluminium, the corresponding atom. In  ${}^2P$  states, (as is shown especially by the HgH type bands)<sup>23</sup> we expect  $\rho \sim 0$ ,  $\sigma = \frac{1}{2}$  ( ${}^2P_1$ ) and  $1\frac{1}{2}$  ( ${}^2P_2$ ). From a study of systematic relations in band spectra,<sup>23</sup> we also expect  $j$  to have integral values for NO, since it has an odd number of electrons. Both of these suppositions are in harmony with the empirical form of the  $\Delta_2 F$ 's, which may





TABLE III (continued)

$j$	$n''$	6	7	8	9	10	11
		$\Delta_2 F_1''$	$\Delta_2 F_2''$	$\Delta_2 F_1''$	$\Delta_2 F_2''$	$\Delta_2 F_1''$	$\Delta_2 F_2''$
2	12.52		12.39	12.43	12.12	12.11	11.88
3	18.53	19.26	18.50	19.19	18.28	19.08	18.31
4	25.16	25.66	24.87	25.36	24.59	25.13	24.40
5	31.34	32.22	31.07	31.91	30.65	31.50	30.43
6	37.66	38.61	37.27	38.25	36.83	37.77	36.39
7	43.92	45.15	43.43	44.58	42.95	44.12	42.41
8	50.18	51.57	49.68	50.92	49.13	50.41	48.51
9	56.44	58.06	55.89	57.41	55.24	56.59	54.62
10	62.73	64.30	62.07	63.65	61.33	62.96	60.69
11	68.99	70.69	68.28	70.01	67.43	69.19	66.73
12	75.26	77.07	74.48	76.35	73.69	75.50	72.82
13	81.61	83.52	80.61	82.72	79.77	81.70	78.81
14	87.82	90.09	86.94	88.97	85.89	88.02	84.87
15	94.03	96.43	93.07	95.39	91.99	94.26	90.87
16	100.32	102.86	99.23	101.66	98.11	100.53	96.99
17	106.63	109.41	105.54	107.96	104.23	106.72	103.06
18	112.86	115.65	111.51	114.21	110.18	113.04	108.98
19	119.21	122.07	117.81	120.60	116.42	119.30	115.14
20	125.46	128.41	123.85	126.95	122.50	125.49	121.11
21	131.67		129.99	133.13	128.61	131.67	127.21
22	137.98		136.31	139.46	134.80	137.84	133.28
23	144.25		142.60	145.74	140.88	144.08	139.17
24	150.43		148.70	151.85	147.02	150.23	145.22
25			154.75	158.22	153.24	156.40	151.09
26			160.95	164.46	159.18	162.60	157.14
27			167.26	170.64	165.52	168.71	163.32
28			173.20	176.71	171.58	174.90	169.60
29			179.36	183.15	177.75	181.04	175.43
30					183.74	187.16	181.19
31					189.70	193.26	187.09

$j$	$n''$	12	13	14	15	16
		$\Delta_2 F_1''$	$\Delta_2 F_2''$	$\Delta_2 F_1''$	$\Delta_2 F_2''$	$\Delta_2 F_1''$
2	11.74		11.56	11.42	12.32	12.00
3	17.72		17.25	17.87	16.97	17.61
4	23.38	23.91	23.07	23.60	22.73	23.38
5	29.30	30.06	28.88	29.70	28.63	29.24
6	35.13	36.07	34.69	35.62	34.27	35.12
7	40.95	42.01	40.40	41.52	39.97	40.92
8	46.87	47.99	46.22	47.39	45.66	46.78
9	52.67	53.99	51.96	53.32	51.35	52.60
10	58.51	59.97	57.80	59.23	57.11	58.31
11	64.34	65.94	63.56	65.11	62.78	64.32
12	70.14	71.93	69.36	71.01	68.43	70.12
13	76.12	77.90	75.09	76.91	74.17	75.92
14	81.86	83.86	80.87	82.82	79.80	81.76
15	87.72	89.82	86.74	88.69	85.64	87.57
16	93.57	95.83	92.44	94.58	91.21	93.40
17	99.43	101.71	98.14	100.43	96.92	99.19
18	105.16	107.69	103.96	106.33	102.63	104.93
19	110.57	113.63	109.57	112.17	108.17	110.80
20		119.55	115.40	118.03	113.87	116.57
21		125.44	120.76	123.97	119.80	122.26
22		131.35	126.96	129.70		
23			135.54			
24						

A consideration of the missing lines supports the formulation of Eq. (4), with the  $\sigma''$  values  $\frac{1}{2}$  and  $1\frac{1}{2}$ , and also gives the  $\sigma'$  values. Since  $j''$  is limited

to values equal to or greater than  $\sigma$ , the line  $j$  ( $1 \rightarrow 0$ ) should be missing for all bands having the final state  ${}^2P_1$  ( $\sigma'' = \frac{1}{2}$ ). Similarly in the bands with the final state  ${}^2P_2$ , at least three lines should be absent, corresponding to the transitions  $1 \rightarrow 0$ ,  $0 \rightarrow 1$  and  $2 \rightarrow 1$ . Actually we have two lines missing in the first instance and four in the second. This establishes the values of  $\sigma'$ , since the additional missing line ( $0 \rightarrow 1$  in the first case and  $1 \rightarrow 2$  in the second) is evidently due to the exclusion  $j' = 0$  in the first case and  $j' = 1$  in the second. Hence  $\sigma$  must also be  $\frac{1}{2}$  and  $1\frac{1}{2}$  for the components of the upper doublet, and we conclude that this is also a  ${}^2P_{1,2}$  state. The observed transitions then are:

Higher frequency bands:  ${}^2P_1 \rightarrow {}^2P_1$ ;  $\sigma' = \frac{1}{2}$ ;  $\rho' = \rho'' = 0$

Lower frequency bands:  ${}^2P_2 \rightarrow {}^2P_2$ ;  $\sigma' = \sigma'' = 1\frac{1}{2}$ ;  $\rho' = \rho'' = 0$

Therefore the rotational terms of both initial and final states are given by Eq. (4). In support of this picture we have further very strong evidence from the intensity relations (see Part II), since weak  $Q$  branches having intensities in agreement with those observed are required by the theory for transitions where  $\sigma' = \sigma''$ .

*Evaluation of rotational terms.* Since the application of the combination principle has shown that bands with a common  $n'$  (or  $n''$ ) give identical values of  $\Delta_2 F'$  (or  $\Delta_2 F''$ ), we are justified in averaging the appropriate individual values from such bands in order to obtain a more accurate representation of the particular set of rotational terms involved. Table III gives the complete set of combination differences for the four initial and thirteen final vibrational states ( $n' = 0$  to 3;  $n'' = 4$  to 16). The weighted mean has been taken wherever more than one set of data was available. The quantities given in each column of this table have been fitted empirically by equations of the form

$$\Delta_2 F(j) = a + bj + cj^2 + dj^3 \quad (5)$$

For this purpose a method of least squares was used which is particularly suitable for band-spectrum analysis.<sup>31</sup> The accuracy of the data did not appear to justify the inclusion of terms higher than the cubic. The numerical coefficients in Eq. (5) obtained in this way are summarized in Table IV, columns 2 to 5.

To obtain the corresponding equations for  $F(j)$ , a knowledge of the theoretical form of the energy expression is necessary. If we assume merely that the rotational terms may be represented by a power series of the form

$$F(j) = \text{const.} + Aj + Bj^2 + Cj^3 + Dj^4 + \dots \quad (6)$$

we can compute these new coefficients from those of Eq. (5), leaving the value of the constant term undetermined. Thus we have

$$D = d/8, \quad C = c/6, \quad B = b/4 - d/4, \quad A = a/2 - c/6.$$

<sup>31</sup> R. T. Birge and J. D. Shea, "A Method for the Rapid Calculation of the Least Squares Solution of a Polynomial of any Degree," Phys. Rev. **24**, 206 (1924) Abstract; Univ. Calif. Publ. Math. **2**, 67 (1927). We are indebted to Prof. Birge for the use of the tables before publication.

The values of these coefficients are given in the remaining columns of Table IV. With the exception of  $B$ , they show no consistent variations with  $n$ ; and hence have been averaged over the various values of  $n$  for each electronic state.

Since we may assume  $B$  to be given by  $B_0 - \alpha n$ ,<sup>32</sup> the least squares solution of the weighted values for such a linear relation is given in each case

TABLE IV  
Empirical coefficients in rotational energy function.

	$a$	$b$	$c \cdot 10^3$	$d \cdot 10^5$	Wt.	$A$	$B$	$C \cdot 10^3$	$D \cdot 10^5$
${}^2P_1n'=0$	0.0280	4.2802	6.233	-10.85	4	0.0130	1.0701	1.039	-1.356
1	-0.0789	4.2423	6.846	-16.88	2	-0.0408	1.0607	1.140	-2.110
2	0.0684	4.1788	6.468	-11.48	2	0.0331	1.0447	1.077	-1.435
3	-0.0823	4.1492	6.817	-16.98	1	-0.0423	1.0374	1.136	-2.122
				Av.		-0.0006 $\pm 0.0132$	(1.0704 -0.01162 $n'$ ) $\pm 0.0007$	1.081 $\pm 0.017$	-1.626 $\pm 0.149$
$n''=6$	0.0445	6.2595	1.191	-3.520	1	0.0220	1.5649	0.199	-0.440
7	0.0052	6.2159	-0.862	0.154	2	0.0029	1.5539	-0.144	0.019
8	-0.0683	6.1526	-1.608	3.053	3	-0.0340	1.5382	-0.268	0.382
10	0.0886	5.9716	2.000	-7.229	5	0.0438	1.4930	0.333	-0.904
11	0.0839	5.8976	2.500	-9.547	4	0.0415	1.4744	0.417	-1.193
12	-0.0108	5.8558	0.110	-3.854	4	-0.0053	1.4639	0.018	-0.482
13	-0.0637	5.7876	-0.114	-2.309	4	-0.0318	1.4469	-0.019	-0.289
				Av.		0.0071 $\pm 0.0081$	(1.6754 -0.01783 $n''$ ) $\pm 0.0011$	0.106 $\pm 0.064$	-0.506 $\pm 0.137$
${}^2P_2n'=0$	-0.0405	4.6733	-6.871	3.632	8	-0.0190	1.1683	-1.145	0.454
1	0.0534	4.5909	-5.049	0.404	4	0.0276	1.1477	-0.841	0.051
2	0.0612	4.5182	-3.744	-2.236	4	0.0311	1.1296	-0.624	-0.279
3	0.1489	4.4550	-5.373	9.814	1	0.0754	1.1137	-0.896	1.227
				Av.		0.0093 $\pm 0.0150$	(1.1678 -0.01892 $n'$ ) $\pm 0.0006$	-0.936 $\pm 0.076$	0.232 $\pm 0.224$
$n''=6$	0.0869	6.4255	0.110	-2.336	1	0.0436	1.6063	0.018	-0.292
7	0.0024	6.3864	-1.778	-1.736	3	0.0015	1.5966	-0.296	-0.217
8	0.0512	6.2843	1.315	-10.05	6	0.0253	1.5711	0.219	-1.260
9	-0.0693	6.2349	0.046	-8.824	8	-0.0348	1.5589	0.008	-1.103
11	-0.0776	6.1075	-2.375	-1.329	3	-0.0385	1.5269	-0.396	-0.166
12	0.1913	5.9664	2.160	-10.46	3	0.0954	1.4916	0.360	-1.307
13	0.0444	5.9250	-0.124	-5.617	5	0.0223	1.4812	-0.021	-0.702
				Av.		0.0070 $\pm 0.0121$	(1.7239 -0.01866 $n''$ ) $\pm 0.0015$	0.010 $\pm 0.069$	-0.871 $\pm 0.135$

in place of the average. The occurrence of an exceptionally large range of  $n''$  values in the  $\beta$  bands shows well the effect of increasing vibration on the spacing of the rotational terms. The value of  $B_0''$  obtained from the  $\gamma$  bands by Frl. Guillery<sup>17</sup> (1.663 for  ${}^2P_1$  and 1.694 for  ${}^2P_2$ ) are slightly lower than those of Table IV, due probably to the method of evaluation, which

<sup>32</sup> A. Kratzer, Zeits. f. Physik 3, 289 (1920).

neglects higher power terms and would be expected to give lower values than the more accurate procedure used here.

*Rotational doubling.* As stated in an earlier section (cf. p. 155), the lines of the  ${}^2P_1$  band are double. In the analysis just given, this doubling has been left out of account. An investigation of the doublet separations in the (0, 10) and (0, 11) bands shows that their value,  $\Delta\nu$ , is practically the same for corresponding lines of the two bands, and can be represented within experimental error by

$$\Delta\nu_R = 0.0154j \quad \Delta\nu_P = 0.0138j \quad (7)$$

The analysis of the  $\gamma$  bands<sup>17</sup> shows that the rotational doubling in the  $F_1''$  levels may be represented (with reference to the *mean*  $F_1''$  values) by  $\pm 0.005 j''$ . If we take Eqs. (7) to hold within the range of measurements ( $j = 16$  to 22), the rotational doubling in the initial ( $F_1'$ ) states becomes  $\pm 0.0123 j'$ . In the data for the  $\gamma$  bands, there are also indications of a small combination defect, hence of a small rotational doubling, in the  ${}^2S \rightarrow {}^2P_2$  bands, which is practically constant with increasing  $j$ . If this is real, there must also be a doubling of equal magnitude in the initial  ${}^2P_2$  levels of the  $\beta$  bands, since the lines of the  ${}^2P_2$  bands are strictly single on our plates. Presumably at least a *latent* doubling is present in *all* ( $F_1$  and  $F_2$ ) levels and in all the  $P$ ,  $Q$ , and  $R$  branches, as would be expected from the theory. Probably the branches in each sub-band are given by a scheme (Eq. (2) of p. 1206 of ref. 23) involving "crossing over" in the  $Q$  branches.

*Band-origins and equations for vibrational terms.* For the calculation of band-origins, and conversely for the empirical representation of the lines, we employ Eqs. (2), evaluating the  $F(j)$  terms by Eq. (6) with the mean values of the coefficients given in Table IV. If the rotational terms are represented by Eq. (4),<sup>33</sup> the term  $F(0)$  equals  $-B\sigma^2 + D\sigma^4$ . We therefore give this value to the constant term of Eq. (6).<sup>34</sup> In this way the position of the origin of each band was computed, using the first three accurately measured lines of the  $R$  branch and the first four of the  $P$  branch. The mean of the seven values of  $\nu^0$  thus obtained, which never differed among themselves by more than a few hundredths  $\text{cm}^{-1}$ , is recorded in Table V as  $\nu^0$  (*obs.*), for each band. Under  $\nu^0$  (*calc.*) are entered the values given by the following equations for band origins

$$\begin{aligned} {}^2P_1 \quad \nu^0 &= 45,486.12 + 1029.429n' - 7.460n'^2 + 0.1017n'^3 - 1892.119n'' \\ &\quad + 14.4243n''^2 - 0.04021n''^3 + 0.001351n''^4 \\ {}^2P_2 \quad \nu^0 &= 45,394.58 + 1030.883n' - 7.455n'^2 + 0.0917n'^3 \\ &\quad - 1891.976n'' + 14.4543n''^2 - 0.04229n''^3 + 0.001423n''^4 \end{aligned} \quad (8)$$

<sup>33</sup> E. C. Kemble, Report on Molecular Spectra Ch. VII, part 2A, p. 310. (Derivation of Kramers and Pauli formula).

<sup>34</sup> In the formulation of the new quantum mechanics, Eq. (4) becomes

$$F(j) = B[j^*(j^*+1) - \sigma^2] + D[j^*(j^*+1) - \sigma^2]^2 + \dots$$

If  $j^*$  is taken  $\frac{1}{2}$  unit lower than the integral  $j$  used here,  $F(0)$  should be taken as  $-B(\sigma^2 + \frac{1}{4}) + D(\sigma^4 + \frac{1}{2}\sigma^2 + 1/8)$ . Hence the essential result of this change would be a small shift in the  $\nu^0$  values obtained below of approximately  $\frac{1}{4}C(C = B' - B'')$ . The new mechanics also requires that the vibrational quantum numbers,  $n$ , used here be replaced throughout by  $n + \frac{1}{2}$ .

Combining these expressions with the empirical coefficients for Eq. (6) given in Table IV, and defining the band lines by Eqs. (2), we obtain a precise representation of all the frequencies found in this extensive band system. No evidence was found for perturbations in either rotational or vibrational terms.

TABLE V  
Frequencies of band origins.

Band	$\nu^0$ (obs)	$\nu^0$ (calc)	$o-c$	Band	$\nu^0$ (obs)	$\nu^0$ (calc)	$o-c$
(0, 4)	38,146.21 38,055.59	38,146.21 38,055.59	$\pm 0.00$ $\pm 0.00$	(0, 10)	27,980.71 27,892.16	27,980.67 27,892.19	+0.04 -0.03
(0, 5)	36,382.00 36,291.68	36,382.08 36,291.66	-0.08 +0.02	(0, 11)	26,384.44 26,296.40	26,384.42 26,296.36	+0.02 +0.04
(0, 6)	34,645.74 34,555.77	34,645.75 34,555.78	-0.01 -0.01	(1, 11)	27,406.57 27,319.95	27,406.49 27,319.92	+0.08 +0.03
(1, 6)	35,667.69 35,579.24	35,667.82 35,579.30	-0.13 -0.06	(0, 12)	24,816.31 24,728.69	24,816.23 24,728.72	+0.08 -0.03
(0, 7)	32,937.54 32,847.91	32,937.53 32,847.91	+0.01 $\pm 0.00$	(1, 13)	24,298.63 24,212.95	24,298.62 24,212.95	+0.01 $\pm 0.00$
(0, 8)	31,257.27 31,168.04	31,257.28 31,168.02	-0.01 +0.02	(2, 13)	25,306.41 25,222.10	25,306.38 25,222.11	+0.03 -0.01
(3, 8)	34,281.14 34,196.07	34,281.17 34,196.07	-0.03 $\pm 0.00$	(2, 14)	23,795.06 23,711.28	23,795.04 23,711.26	+0.02 +0.02
(0, 9)	29,604.99 29,516.10	29,604.97 29,516.10	+0.02 $\pm 0.00$	(2, 15)	22,312.40 22,229.13	22,312.48 22,229.16	-0.08 -0.03
(2, 9)	31,634.78 31,548.80	31,634.80 31,548.78	-0.02 +0.02	(3, 16)	21,852.65 21,771.36	21,852.60 21,771.36	+0.05 $\pm 0.00$

#### DISCUSSION OF RESULTS

*Form of rotational energy function.* The term-form  $B(j^2 - \sigma^2) + D(j^2 - \sigma^2)^2 + \dots$ , involving only even powers<sup>16</sup> of  $m = (j^2 - \sigma^2)^{1/2}$  does not successfully represent the empirical form of the rotational terms found in the  $\beta$  bands. Thus  $C$ , the coefficient of the cubic term is relatively large in the initial electronic state, and is positive for the  ${}^2P_1$  and negative for the  ${}^2P_2$  level. Also the quantity  $B$ , which should be substantially equal to  $h/8\pi^2I$ , and would be expected to be practically the same for  ${}^2P_1$  and  ${}^2P_2$ , is decidedly greater for  ${}^2P_2$ . Both of these effects tend to bring the lines  $P_1(j)$  and  $P_2(j-1)$ , together for high  $j$  values, likewise the lines  $R_1(j)$  and  $R_2(j-1)$ ; and similarly with the  $F$  and  $\Delta_2F$  values (cf. Table 3). Such a drawing together of the branches is found to a more pronounced degree in other bands involving multiplet electronic states (OH, MgH, CaH(A), CH,  $N_2$  (second positive) and Swan bands).

The above phenomena are qualitatively accounted for by Hund's theory of molecular electronic states.<sup>35</sup> In the initial state of the  $\beta$  bands

<sup>35</sup> F. Hund, Zeits. f. Physik **36**, 657 (1926).

of NO we evidently have an example of a  ${}^2P$  doublet electronic state which approaches Hund's case *a* for low values of  $j$ , but case *b* for high  $j$  values, corresponding to a gradual change of the orientation of the electron spin vector from positions parallel and anti-parallel to  $\sigma_k$  for low  $j$ , to an orientation parallel and anti-parallel to  $j_k$  (resultant of  $\sigma_k$  and  $m$ ) for large values of  $j$  (cf. Hund's paper and discussion by Kemble<sup>36</sup> and by Mulliken.<sup>37</sup>)

From the  $B$  and  $C$  values of Table IV, it is evident that the transition from case *a* toward case *b* proceeds much less rapidly in the *final* than in the initial  ${}^2P$  state. This justifies the conclusion that the doublet separation (which is a measure of the energy of orientation) is considerably less in the initial than in the final  ${}^2P$  state. This lends support to our original assumption that the separation of 91.54 wave-number units between the origins ( $n' = n'' = 0$ ) of the  ${}^2P_1$  and  ${}^2P_2$  systems, as given in Eqs. (8), represents the *difference*, rather than the sum, of the initial and final electronic doublet separations. Since from the  $\gamma$  bands the final  $\Delta\nu$  is 124.4 units,<sup>38</sup> the initial  $\Delta\nu$  is thus evaluated as 32.9 units. It then also follows, from the relative position of the two sub-bands and the preceding analysis, that the  ${}^2P$  doublets are *normal* (not inverted) in both cases. (cf. Fig. 1).

The effect on the rotational term formulae of the transition from case *a* to case *b* has been carried through quantitatively by Professor E. C. Kemble for the case of doublet states. At his suggestion, the resulting equations were tested by one of the writers with the data reported here, and found to give satisfactory agreement.<sup>39</sup> A more complete consideration of these quantitative results will be given in a later paper.

The assumption that for low values of  $j$  the terms are given by  $F(j) = \text{Const.} + Bj^2$  permits an approximation from the equations, making possible the evaluation of the true moment of inertia,  $I$ , from the empirical  $B$ . Thus Kemble has found:

$$B = \frac{h}{8\pi^2 I} (1 \mp z)^2 \pm z^2 \Delta\nu$$

where

$$z = \frac{h}{8\pi^2 I \Delta\nu - 2h \pm 2h} \quad (9)$$

and  $\Delta\nu$  = term difference for zero rotation. The upper sign goes with the lower level of the pair. First taking  $h/8\pi^2 I$  as given approximately by the mean value of  $B$  for  ${}^2P_1$  and  ${}^2P_2$ , Eq. (9) gives the true values as follows ( $B_0$  = value of  $B$  for  $n = 0$ , obtained by extrapolation in Table IV).

<sup>36</sup> E. C. Kemble, Report on Molecular Spectra, p. 326.

<sup>37</sup> R. S. Mulliken, Phys. Rev. **29**, 637 (1927.)

<sup>38</sup> This was obtained from the results of Miss Guillery (Ref. 17) on the separation of the null lines by extrapolation to  $n'' = 0$  and addition of  $9/4B_2'' - 1/4B_1''$ .

<sup>39</sup> Cf. preliminary report, E. C. Kemble and F. A. Jenkins, Phys. Rev. **29**, 607 (1927) Abstract.

	B <sub>0</sub> values from Table IV.		Values of $h/8\pi^2 I_0$ by Eq. (9)	
	B <sub>0</sub> '	B <sub>0</sub> ''	$h/8\pi^2 I_0'$	$h/8\pi^2 I_0''$
<sup>2</sup> P <sub>1</sub>	1.070	1.675	1.122	1.701
<sup>2</sup> P <sub>2</sub>	1.168	1.724	1.112	1.700

Thus the apparently anomalous difference in the moment of inertia for the doublet components is quantitatively accounted for.

As already noted, the final state doublet separation ( $\Delta\nu = 124.4$ ) is much less affected by the rotation than is that of the initial state ( $\Delta\nu = 32.9$ ). Kemple's equations show that the rate of transition from case *a* to case *b* is determined by the ratio  $\Delta\nu/B$ , so it is evident that the wider doublet should show the smaller rate. In a limiting case where the rotation has no effect on the electronic separation, the coefficient of  $j^4$  (and of  $m^4$ ) should satisfy a theoretical relation derived by Kratzer,<sup>40</sup> namely

$$D_0 = -4B_0^3/\omega_0^2.$$

This relation is approximately fulfilled for the final state, where the observed values for the mean *D* from Table IV are  $(-5.0 \pm 1.4) \times 10^{-6}$  and  $(-8.7 \pm 1.4) \times 10^{-6}$  for <sup>2</sup>P<sub>1</sub> and <sup>2</sup>P<sub>2</sub> respectively. The theory predicts  $-5.49 \times 10^{-6}$ . In the initial state the two observed values are widely different.

*Constants of the nitric oxide molecule.* The true values of  $h/8\pi^2 I_0$  obtained above now permit the calculation of the moment of inertia, *I*<sub>0</sub>, for the vibrationless molecule in its initial and final electronic states. The values of *I*<sub>0</sub> are given in Table VI, together with computed values of *r*<sub>0</sub>, the internuclear distance.

TABLE VI  
*Molecular constants of nitric oxide.*

	Initial electronic state		Final electronic state	
	<sup>2</sup> P <sub>1</sub>	<sup>2</sup> P <sub>2</sub>	<sup>2</sup> P <sub>1</sub>	<sup>2</sup> P <sub>2</sub>
$\omega_0$	1029.43 cm <sup>-1</sup>	1030.88	1892.12	1891.98
$x\omega_0$	7.460+ cm <sup>-1</sup>	7.455+	14.424+	14.454+
$Q_D$			6.810 volts	6.775
<i>I</i> <sub>0</sub>	$(24.80 \pm 0.02) \times 10^{-40}$ gr cm <sup>2</sup>		$(16.30 \pm 0.02) \times 10^{-40}$	
<i>r</i> <sub>0</sub>	$1.418 \times 10^{-8}$ cm		$1.150 \times 10^{-8}$	

The table also gives  $\omega_0$ , the frequency of vibration for infinitesimal amplitudes, and  $x\omega_0$ , which measures the rate of change of the vibration frequency with *n*. It is noteworthy that the admission of cubic and biquadratic terms in  $n''$  in deriving Eqs. (8) brings the experimental values of  $\omega_0''$  for <sup>2</sup>P<sub>1</sub> and <sup>2</sup>P<sub>2</sub> much closer together (perhaps equal within experimental error) than those obtained if a parabolic law is assumed. This suggests that the larger difference which we find for the two values of  $\omega_0'$  may result from our inability to evaluate sufficient higher power terms in this case, owing to the limited number of experimental values. In this connection it is of interest

<sup>40</sup> A. Kratzer, Ann. d. Physik **71**, 72 (1923).

that in the final state (probably  ${}^2P$ ) of the SnCl bands as analysed by Jevons,<sup>41</sup>  $\omega_0$  is greater for the upper (probably  ${}^2P_2$ ) state by 2.1 parts in 350; in these bands the doublet separation is very large ( $\Delta\nu \sim 2360$ ) so that the  ${}^2P$  state should closely approximate Hund's case *a*.

For the final state of the NO  $\beta$  bands the heat of dissociation into atoms,  $Q_D$ , obtained by analytical extrapolation of the  $\omega_n:n$  curve<sup>42</sup> and integration to  $\omega_n=0$ , is also given in Table VI. The result is considerably lower than that obtained by Birge and Sponer,<sup>21</sup> which was 7.93 volts. The discrepancy arises from the fact that we have here carried the experimental curve to somewhat higher values of  $n''$  and taken into account the quadratic and cubic terms, while Birge and Sponer assumed a linear relation. Direct measurements of the heat of dissociation of NO into  $N_2$  and  $O_2$ , combined with the heats of dissociation of  $O_2$  and  $N_2$  obtained from band spectrum data,<sup>21</sup> give  $Q_D$  as 8.3 volts, so that it is doubtful whether the band spectrum method in this case is capable of yielding more than a rough approximation. The rule of Birge<sup>43</sup> and Mecke,<sup>44</sup> which states that a decrease in the moment of inertia is invariably accompanied by an increase in the vibration frequency  $\omega_0$ , holds true in the  $\beta$  bands. It is interesting to note that the semi-quantitative relations found by Mecke<sup>44</sup> are supported in this extreme case where the changes in  $\omega_0$  and in the moment of inertia between the initial and final states are exceptionally large. Applying them in the form given by Birge,<sup>16</sup> if we denote by a subscript *m* the mean value over the initial and final states, we find

$$\omega_m/(\omega_0' - \omega_0'') = -1.70, \quad I_m/(I_0' - I_0'') = -2.43.$$

A further relation found by Mecke also holds approximately in this case:  $I_m \times \omega_m$  nearly equals  $I_0'' \times \omega_0''$ , and the resulting quantities, 29,970 and 30,830 respectively, lie very near those found<sup>16</sup> for several other molecules having molecular weights of the same order of magnitude.

Since the energy levels of the normal state of NO are given (at least by extrapolation) by the data presented here, it should be possible to calculate from them accurate values of the specific heat of gaseous nitric oxide, and its variation with temperature. Preliminary results<sup>45</sup> show that the existence of a doublet normal state results in an appreciable contribution to the specific heat at low temperatures which are within the range subject to experimental test. Unfortunately no measurements have yet been made at these temperatures.

The magnetic susceptibility of the gas is another property whose theoretical evaluation has been made possible by a knowledge of the molecular electronic states.<sup>46</sup>

<sup>41</sup> W. Jevons, Proc. Roy. Soc. **110A**, 365 (1926).

<sup>42</sup> This is obtained directly from Eqs. (8) by differentiation with respect to *n* of the appropriate expression for  $E_n$ .

<sup>43</sup> R. T. Birge, Phys. Rev. **25**, 240 (1925) Abstract.

<sup>44</sup> R. Mecke, Zeits. f. Physik **32**, 823 (1925).

<sup>45</sup> E. E. Witmer, Paper before the Washington meeting of the American Physical Society, Apr. 1927 (Preliminary report of more accurate calculations).

<sup>46</sup> J. H. Van Vleck, Phys. Rev. **29**, 613 (1927) Abstract; Nature **119**, 670 (1927).



*Relation of NO  $\beta$  bands to theory of band-structure and electronic states.*

The NO  $\beta$  bands constitute the first band system for which the existence of integral effective rotational quantum numbers ( $T$ ) in both initial and final states has been established. The existence of integral  $j$  values ( $T=j$ ), and of  $\sigma$ -type terms with  $\sigma = \frac{1}{2}$  and  $1\frac{1}{2}$  give strong support to previous generalizations of one of the writers,<sup>23</sup> according to which the  $j$  values are integral for all odd molecules, and the  $j_e$  (here =  $\sigma$ ) values are the same as Sommerfeld's  $j$  values for the corresponding atomic electronic states.

The NO $\beta$  bands are in all respects in agreement with Hund's theory.<sup>35</sup> The existence of a  ${}^2P \rightarrow {}^2P$  transition, which would have been very surprising in the case of an atom, is in harmony with the theory. The occurrence of the transitions  ${}^2P_1 \rightarrow {}^2P_1$  and  ${}^2P_2 \rightarrow {}^2P_2$ , without  ${}^2P_1 \rightarrow {}^2P_2$  and  ${}^2P_2 \rightarrow {}^2P_1$ , gives striking confirmation of Hund's selection rule  $\Delta\sigma_s = 0$ . The detailed intensity relations agree excellently with the theory, as will be shown in Part II of this paper. The presence, in the  ${}^2P_1$  bands at least, of a fine-scale doubling ( $\sigma$ -type doubling) with equal *a priori* probabilities (as indicated by the relative intensities of the components of the double lines, cf. p. 155) of the doublet components, is in agreement with Hund's theory.

*Classification of O $_2^+$  and SiN bands.* The ultraviolet O $_2^+$  bands,<sup>47</sup> and also certain SiN bands,<sup>48</sup> have the same obvious structure,—just two well-separated heads of approximately equal intensity, in each band,—as the NO $\beta$  bands, and may be tentatively classified as  ${}^2P \rightarrow {}^2P$  transitions ( ${}^2D \rightarrow {}^2D$  might also be a possibility). If these bands were  ${}^2S \rightarrow {}^2S$ , there would be no doubling of the heads; if they involved a change in  $\sigma_k$  (e.g.  ${}^2S \rightarrow {}^2P$  or  ${}^2P \rightarrow {}^2D$ ), strong  $Q$  branches should be present, giving quadruple heads as in the NO $\gamma$  or CO $^+$  comet-tail bands.

In conclusion we wish to thank Professor E. C. Kemble for valuable suggestions and for the interest he has taken in this work.

JEFFERSON PHYSICAL LABORATORY,  
HARVARD UNIVERSITY,  
WASHINGTON SQUARE COLLEGE,  
NEW YORK UNIVERSITY,  
April, 1927.

<sup>47</sup> R. C. Johnson, Proc. Roy. Soc. **105A**, 683 (1924); V. M. Ellsworth and J. J. Hopfield, Phys. Rev. **29**, 79 (1927); etc.

<sup>48</sup> R. S. Mulliken, Phys. Rev. **26**, 334 (1925).

