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THE NEAR INFRARED SPECTRUM OF NITRIC OXIDE

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Nathan Lankford Nichols

AN ABSTRACT

Submitted to the School of Graduate Studies of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements

for the degree of

DOCTOR OF PHILOSOPHY

Department of Physics and Astronomy

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ABSTRACT

A study has been made of the overtone rotationvibration absorption bands of nitric oxide occurring in the near infrared. Complete rotational analysis was possible for the 2-0 and 3-0 bands but not for the 4-0 band as the envelope only was obtained. The infrared data confirms the data from the electronic transitions involving the ground state.

An absorption cell containing a multiple traverse mirror system of the J. U. White type was constructed with the mirrors separated 35 centimeters. The absorption cell was used in conjunction with a vacuum infrared spectrograph built by R. H. Noble which consisted essentially of a rock-salt fore-prism monochromater and a plane grating to provide the dispersion for the lead sulfide photoconducting detector.

The 2-0 and 3-0 bands were obtained with absorbing paths of about four meter-atmospheres. The 4-0 band required an absorbing path of about 60 meter-atmospheres. The ground state of NO is a doublet II state and each branch of a band consists of two components. It was possible to resolve the P components for both overtone bands, but not all the R components.

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Careful reduction of the data gave values for the rotational constants as: $B_0 = 1.6965 \text{ cm}^{-1}$; $B_2 = 1.6631 \text{ cm}^{-1}$; and $B_3 = 1.6408 \text{ cm}^{-1}$. The equilibrium rotational constant B_e was determined as 1.7060 cm⁻¹ which gave the equilibrium moment of inertia I_e as 16.404 x 10⁻⁴⁰ gm-cm² and the equilibrium separation of the atoms as 1.1503 x 10⁻⁸ cm. The band origins were determined as 3724.16 cm⁻¹ and 3723.48 cm⁻¹ for the two components of the 2-0 band, and as 5544.28 cm⁻¹ and 5543.69 cm⁻¹ for the two components of the 3-0 band.

There were no evidences of any extreme perturbations to the rotational structure of the NO molecule nor was there any evidence of a transition from one coupling scheme to another. It is felt that the molecular constants presented here are more representative of the molecule than those previously determined from the electronic data and from the infrared fundamental band.

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by

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INTRODUCTION

General

Nitric oxide is a colorless, slightly heavier-thanair gas which is toxic in very small quantities and poisonous in moderate quantities. Upon exposure to air, it immediately becomes reddish-brown nitrogen dioxide (NO_2) , which is also a poisonous gas. The nitric oxide molecule is diatomic (NO), has a molecular weight of 30.01 and the sum of the atomic numbers is 15. Its normal freezing and boiling points are -161.0°C and -151°C.

Nolecular constants for the nitric oxide molecule have been determined from fine structure analyses of the electronic transitions occuring in the ultraviolet, but only the fundamental vibration transition has been done with sufficient rotational fine-structure resolution to yield these constants. The object of the present work has been to investigate the rotational fine structure of as many of the vibrational overtones as possible to re-evaluate the rotational constants for the ground state and to determine these constants for the upper vibrational states. A critical re-examination of the electronic data involving transitions to the ground state has been carried through and calculations have been made using the electronic data in order to determine the rotational constants. The presently accepted vibrational constants for NO, computed largely from the electronic data, have been checked against the results of the present work.

History of NO Spectra

The infrared spectrum of NO was first observed by Warburg and Leithauser¹ when they obtained the envelope of the fundamental rotation-vibration band and located its center at 5.3 microns. In 1929, Snow, Rawlins, and Rideal² were able to resolve 42 lines in both P and R branches of the fundamental but apparently used only six lines in each branch in determining the rotational constants. Their work on the first overtone³ confirmed the existence of F, Q, and R branches but gave no measurable quantities. In 1939, two papers appeared dealing with the fundamental band of NO, one by Nielsen and Gordy,⁴ the second by Gillette and Eyster.⁵ The rotational constants for NO accepted by Herzberg⁶ are taken from the work of Gillette and Eyster, which seems to be the most thorough infrared work done on NC to date.

The electronic transitions have been studied in great enough detail to make NO one of the best known molecules. In this present work, only the transitions involving the ground state are of interest as they provide a check on the

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data from the infrared transitions. The electronic systems involving the ground state are known as the γ , β , β' , ξ , and ϵ systems and are described later. In the following references to these electronic systems, only those are included for which a rotational anaylsis was made, and which have actually been used here. The γ system was first studied in detail by Guillery, ⁷ then redone by Schmid,⁸ who published 30 pages of tables giving frequencies, combination differences, and other constants. Two years later, Schmid, König, and Farkas⁹ reviewed the two earlier works, redid some of the bands and obtained new bands and recomputed all the combination differences and rotational and vibrational constants. Two new γ bands and one γ band reviewed appeared several years later in a paper by Gerö and Schmid.¹⁰

The first comprehensive study of the β bands was by Jenkins Barton, and Wulliken¹¹ who published the rotational lines for 18 different bands and computed combination differences and empirical coefficients. Schmid, König, and Farkas⁹ included in their comprehensive study a re-evaluation and some additional work on the β bands. The β system has been studied, but only the band head frequencies have been published, so are of no value here. The ϵ system has been analyzed by Gerö, Schmid, and von Szily¹² and by Gaydon,¹³ although they were able to obtain only four bands in the two investigations.

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THEORY

Ground State of Nitric Oxide

Most diatomic molecules have an even number of electrons (e.g. CO, N₂, H₂, HCl, etc.), indicating that the total electron spin S of the molecule must be zero or integral, since the electron spin unit is $\frac{1}{2}(h/2\pi)$. Since the resultant electronic orbital angular momentum vector L could be 0, 1, 2, etc., it can be seen that the lowest possible energy state, or ground state, for a molecule having an even number of electrons, would involve zero spin and zero orbital angular momentum, resulting in what is called a Σ state which is a singlet state.

The nitric oxide molecule is the only stable diatomic molecule to have an odd number of electrons (15) indicating that the resultant spin, and therefore its projection on the internuclear axis Σ , must be half-integral. Since this spin vector can combine with Λ , the projection of L on the internuclear axis, in either of two directions, the ground state of NO must be a doublet state, or ${}^{*}\Pi_{1/2}$, ${}^{*}\Pi_{3/2}$ state, indicating a Λ value of 1. The separation of the two substates is 121 cm⁻¹.

Vector Models

If the rotation of the molecule about a perpendicular to its internuclear axis is considered along with the above discussion of electronic orbital angular momentum and spin, it becomes possible to combine in several different modes the vectors for the total electronic orbital angular momentum L (and therefore its projection on the internuclear axis Λ), the total electron spin S, and the angular momentum of nuclear rotation N, all of which combine to give a final resultant J which is fixed in space. This was first done by Hund, so the different coupling schemes are known as Hund's cases "a", "b", "c", etc.

In case "a" coupling, ¹⁴ the electronic and nuclear rotations are weakly coupled in such a manner that the total spin vector S is coupled to the internuclear axis (see figure 1a) and combines with the electronic orbital angular momentum vector \mathbf{A} to form a resultant $\mathbf{\Omega}$ which in turn combines with the nuclear rotation vector N to give a final resultant J which is the total angular momentum of the molecule including electron spin. Since J is constant in magnitude and direction, the internuclear axis must rotate about this vector (nutation) and the vectors L and S must precess about the internuclear axis. (The precession of L and S is much faster than the nutation of the axis about J for case "a" coupling).



b. Case D Coupling

Figure 1.

In case "b" coupling, the revolution of the nucleii about a common center is enough greater so that the spin vector S no longer couples with the internuclear axis but instead couples to the resultant of the electronic orbital angular momentum vector \mathbf{A} and the nuclear rotation vector N. This resultant of \mathbf{A} and N is called K and is illustrated in figure 1b. The resultant of K and S is J, the total angular momentum of the molecule and is represented by a vector which is fixed in space. (The nutation of \mathbf{A} about K is much faster than the precession of K and S about J). The nitric oxide molecule is between cases "a" and "b", although for low rotation, it has practically pure case "a" coupling.

Potential Curves

The total energy of a diatomic molecule is determined by both the kinetic and the potential energies, where the potential energy depends upon the internuclear separation of the two atoms, which in turn depends upon the vibration of the molecule. Since the vibration of a diatomic molecule is essentially that of an anharmonic oscillator, the usual potential "well" for the simple harmonic oscillator must be modified, as was first done by Morse. to better fit the observed data. Geydon¹⁵ has developed the potential wells for NO as shown in figure 2. The state labeled X is the ground state, the one of primary interest here. The



Figure 2.

ground state actually consists of two potential curves separated by 121 cm⁻¹, making the separation too small to be shown with the scale used. Transitions from the X ²II ground state to the A ²X⁺ state give the electronic γ bands; to the B ²II state give the electronic β bands; to the C ²X⁺ state give the electronic ϵ bands; and to the D ²X⁺ state give the electronic ϵ bands. The dissociation limits are shown at the right. The present problem has been to investigate the absorption transitions from the zero vibrational level of the X ²II ground state to the 2, 3, 4, and 5 vibrational levels within this same ground state. All of these transitions occur in the near infrared spectral region.

Since the molecule is rotating at the same time it is vibrating, the rotational levels are superposed on the vibrational levels, just as the vibrational levels are superposed on the electronic levels. The vibrational transitions from any upper vibrational level to a lower level will show, if there is sufficient resolution, rotational fine structure, an analysis of which leads to the rotational constants of the molecule.

Hill and VanVleck Energy Relations

Hill and VanVleck¹⁶ have derived an expression for the energy of a molecule which is intermediate between cases "a" and "b" which may be written, neglecting the small term f(K, J-K), as:

$$T_{1}(J,v) = T_{e}+G_{1}(v)+B_{v}\left\{ (J+\frac{1}{2})^{2}-1+(-1)^{1}\left[(J+\frac{1}{2})^{2}-A/B_{v}+A^{2}/4B_{v}\right]^{\frac{1}{2}} \right\}$$

-D_{v}J^{2}(J+1)^{2}+\cdots eq 1

in which T_i represents the total energy term value, J is the rotational quantum number, v the vibrational quantum number, T_e the term value for the equilibrium position, B_v a rotational constant which is inversely proportional to the moment of inertia of the molecule and approximately half the separation of successive rotational levels (and one of the important constants to be determined here), A the separation of the two substates. The ratio A/B gives a measure of the type of coupling, a large number indicating case "a", a small value, case "b". D represents the centrifugal stretching term, which arises because of the nonrigidity of the rotating molecule. When i is 1, equation 1 refers to the first component, ${}^{*}\Pi_{1/2}$; when i is 2, the equation refers to the second component, ${}^{*}\Pi_{3/2}$. The subscript i is also added to the vibrational energy term G(v), since the two substates are not necessarily identical. Since NO is represented by almost pure case "a" coupling, it is possible to make expansions of the Hill and VanVleck relation which represent the energy adequately:5 $T_1 = T_e - A/2 + G_1(v) + B_v(1)/4 + B_v(1)J(J+1) - D_v(1)J^2(J+1)^* + \cdots$ eqs 2 $T_2 = T_e + A/2 + G_2(v) - 7B_v(2)/4 + B_v(2)J(J+1) - D_v(2)J^2(J+1)^2 + \cdots$

The constants of equations 2 are related to those of equation 1 by: $F_{v} = \left[B_{v}(1) + B_{v}(2)\right]/2 \quad \text{and} \quad D_{v} = \left[D_{v}(1) + D_{v}(2)\right]/2 \quad \text{eq 3}$ (i.e. the averages of the B_{v} and D_{v} values for the two components).

The actual transitions would involve the difference between two such terms as given in equations 2 with different T_0 values for the electronic transitions, different v values for the vibrational transitions, and different J values for rotational transitions. For example, in the NO 3-0 rotation-vibration band in the near infrared (the band done in the most detail here), the two terms would belong to the same electronic system so T_0 would drop out; one term would have v equal to three, the other v equal to zero; and J would assume all possible half-integral values within the restrictions set up by the selection rules that ΔJ can be zero or plus or minus one.

F, Q, and R Branches

The rotational fine structure of a vibrational band consists of three branches, the so-called F, Q, and R branches, which correspond to the selection rules J'-J'' =-1, J'-J'' = 0, and J'-J'' = +1, respectively, where J' is the upper state, and J'' is the lower state. The numbering of the lines of the three branches is determined by the lower state level (e.g. F(3/2) is a transition from J' = 1/2to J'' = 3/2, etc.). Figure 3 shows the transitions involved in these three branches. The fact that NO has a



resultant electronic angular momentum along the internuclear axis causes it to be the only stable diatomic molecule to exhibit a Q branch in the infrared, since for a ${}^{1}\Sigma$ ground state (as found in most molecules) the transition $\Delta J = 0$ is forbidden. For the ${}^{2}\Pi_{3/2}$ component, the first R line, R(1/2) and the first P line, P(3/2), are missing since, for the second component, the lowest J levels in the upper and lower states are J = 3/2.

The structure of the NO molecule corresponds essentially to a symmetric top with the two moments of inertia about an axis perpendicular to the internuclear axis equal and very much greater than the moment of inertia about the internuclear axis. The wave equation solution for the symmetric top then should be sufficient for NO if modified to account for the facts that the NC molecule is also vibrating and (due to this vibration) is a non-rigid rotator. The wave equation for the symmetric top was first solved by Reiche and Rademacher¹⁷ and by Kronig and Rabi¹⁸ giving for the rotational term values the following:

 $F(J) = BJ(J+1)+(A-B)A^{2}$ eq 4 in which $A = h/(8\pi^{2}cI_{A})$ and $B = h/(8\pi^{2}cI_{B})$. I_{A} is the moment of inertia about the internuclear axis and I_{B} is the moment of inertia about a line perpendicular to the internuclear axis. Since I_{B} is very much larger than I_{A} , the value of B is very much smaller than A.

To account for the non-rigidity of the molecule, a centrifugal stretching term $-8DJ^{*}(J+1)^{*}$ has to be added to equation 4, and since this non-rigidity (caused by vibration) is different for different vibrational levels, the B and D of equation 4 must be replaced by effective values B_{v} and D_{v} which are slightly different for different vibrational levels. Equation 4 then becomes:

 $F_V(J) = B_V J(J+1) + (A-B_V) \Lambda^2 - D_V J^2 (J+1)^2 + \cdots$ eq 5 The term containing Λ^2 is constant for any one vibrational level, and the infrared spectrum occurs within one electronic system, so this term may be ignored provided $F_V(J)$ is understood to be the rotational term value measured from the rotational level having J = 0 (rather than the lowest J value of 1/2 in the case of NO).

For the determination of the rotational constants this relatively simple relation is adequate in place of the Hill and VanVleck relation of equations 2, since these constants are based on differences between values in upper and lower states, which means that electronic and vibrational pecularities cancel.

The actual rotational transitions will yield frequencies (in cm^{-1}) for the P, Q, and R branches of:

$$\begin{split} \mathbb{P}(J) &= \boldsymbol{v}_{0} + \mathbb{F}_{\mathbf{v}}^{*}(J-1) - \mathbb{F}_{\mathbf{v}}^{*}(J) = \boldsymbol{v}_{0} - (\mathbb{B}_{\mathbf{v}}^{*} + \mathbb{B}_{\mathbf{v}}^{*})J + (\mathbb{B}_{\mathbf{v}}^{*} - \mathbb{B}_{\mathbf{v}}^{*})J^{*} \\ \mathbb{Q}(J) &= \boldsymbol{v}_{0} + \mathbb{F}_{\mathbf{v}}^{*}(J) - \mathbb{F}_{\mathbf{v}}^{*}(J) = \boldsymbol{v}_{0} + (\mathbb{B}_{\mathbf{v}}^{*} - \mathbb{B}_{\mathbf{v}}^{*})J + (\mathbb{B}_{\mathbf{v}}^{*} - \mathbb{B}_{\mathbf{v}}^{*})J^{*} \\ \mathbb{R}(J) &= \boldsymbol{v}_{0} + \mathbb{F}_{\mathbf{v}}^{*}(J+1) - \mathbb{F}_{\mathbf{v}}^{*}(J) = \boldsymbol{v}_{0} + 2\mathbb{B}_{\mathbf{v}}^{*} + (3\mathbb{B}_{\mathbf{v}}^{*} - \mathbb{B}_{\mathbf{v}}^{*})J + (\mathbb{B}_{\mathbf{v}}^{*} - \mathbb{B}_{\mathbf{v}}^{*})J^{*} \\ J \text{ is the rotational quantum number for the lower state, and} \end{split}$$

 \mathbf{V}_{0} is the band origin or zero line, corresponding to the (unrealizable) transition J' = 0 to J'' = 0.

The P and R branches actually form a single series according to the relation:

$$\mathbf{V} = \mathbf{V}_0 + (\mathbf{B_V}^* + \mathbf{B_V}^*)\mathbf{m} + (\mathbf{B_V}^* - \mathbf{B_V}^*)\mathbf{m}^*$$
 eq 7
where m is -J for the P branch and m is J+1 for the R
branch. The P and R lines of any one of the NO vibrational
bands form a single series with two missing lines at the
positions for which m would be -1/2 and +1/2. These would
correspond to P(1/2) and R(-1/2) which of course are non-
existent. The second component has a gap in the center
with four missing lines at m = -3/2, -1/2, +1/2, and +3/2
since for this component there is no P(3/2) line and no
R(1/2) line. The lines set closer together in passing
through the P branch toward the center and on into the R
branch. This direction of convergence, which is called
degrading toward the red in this case, is caused by the
fact that $\mathbf{B_V}^*$ is greater than $\mathbf{B_V}^*$ for NC. This convergence
is shown in the spectrogram for the 3-0 band, figure 12.

Determination of B_{v} "

While it would be possible to determine the rotational constants of equation 7 (and therefore equations 6) by getting an empirical relation of the form $\mathbf{V} = \mathbf{a} + \mathbf{b}\mathbf{m} + \mathbf{c}\mathbf{m}^2$, where the a, b, and c correspond to the constants in equation 7, more accurate results are had by obtaining the upper and

lower state constants separately by a method using the socalled combination differences. The lower state constant, B_V ", may be found from the combination differences formed by subtracting the frequencies (in cm⁻¹) of the P lines from the frequencies of the R lines which have the same upmer state levels. Thus, the first R line, R(1/2), has the same upper level as the second P line, F(5/2); the second R line R(3/2) has the same upper level as the third P line, F(7/2), etc. Figure 4a shows that the difference between these corresponding R and P lines gives the separation of alternate rotational levels in the lower state -- (e.g. the first R line frequency minus the second F line frequency gives the separation of the two lower state levels with J = 1/2 and J = 5/2). This combination difference relation may be written as:

 $\Delta_{2} F''(J) = R(J-1) - P(J+1) = F_{v}''(J+1) - F_{v}''(J-1). \quad eq 8$

By substituting the values for F_v from equation § into equation 8, the following relation is obtained:

$$\Delta_{2} F''(J) = \left[B_{V}''(J+1)(J+2) - D_{V}''(J+1)^{2}(J+2)^{2} \right]$$

$$- \left[B_{V}''(J-1)J - D_{V}''(J-1)^{2}J^{2} \right] \qquad eq 9$$

which reduces to:

$$\Delta_{2} \mathbf{F}^{"}(\mathbf{J}) = (4B_{\mathbf{v}}^{"}-6D_{\mathbf{v}}^{"})(\mathbf{J}+\frac{1}{2})-8D_{\mathbf{v}}^{"}(\mathbf{J}+\frac{1}{2})^{3}. \quad eq \ 10$$

Since $D_{\mathbf{v}}$ " is very much smaller than $B_{\mathbf{v}}$ ", it may be neglected in the first term of equation 10, giving:

 $\Delta_{2} \mathbf{F}^{"}(\mathbf{J}) = 4 \mathbf{B}_{\mathbf{V}}^{"}(\mathbf{J} + \frac{1}{2}) - S \mathbf{D}_{\mathbf{V}}^{"}(\mathbf{J} + \frac{1}{2})^{3}. \qquad \text{eq 11}$

If the value of D_v is known from other sources, such as the



Figure 4.

data of the electronic transitions, the last term, $8D_v(J+\frac{1}{2})^3$, may be added to the left hand member so that the slope of the curve of the new left hand member plotted against $J+\frac{1}{2}$ will give directly $4B_v$ ". If D_v " is negligible (as was found to be true for NO for the first component), then, of course, the second term of equation 11 may be omitted.

A second method for determining B_v " would be to average the values of $\left[\Delta_2 F^*(J) + 8D_v(J + \frac{1}{2})^3\right]/4(J + \frac{1}{2})$ for the individual cases. However, a method which gives more accurate results than either of those mentioned, is to assume an approximate B_v " value, $\widetilde{B_v}$ ", which is close to the expected value, and then make use of the equation:

 $\Delta_2 F''(J) = (4B_v''+4\Delta B_v'')(J+\frac{1}{2})-8D_v(J+\frac{1}{2})^3 \quad eq 12$ in which the B_v'' of equation 11 has been replaced by $\widetilde{B_v''}+\Delta B_v''$. Rearranging then gives:

 $\Delta_2 \mathbf{F}^*(\mathbf{J}) - 4 \widetilde{\mathbf{B}}_{\mathbf{V}}^* "(\mathbf{J} + \frac{1}{2}) + 8 \mathbf{D}_{\mathbf{V}} (\mathbf{J} + \frac{1}{2})^3 = 4 \Delta \mathbf{B}_{\mathbf{V}}^* (\mathbf{J} + \frac{1}{2})$ eq 13 The subtraction of the term $4 \widetilde{\mathbf{B}}_{\mathbf{V}}^* "(\mathbf{J} + \frac{1}{2})$ from the left hand member of equation 11 allows plotting to a much larger scale and gives, from the slope, the corrective term $\Delta \mathbf{B}_{\mathbf{V}}^*$ which, when added to $\widetilde{\mathbf{B}}_{\mathbf{V}}^*$, results in the true value of $\mathbf{B}_{\mathbf{V}}^*$.

The above procedure is applied in the same manner to both the ${}^{*}\Pi_{1/2}$ and ${}^{*}\Pi_{3/2}$ components yielding two different values with the second value larger than the first. The average of these two values gives the true B_{v} " with the splitting effect due to the resultant electronic angu-

lar momentum about the internuclear axis removed; that is, it gives the value for rotation only, without any electronic effects.

Determination of B_{v} '

The upper state rotational constants are determined by a similar graphical means except that the combination differences used here must be the difference between the frequencies of R lines and T lines having a common lower state level. Thus, the second R line, R(3/2), minus the first P line, F(3/2), gives the separation of the upper levels for which J equals 1/2 and 5/2. Figure 4b shows the method by which the separation of alternate levels in the upper state is obtained. Equation 8 for the upper

 $A_2F'(J) = R(J)-P(J) = F_v'(J+1)-F_v'(J-1)$. eq 14 When the values for F_v' are substituted from equation 5 into equation 14, the resultant equation is identical to equation 9, which reduces to equation 10, except, of course, the superscripts must now refer to the upper state.

The determination of B_v ' then becomes the same as for B_v ". Equations 11, 12, and 13 all apply to the treatment of the combination differences, and the slope of the graph again determines the correction ΔB_v ' to be added to the approximate $\widetilde{B_v}$ ' to get the true B_v '. Two values are obtained, one for each component as before, with the second

component value the larger. Again the average of the two component values gives the true rotational constant with the electronic influence removed.

Determination of B_e, \propto_e , I_e , and r_e

After the B_v values are obtained for two or more vibrational states, it then becomes possible to determine the equilibrium constant, B_e , from the relation:

$$B_v = B_e - \alpha_e(v + \frac{1}{e}) \qquad eq 15$$

where $\boldsymbol{\alpha}_{e}$ is a measure of the change in the rotational constant B_{v} with changes in vibration, and B_{e} is given by the relation:

 $B_{e} = h/(8\pi^{2}cI_{e}) = h/(8\pi^{2}c\mu r_{e}^{2})$ eq 16

where I_e is the moment of inertia for the equilibrium separation of the two atoms, c is the velocity of light, h is Planck's constant, and μ is the reduced mass of the NO molecule (in grams) and is equal to the product divided by the sum of the individual masses of the two atoms. The usual method for determining B_e is to plot the various B_v values against $(v + \frac{1}{2})$, the Y intercept giving directly B_{Θ} , and the slope giving ee. An examination of equation 5 in which the small D_v term is neglected, $[F_v(J) = B_v J(J+1) + \cdots]$, shows that the difference between two energy term values, each given by this equation, one with J = 3/2, the other with J = 1/2, gives $3B_v$. This constant (B_v) could then be defined as one-third the separation of the first two NO rota-

tional levels. It usually is defined as one-holf the separation of the rotational levels with J = 1 and J = 0, which, of course, has no significance for NO with its halfintegral values of J.

Once the value of B_e has been determined, the computation of the equilibrium moment of inertia is a simple matter, using the first part of equation 16. From the value of the moment of inertia, the internuclear equilibrium distance may then be determined from:

$$I_e = \mu r_e^*$$
. eq 17

Electronic Confirmation of Infrared Data

The NO combination differences can be checked from any rotational fine structure data involving the ground state and having the proper vibrational level. For example: B_0 " could be determined from any of the following sets of combination differences: 1-7, 2-0, 3-0, 4-0, etc. bands of the infrared; also the 1-0, 2-0, 3-0, etc. bands of <u>any</u> of the electronic transitions involving the ground state, such as the γ , β , β , and ϵ systems. B_3 ' could be determined from the combination differences of any of the above electronic systems involving the ground state with the lower vibrational level v = 3, such as the 0-3, 1-3, 2-3, 3-3, 4-3, etc. bands. B_2 ' could be checked by electronic bands involving 0-2, 1-2, 2-2, etc. transitions to the ground state.

Band Origins

Of the various vibrational constants, the only ones of real interest in this problem are the band origins for the 3-0 and 2-0 bands. The band origin represents the energy level term value for the upper state which has the rotational quantum number zero. In the case of NO, the band origin has no physical significance, since the lowest J value is one-half. It also represents the energy involved in the unrealizable transition between J = 0 in the upper state and J = 0 in the lower state.

A band origin could be determined from the relations of equations 6 using the values for the frequencies of the F and R lines and setting up as many equations as the number of known lines. This would obviously be a tedious task and would require a precise knowledge of the rotational constants.

The usual (and much simplier) way to determine the band origin is a graphical method making use of combination sums which involve only the frequencies of the lines and does not require an exact knowledge of the rotational constants. The combination sums needed involve the addition of the frequencies (in cm⁻¹) of corresponding P and R lines, the first P plus the first R; the second P plus the second R, etc. Substituting from equations 6, the combination sums simplify to the following:

 $R(J-1)+F(J) = 2p_0+2(B_v'-B_v'')J^2$. eq 18
A rlot of the left hand member against J^2 gives $2V_0$ as the Y intercept. A refinement which adds much to the accuracy of the result is to assume an approximate value for $(B_v'-B_v'')$ which is close to the expected value and then make use of the relation:

 $R(J-1)+P(J) = 2\nu_0+2\left[(B_v'-B_v'')+\Delta(B_v'-B_v'')\right]J^2$ eq 19 in which the $B_v'-B_v''$ of equation 18 has been replaced by an approximate value plus a corrective term shown in the brackets of equation 19. Rewriting equation 19 and dividing by 2 gives:

 $\frac{1}{2} [R(J-1)+P(J)-2(\overline{B_V}'-B_V'')J^2] = V_0 + \Delta(B_V'-B_V'')J^2 . eq 20$ The left hand member can now be plotted to a much larger scale and the Y intercept gives the band origin directly. Actually the effect of non-rigidity, the D correction, should add a corrective term involving $(D_V'-D_V'')$ to the above, but for NO, the D values for the different vibrational states are practically identical and the term may be neglected.

AFFARATUS

Multiple Traverse Mirror System

<u>Construction of mirror mountings</u>. In absorption spectroscopy, there are two ways of increasing the amount of absorption, one by increasing the length of the light path in the gas, the other by increasing the pressure. Both methods effectively increase the number of gas molecules encountered by the beam of light. But increasing the pressure causes "pressure broadening" of the lines and the resolution of the lines is lowered. Increasing the path length has obvious physical limitations. However, it is possible to get a long path length in a short tube by using an ingenious multiple reflection system of concave mirrors originally devised by White.¹⁹

The multiple traverse mirror system as used here consists of three mirrors with identical radii of curvature, one of 4 3/4 inch diameter with two ledges cut from its edge as shown in figure 5b, the other two formed by sawing a 4 3/4 inch mirror in two as shown in figure 5c. The mirrors are mounted within a 6 1/2 inch brass cylinder, as shown in figure 6, at a distance of 35.7cm apart, this distance being the radii of curvature of the mirrors. The top of the cylinder is cut to facilitate visual observation dur-



Figure 5



Figure 6. Absorption Cell

ing adjustment of the mirrors. The mirrors themselves are mounted on brass rings held to the cylinder with Allen screws. The front mirror (figure 7a) has one-half inch notches cut from each side above the center to allow the beam of light to enter and leave the system. The cuts were made with a diamond impregnated rock saw made available by the Geology Department. The mirror is supported at three points by six soft-solder-tipped screws, to give adjustment from either face of the mirror. The back "half" mirrors are supported on aluminum semicircular supports as shown in figure 8. These in turn are mounted on a three-sixteenths inch steel rod fastened to a brass ring which just fits within the cylinder. The steel rod coincides with the pole of the mirrors when they are adjusted to have the same center of curvature. Screws through the brass ring, plus spring tension, allow the adjustment of the rotation of the mirrors about the steel post, (figure 7b).

<u>Optical alignment</u>. The optical arrangement is shown in figure 5a for the simple case of four traversals. A source placed at S_1 forms an image at S_2 on the edge of the mirror ledge as shown in figure 5b. With the center of curvature of half-mirror A at C_A , the cone of light 1 reflects as cone 2 from the mirror A and converges to point S_3 which is as far below the center of the mirror as S_2 is above. Foint S_3 then is a source giving cone 3 which reflects from mirror B as cone 4, converging to S_4 . Finally, S_5 repre-



Figure 7. Absorption Cell Mirrors

sents the slit of the spectrograph. The extreme upper and lower parts of the mirrors octually are not used. In the initial adjustment, cone 1 of light is made large enough to slightly overlap mirror B, giving a faint image which falls outside the front mirror beyond S_4 , greatly facilitating the adjustment of mirror B.

If the mirrors A and B are rotated so that their centers of curvature C_A and C_B are closer together, the number of traversals is increased in steps of four with the distance between these two points always giving twice the separation of successive images either above or below the center. Figure 5d shows the conditions for 16 traversals with the numbers by the images representing the number of traversals of the light beam. In this case, the separation of the centers C_A and C_B would be twice the separation of two images such as 6 and 10. It is not necessary to have the images below the center spaced exactly between the ones above the center; in fact, the final adjustments have always been made with mirror A only.

Since the initial beam enters the mirror system far off axis, the astigmatism is very great, causing a vertical enlargement. This actually is a welcome feature, allowing a point source to give a vertical image to illuminate the slit of the spectrograph.

There are two limiting factors restricting the number of traversuls in this type of optical system. First, there



Figure 8. Half-mirror Mountings

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is a loss of energy at each reflection (e.g. a 5% loss on each of 100 reflections would result in a final image having an intensity of only about 0.6 of 1% of the initial intensity!). The second limiting factor is the minimum separation of images 0 and 4 (figure 5d). If the edge of the ledge is rough or chipped, or if the source does not give a narrow image, some intensity will be lost.

Absorption cell. The cylinder containing the mirror system is so fixed that it slides into a second, larger, seven inch cylinder (the absorption cell itself), as shown in figure 6b. This outer cylinder is fitted with two legs at the back and one at the front, all three being adjust-The front face is equipped with two two inch diameable. ter cuartz windows to allow the light to enter and leave, and a half-inch brass tube leading to a brass-to-glass tapered joint connected to a mercury manemeter and a stopcock, the stopcock in turn being connected to a vacuum pump. The manometer is fastened to the cell itself so that the cell may be moved without danger of breaking the glass tubing. The absorption cell is made vacuum-tight by means of a brass disk at the back end, which fits over a collar having a groove with an eight inch neoprene "O" ring. The back is held on by means of six large machine screws. A half-inch brass tube with a brass-to-glass tapered joint connects the back of the cell to the cylinder containing the gas.

The nitric oxide gas was obtained from the Matheson Gas Company and was claimed by them to be better than 99 percent pure. The chief impurity was found to be nitrous oxide (N_20) . The gas was used without further purification, although it was found that upon standing for several weeks in the brass absorption cell, it gradually deteriorated, presumably into N_20 .

Vacuum Infrared Spectrograph

Optical alignment. The vacuum infrared spectrograph was designed and constructed by Dr. Robert H. Noble²⁰ and consists essentially of the following parts: rock salt prism to serve as a monochrometer; grating to give the diffraction; lead sulfide detector to detect the radiation from the grating; amplifier and recorder to give a permanent record of the absorption spectrum; plus the necessary mirrors used in conjunction with the prism and grating.

Referring to figure 9, the initial slit S_1 corresponds to the final image S_5 from the absorption cell (figure 5a) and is the entrance slit to the monochromator section of the spectrograph. This slit lies just within the wall of the steel vacuum chamber which houses the spectrograph proper (see figure 10). The cone of light from the slit S_1 reflects from the plane mirror M_1 to the off-axis parabaloidal collimating mirror M_2 (of six inch diameter), which is placed so that S_1 is at its principal focus, the focal







Figure 10. Spectrograph with Absorption Cell

length of M_2 being 49.7 centimeters. The parallel light from M_2 strikes the rock salt prism which acts essentially as a monochromator passing only a small band of wave lengths and eliminating the troublesome over-lapping of several different orders. The prism is of the Littrow type with the back side aluminized to effectively double the prism angle, and to return the light very nearly along its incident path.

The parallel light returning to M_2 is de-collimated and focussed at the slit S_2 . This slit is both the exit slit of the monochromator section, and the entrance slit to the spectrograph section of the instrument. If all the light traveled through the monochromator as horizontal rays, a straight entrance slit S_1 would produce a straight image in the plane of the exit slit. However, some of the light enters the prism at a slight angle to the horizontal and travels farther through the prism material than a similar horizontal ray. Thus, the prism angle "seems" greater to this oblique ray and a curved image results. This effect is minimized by using a very short slit.

The large plane mirror M_4 has a three-fourths inch hole in its center which allows the cone of light from S_2 to pass through to the parabaloidal mirror M_3 . Since the incident and reflected beams have the same axis, the pole of the mirror M_3 is at its center and not near the edge as with M_2 . The distance from S_2 to M_3 is the focal length of M_3 (100.4 centimeters), so the beam is collimated by M_3 , returns to

the plane mirror M_4 , and is reflected to the grating. The mirrors M_3 and M_4 have diameters of eight inches. Figure 9 shows the grating in position for the central image.

The parallel beam of light coming from the grating is reflected from plane mirror M_5 (identical to M_4) to parabaloidal mirror M_{6} (identical to M_{3}) which decollimates the beam and focusses it through the hole in M_5 onto the slit S_3 , which is the exit slit for the grating section. The slit S3 is at the far focal point of an ellipsoidal mirror M_7 so that the cone of light from S_3 is re-focused to the detector placed at the near focal point of the ellipsoidal mirror. The ellipsoidal mirror has a diameter of six inches and focal lengths of 7.7 centimeters and 40 centimeters. It has been found that the sensitized area of the lead sulfide detector (about 1.5mm^2) used in all the present work is large enough so that the ellipsoidal mirror can be eliminated and the sensitive surface placed directly at the position S3. The chief advantage in using the ellipsoidal mirror is to diminish the size of the image in going from the far to the near focal points. This ratio would be the ratio of the focal lengths, viz. 40 to 7.7. In using a thermocouple detector, where the radiation must fall on a very small area, the ellipsoidal mirror would be a necessity.

Rotation of prism and grating. The prism is rotated by means of a Selsyn motor mounted inside the spectrograph tank and controlled by a similar motor mounted outside the



tank behind the control panel and connected to a mechanical counter. The Selsyn inside the tank is lubricated with vacuum oil to avoid the high vapor pressure of ordinary motor oil. The prism measures three and one-half by five inches for its aluminized back, and is approximately a 30-60-90 degree triangle. In measuring the 3-0 band, it has been found that there are no over-lapping orders in the region of sensitivity of the lead sulfide detector, and that the prism can be replaced by a plane mirror.

The grating is also rotated by means of a Selsyn motor mounted inside the spectrograph tank, and controlled from outside. The grating circle is so arranged that two gratings placed back to back may be used interchangeably, without opening the vacuum tank, by simply rotating the entire mount 180 degrees. A cam on the worm gear driving the grating circle actuates a micro-switch which discharges a condenser in such a way as to put a "pip" on the recorder paper for each revolution of the worm gear, corresponding to a tenth of a degree of rotation of the grating. This pip has very greatly facilitated the calibration of the instrument and the analysis of the spectrograms. The grating may be rotated at six different speeds by means of gears, each successive speed being 1/6, 1/6, 1/6, 1/4, and 1/4 of the preceding speed. These six values correspond to grating rotations of 1080, 180, 30, 5, 1.25, and 0.3125 minutes of arc per minute of time. It is interesting to note that the

gears causing the slowest rotation would require approximately 48 days for a complete revolution, whereas at the fastest speed a complete revolution may be had in a matter of 20 minutes. A mechanical counter is attached to the control panel indicating the rotation in one-hundredths of a degree.

Two plane gratings have been used with the instrument so far, one 1800 lines per inch, the other 7200 lines per inch. The 1800 grating has a useable surface area of six by eight inches, implying a total number of lines of about 14,000. It is blazed at 27 degrees so was used in the higher orders so as to take advantage of the glaze. The 7200 grating is on loan from the University of Michigan by the courtesy of Dr. E. F. Barker and has a useable surface area of four by five inches. It is blazed at 15 degrees which fortunately corresponds to the 3-0 region of nitric oxide in the first order.

Detector, amplifier, and recorder. The electronic circuit associated with the detector consists essentially of three parts, a pre-amplifier, a 10-cycle tuned amplifier, and a lock-in amplifier. The beam of light entering the spectrograph at the entrance slit is "chopped" by a sectored circle which allows light to pass half the time, the successive pulses being one-tenth of a second apart. The detector, then, receives 10-cycle pulses of light which have passed through the spectrograph. The pre-amplifier



is placed as close to the detector as possible, outside the vacuum tank, so as to make possible short lead wires to minimize stray pick up. The second component is a conventional plate-tuned amplifier which is designed to pass only the 10-cycle signal. The chopper has a small flashlight-size bulb and a photocell attachment connected so that the photocell receives 10-cycle pulses of light of the same duration as those received by the detector.

The third component contains three additional stages of amplification, a phase-splitter stage, and a lock-in amplifier stage. The lock-in stage consists of two double tubes (6SN7's), the first of which has the two cathodes tied together and with one grid connected to the chopper photocell, and the second connected through the amplifiers to the detector. The first grid receives a 10-cycle square wave pulse from the chopper, the second a 10-cycle signal upon which is superposed the variations caused by the grating. The two plates of this tube are connected to the two grids of another 6SN7. The cathodes of this second tube are tied together, as are their plates. Therefore, if the two grids receive signals that are out of phase, each will nullify the other. However, if the two grids receive signals that are in phase, the two will add and amplification will result. This implies that the first of the above tubes must have signals on the two grids that are in phase, or that the square wave signal from the chop-

per must be in phase with the signal from the detector. Stray noise that is not in phase with the chopper signal will be minimized, since the lock-in amplifier will pass a signal only during the half of each cycle that the chopper is allowing light to enter the spectrograph. The lockin amplifier is connected through a resistive-capacitive filter to a Leeds and Northrup Speedomax recorder which has a paper speed of one-half inch per minute.

The detector itself is a lead sulfide photo-conducting tube which has a small area that is exposed to the radiation. A 45 volt battery causes a very small current to flow through the high resistance of the lead sulfide surface. This current changes as the conductivity of the surface changes due to variations in the light beam coming from the grating. These fluctuations in current cause changes in voltage which are amplified by the above-mentioned amplifiers. The detector is many times more sensitive at low temperatures so is cooled by running chilled acetone through the brass block supporting the cell. This acetone "pump" is self-acting, the acetone running in to the detector by gravity. As it warms slightly, some of the dissolved carbon dioxide from the dry ice comes out of solution causing bubbles which actually force the acetone above its original level and back into the container holding the dry ice.

Vacuum tank. The vacuum tank which holds the spectrograph proper is essentially a steel cylinder 42 inches in diameter and about six feet long with the ends rounded, (volume of about 55 cubic feet). It is sliced in a horizontal plane about eight inches above the center and fitted with flat steel pieces, one of which contains a rectangular groove. A square neoprene gasket fits into the groove and provides the vacuum seal. The tank is supported at three points on a cement pier with two additional supports which contact the cement only when the heavy lid is open. The lid is raised by an electric motor about its hinge, which runs along one side of the tank, as may be seem at the extreme right of figure 10.

The inside of the tank is criss-crossed with steel supports at the top and bottom, the bottom cross pieces acting as the supports for the aluminum table upon which the optical system is fastened. This table is approximately three feet by five feet and one inch thick with one and one-half inch channel aluminum around the four edges. It is supported at only three points, these points being directly above the points of support of the tank. This coincidence of supporting points is necessary, as evacuating the tank causes some distortion, and changes in the optical alignment must be avoided. The connecting wires to the Selsyn motors, chopper, etc. are sealed through the side of the tank, as are the tubes which supply the cold acetone

to the detector. The vacuum tank window is a circular piece of quartz fastened with piecine to the flat end of a section of 2 inch brass pipe which has a tapered thread and screws into the side wall of the tank. The tank is evacuated with a megavac pump which pumps out most of the air and water vapor in a matter of a half hour. Up to the present time, it has not been found necessary to install a diffusion pump, although one would be necessary if an extremely high percentage of water vapor were to be removed.

Absorption cell positioning. The initial alignment of the entire system, absorption cell and spectrograph, is done as follows: the inner cylinder containing the mirrors is removed, and its adjustment made out in the room where the images formed on the front mirror can be seen. The mirror system is then replaced in the absorption cell. Next. a small source (such as an auto head light) is placed inside the spectrograph somewhere along the optical axis of the spectrograph. With no lenses in the system, the absorption cell is moved until the beam from this source enters at the proper angle. The real source is then placed in line with this beam where it emerges from the absorption cell. The lenses are then positioned and the final adjustments are made on them with no further changes in the mirrors.

EXPERIMENTAL DETAILS

3-0 Band

The 3-0 band which was known to be near 1.8 μ was obtained by adjusting the mirror system to 40 traversals and the NO pressure to about 25 centimeters of mercury, giving an absorbing path of about $4\frac{1}{2}$ meter-atmospheres. With the slits set at 20 microns (0.4 cm⁻¹) the absorption was about 15-20 percent.

The source used for this region was a Western Union 100 watt concentrated zirconium oxide arc operated at 6.25 amperes. Since this type of arc has a negative temperature resistance coefficient, it was necessary to insert a large ballast resistor in series with the arc. A large inductance coil (actually a heavy-duty auto-transformer) was placed in series with the arc in an attempt to minimize fluctuations in the current. The total voltage drop was about 80 volts from the D C generators, approximately 60 volts being the drop in the ballast resistors. The glass envelope around the arc was air cooled. Since the arc operated in an atmosphere of argon, the argon emission lines were present on every spectrogram, aiding in the analysis.

With the grating rotating at speed 6 (0.3125 minutes of arc per minute of time), the linear dispersion on the

recorder paper was about 0.0002 degree per millimeter, corresponding to about 0.08 cm⁻¹ per millimeter. It was possible under the conditions used to get lines in the P and R branches out to J values of 37/2.

This spectral region at 1.8 μ was favorable in three respects: the 7200 lines per inch grating was blazed at 15 degrees which corresponded to 1.8 μ in the first order; the 100 watt concentrated arc source had its maximum radiation at 1.6 μ ; and the lead sulfide detector had very high sensitivity in this region.

Figure 12 shows a typical 3-0 spectrogram taken at a fairly fast grating speed making the spectrogram more easily photographed. The doubling of the lines due to the doublet nature of the ground state is evident for all the lines of the P branch and for some in the R branch. The ${}^{s}\Pi_{1/2}$ component can easily be identified by its relatively greater intensity. In the spectrograms actually measured, taken at slower grating speeds, the doublets were resolved for all J values beyond 13/2 in the R branch and for all the P lines. Only the envelope of the Q branch was obtained. High orders of well known visible argon and neon lines were superposed on the spectrograms to aid in the calibration. It was necessary to have the neon source off at one side and to use a hinged mirror so that the beam from the neon replaced that through the NO gas only in regions where known neon lines existed, as determined by prelimin-





ary trials. The NO lines missing in these regions were then determined from another tracing on the spectrogram taken without superposing the neon.

2-0 Band

The 2-0 band at 2.69 μ presented difficulties because of the fact that glass becomes opaque beyond about 2.7 μ . It was found that the best results for the R branch were obtained with the 100 watt concentrated arc using the 7200 grating, but that it was necessary to change to a carbon arc and to the 1800 grating for the P branch.

For the R branch, the spectrograph slits were set for 50 microns, corresponding to 0.4 cm⁻¹ with the 7200 grating, and the absorption cell was set for 40 traversals with the pressure at 14 centimeters of mercury. With the grating rotating at speed 5 (1.25 minutes of arc per minute of time), the linear dispersion on the recorder paper was about 0.0008 degree per millimeter or 0.11 cm⁻¹ per millimeter. It was possible to get R lines with good resolution to J values of 139/2. Figure 13 shows a typical spectrogram of the 2-0 R branch but at a faster grating rotation speed than used on the spectrograms measured. It is readily seen that the glass envelope on the source became opaque soon after passing through the Q branch.

In order to obtain the P branch of the 2-0 band, it Was necessary to change all the glass lenses and the win-





dows on the absorption cell and the spectrograph to quartz, and to eliminate the glass surrounding the source by using a carbon arc. It was also found that better results were obtained with the 1800 grating which was used in the fifth order to take advantage of its blaze at 27 degrees. With the 1800 grating it was necessary to use the fore-prism monochromater. With the slits set at 200 microns $(\frac{1.3}{6.4} \text{ cm}^{-1})$, it was possible to get P lines out to J values of 33/2 before the thin glass envelope on the lead sulfide detector became completely opaque.

4-0 Band

In an attempt to resolve the 4-0 band at 1.36 μ , an estimate was made from the absorption in the 3-0 band as to the necessary absorbing path. This was of the order of 100 meter-atmospheres to give even 5-10 percent absorption. The mirrors were adjusted for 100 traversals and the pressure was increased to almost two atmospheres, giving an effective absorbing path of about 60 meter-atmospheres. Since this region was off the blaze of the 7200 line grating, it was necessary to open the slits to 400 microns (15 cm⁻¹) to get much indication of absorption. Figure 14 is a tracing made from a spectrogram and shows that the en-, Velope of the 4-0 band only was obtained . Two argon emission lines from the 100 watt arc, one on each side of the band, aided in the location of its center at 7337 cm⁻¹.





4-0 Envelope of NO at 1.36, Slit 400.

5-0 Band

An attempt was made to obtain the 5-0 band in the photographic infrared region at 1.10 μ , but with the absorption cell mirrors silver-plated and set for 120 traversals and the NO pressure at two atmospheres (an absorbing path of about 80 meter-atmospheres), no absorption was evident even with 48 hour exposures. The spectrograph used for this part was a photographic, concave-grating instrument built by C. F. Clarke.²¹ Its concave grating is an original made by R. W. Wood and has a radius of curvature of 100 centimeters. It has 30,000 lines per inch over a two inch by four inch surface. The grating was used in an Eagle mount on a Rowland circle of one meter diameter. The photographic plates were Eastman Z plates which were hyper-sensitized with a 4 percent ammonia solution immediately before exposure in the spectrograph. The background fogging was found to be rather intense, so that the time of exposure had to be limited.

RESULTS AND DISCUSSION

Wave Numbers for the 3-0 and 2-0 Bands

The determination of the actual wave number for a line involved knowing the angle through which the grating rotated in giving the line. This can be seen from the grating equation:²²

$$\pm n\lambda = d(\sin \alpha + \sin \beta)$$
 eq 21

in which n is the order number, d is the separation of successive grating rulings, d is the angle of incidence, and β is the angle of diffraction.

In the Noble spectrograph, the directions of the incident and diffracted light remain fixed in space and the grating is rotated. In Figure 15 the grating is shown in the pos-



Figure 15. Grating Equation Angles

ition for the central image by the dotted lines and rotated through an angle Θ by the solid lines. N₀ is the normal for the central image and N is the normal for the grating after being rotated through the angle Θ . From the figure it can be seen that $\mathbf{d} = \Theta - \beta_0$, and that $\boldsymbol{\beta} = \Theta + \boldsymbol{\beta}_0$. With these substituted into equation 21, and the usual expansion of the sine of the difference of two angles and the sine of the sum of two angles, the grating equation becomes:

$$\pm n\lambda = 2d\cos\beta_0\sin\theta$$
 eq 22

from which the wave number becomes:

$$\mathcal{V} = 1/\lambda = n/(2\cos\beta_0\sin\theta) = K_{\nu}/\sin\theta$$
 eq 23

The angle of rotation of the grating for each line was determined as follows: One of the "pips" near one end of the spectrogram was selected as the zero meter stick reading and the number of millimeters to each of the spectral lines from this zero was observed and recorded. The counter on the spectrograph indicated the number of degrees (or tenths of a degree, since the pips were one-tenth of a degree apart)from the zero meter stick reading to the pip mearest to the central image. For the 3-0 band this was a bout 15 degrees: for the 2-0 it was about 22 degrees for the 7200 grating and 29 degrees for the 1800 grating. The Strating angle for the 4-0 band with the 7200 grating was a bout 11 degrees. The linear dispersion in degrees per millimeter was then computed by dividing the linear disance on the recorder paper into the number of degrees be-
tween the pips used. Averaged values were always used. The spectrograph counter reading corresponding to the central image was then computed from this linear dispersion. and the distance from several pips to the central image. With the counter reading for the central image known, a simple subtraction then gave the accurate angle from the central image to the pip which was taken as the zero meter stick reading (i.e. the angle of grating rotation for the zero meter stick reading was then known). The linear dispersion in degrees per millimeter was then used to determine the angles from the meter stick zero to each line and these were added to the angle of grating rotation for the zero of the meter stick, so that the results then gave the angles of grating rotation from the central image to each of the lines on the spectrogram. It was then a simple matter to look up the sines of the angles.

The grating constant for each line was determined from a graph of $K_{\mathcal{V}}$ vs. Θ where the values of $K_{\mathcal{V}}$ were determined from the spectrograms of mercury, neon, and argon in this region. Most of these lines were higher orders of wellknown visible lines so that the \mathcal{V} 's were accurately known and with the angles Θ determined as above, equation 23 gave the values of $K_{\mathcal{V}}$. Equation 22 would indicate that $K_{\mathcal{V}}$ should be the same for all angles of rotation of the grating; however, it was found that there was a periodic variation occurring with a period of one degree caused by the

worm gear which drove the wheel upon which the grating was mounted. The teeth on the wheel are one degree apart, so with the shaft of the worm gear very slightly off-axis, the periodic error was introduced, necessitating the correction graph. The sines of the angles for each line divided into their grating constants (equation 23) then gave the wave numbers of the lines.

It was noted that the humidity of the air was an important factor in the linear dispersion of a spectrogram as the paper stretched noticibly on moist days. However, if all readings were taken at one time, this introduced no error.

Table I shows the wave numbers for the 3-0 band, the ${}^{2}\Pi_{1/2}$ lines being labeled R_{1} and P_{1} and the ${}^{2}\Pi_{3/2}$ lines being labeled R_{2} and P_{2} . The parentheses indicate that the R lines were unresolved for J values up to 13/2. Although the envelopes of most of these unresolved lines showed asymmetry, only those for which the two peaks were visible were actually separated into the two components. Three of the R_{2} lines (19/2, 21/2, and 25/2) were masked by amplifier noise so were omitted. It was discovered that maximum resolution was obtained for the P branch lines on a spectrogram dated 4-7-53, whereas maximum resolution for the R lines occurred on a spectrogram dated 5-29-53. Since the P line frequencies for the spectrogram dated 5-29-53 were higher on the average by 0.39 cm⁻¹ than the corresponding lines on the spectrogram

TABLE I

WAVE NUMBERS FOR 3-0 BAND

.

(R components are from spectrogram dated 5-29-53) (P components are from spectrogram dated 4- 7-53)

J+1	R ₁ (J)	P 1(J)	R ₂ (J)	P ₂ (J)
1	5548.81			
2	(5551.81)*	5538.95	(5551.81)*	
3	(5554.79)	5535.69	(5554.79)	5534.80
4	(5557.81)	5532.19	(5557.81)	5531.11
5	(5560.63)	5528.40	(5560.63)	5527.30
6.	(5563.41)	5524.64	(5563.41)	5523.44
7	(5565.97)	5520.80	(5565.97)	5519.39
8	5568 .26	5516.80	5568.51	5515.28
9	5570 .64	5512.53	5570.92	5510.78
10	5572.71	5508.22		5506.50
11	5574.88	5503.88		5502.03
12	5576.89	5499.46	5577.43	5497.49
13	5578.92	5494.92		5492.85
14	5580.71	5 49 0.13	5581.18	5488.03
15	5582.43	5485.57	5582.90	5483.13
16	5584.01	5480.48	5584.52	5478.03
17	5585.41	5475.41	5585.80	5472.90
18	5586.79	5470.50	5587.30	5467.51
19	5588.04	5465.30	5588.51	5 462. 32

*Two R components unresolved. Maximum of unresolved Q1 and Q2 branches at 5543.0

0.19 cm⁻¹ from the R lines and adding 0.20 cm⁻¹ to the P lines as they were computed from their separate spectrograms.

Table II shows the wave numbers for the 2-0 band, the parentheses indicating that the two R components were unresolved for values of J up to 25/2. It was impossible to resolve the first of the F lines. The P lines were obtained from a spectrogram dated 2-21-52 for which the 1800 lines per inch grating and the 100 watt concentrated arc were used. The R lines were obtained from a spectrogram dated 2-8-53 for which the 7200 lines per inch grating and the **carbon** arc were used. As was mentioned previously, it was possible to measure R lines out to J values of about 139/2, but P lines only to about 33/2.

Upon comparing the data from the 3-0 and 2-0 bands and making use of Gillette and Eyster's data on the 1-0 band,⁵ it was discovered that the average separation of the two F components was greatest in the 3-0 band, less in the 2-0 and least in the 1-0 band; also that the separation of the R components was least in the 3-0 band, more in the 2-0, and greatest in the 1-0 band. This would indicate that a grating with much greater resolution would be necessary if an attempt is to be made to obtain the fine structure of the 4-0 R branch.

TABLE II

WAVE NUMB	ERS FOR	2-0	BAND
-----------	---------	-----	------

(P components from spectrogram 2-21-53 using 1800 grating) (R components from spectrogram 2- 8-53 using 7200 grating)

J+≵	R _l (J)	P ₁ (J)	R ₂ (J)	P ₂ (J)
1	3729.10		9000	
2	(3732.09)*	3719.28	(3732.09)*	
3	(3735.14)	(3715.71)*	(3735.14)	(3715.71)*
4	(3738.18)	3712.63	(3738.18)	3711.85
5	(3741.10)	3708.93	(3741.10)	3707.87
6	(3744.26)	3704.88	(3744.26)	3703.67
7	(3746.96)	3700.97	(3746.96)	3699.77
8	(3749.66)	3697.26	(3749.66)	3696.08
9	(3752.37)	3693.29	(3752.37)	3692.01
10	(3755.11)	3689.37	(3755.11)	3687.92
11	(3757.56)	3685.18	(3757.56)	3683.75
12	(3760.01)	3681.07	(3760.01)	3679.29
13	(3762.39)	3676.95	(3762.39)	3675.13
14	3764.83	3672.87	3765.63	3670.93
15	3767.02	3668.59	3767.74	3666.60
16	3769.25	3664.09	3770.07	3661.98
17	3771.23	3659.86	3771.83	3657.54

*Two components unresolved. Maximum of unresolved Q_1 and Q_2 branches at 3724.0

Rotational Constants

Evaluation of B_0 . The combination differences $\Delta_2 F(J) = R(J-1)-P(J+1)$ which were used to determine B_0 " for both components are shown in Table III for the 3-0 and 2-0 bands. The average of the 3-0 and the 2-0 bands for each component is also given in Table III with the 3-0 values having been given a weight of two and the 2-0 values a weight of one, since the 3-0 data, in general, was much better than the 2-0. The parentheses indicate the combination differences which involve unresolved R lines.

Figure 16 shows the graphical solution of equation 13 for $B_0"(1)$ in which $\widetilde{B_0}(1)$ was taken as the final value proposed here for $B_0"(1)$, namely 1.6706 cm⁻¹, and D_0 was considered negligible. With the approximate value equal to the final value, the slope, or $4\Delta B_0$, is zero and the line becomes horizontal. Also shown in Figure 16 are the results from Gillette and Eyster for the fundamental⁵ and from Gerö and Schmid for the electronic γ 1-0 and 2-0 bands.¹⁰ The dotted line in the 1-0 graph represents the line corresponding to Gillette and Eyster's final value, 1.6696 cm⁻¹. Beyond the first few points the scattering in the 3-0, 2-0 data is less than for either of the other two. All three lines represent the best fit through the zero ordinate as determined by least squares calculations.

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TABLE III

B₀ COMBINATION DIFFERENCES

(R	lines	from	spectrogram	5-29-53:	Ρ	from	4-7-53)
1 * *	1100	T T Om	opoour ogrum	0-22-00,	•	T T OW	1 00

J+ _춘	∆ ₂ F ₁ (3-0)	∆ 2 ^F 1 (2-0)	▲ ₂ F1 (Avg)ª	▲ ₂ F ₂ (3-0)	▲2 ^F 2 (2-0)	▲ ₂ F ₂ (Avg)
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18	$13.12 (19.62)^{b} (26.39) (33.17) (39.83) (46.61) (53.44) 60.04 66.76 73.25 79.96 86.76 93.35 100.23 107.02 113.51 120.11$	13.39 (19.46) (26.21) (33.30) (40.13) (47.00) (53.67) (60.29) (67.19) (74.04) (80.61) (87.14) (93.80) 100.74 107.16	13.21 19.57 26.33 33.21 39.93 46.74 53.52 60.12 66.90 73.51 80.18 86.89 93.50 100.40 107.07 113.51 120.11	(20.70) ^b (27.49) (34.37) (41.24) (48.13) (55.19) 62.01 68.89 89.40 103.15 110.00 117.01 123.48	(20.24) ^b (27.27) (34.51) (41.33) (48.18) (54.95) (61.74) (68.62) (75.82) (82.43) (89.08) (95.79) 103.65 110.20	20.55 27.42 34.42 41.27 48.15 55.11 61.92 68.80 75.82 82.43 89.35 95.79 103.32 110.07 117.01 123.48
	A		· · · · ·			

a(3-0) values given weight 2; (2-0) given weight 1. ^bTwo R components unresolved.

TABLE IV

Bo	INFRARED	AND	ELECTRONIC	VALUES
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B ₀ (1)	B ₀ (2)	Bo	Source
1.6680	1.7222	1.6951	Infrared 3-0
1.6762	1.7207	1.6985	Infrared 2-0
1.6706	1.7224	1.6965	Infrared 3-0,2-0 ^a
1.6696	1.7200	1.6948	Infrared 1-0
1.6703	1.7182	1.6943	Electronic 7 1-0,2-0
1.6706	1.7239	1.6973	Electronic 7 0-0,1-0



Figure 16.

The first column of Table IV gives a comparison between the $B_0(1)$ values from the infrared data and the values determined from the electronic data. It is to be noted that the 3-0 $B_0(1)$ alone is lower than the others and that the value from the 2-0 band alone is higher than the others but that the average of the 3-0 and 2-0 is about the same as the other three.

A graph of equation 13 using the electronic γ 1-0, 2-0 data of Gerö and Schmid (not included here) shows that for values of J up to about 59/2, the centrifugal stretching term D_o is negligible. Beyond this value, the curvature suddenly becomes great enough to indicate the possibility of an additional term involving $(J+\frac{1}{2})^5$ in equations 11 and 13. This would indicate the addition of a cubic term $H_{\nu}J^3(J+1)^3$ to equation 5 with H_{ν} of opposite sign to D_{ν} .

The centrifugal stretching term $D_0(2)$ is not a negligible quantity so was computed from the 71-0, 2-0 electronic data of Gerö and Schmid using equation 13 with B_0 as 1.65 cm⁻¹. Figure 17 shows the results for J values to 69/2 and the influence of this centrifugal stretching can be seen to be appreciable. A least squares fit of equation 13 to the points indicated a value for $D_0(2)$ of 6.63 x 10⁻⁶ wave numbers. Similar graphs and least squares calculations (not shown here) for the electronic \notin 0-2 band of Gerö, Schmid, and von Szily¹² gave $D_2(2)$ as 6.88 x 10⁻⁶ cm⁻¹. The same treatment of the electronic \notin 0-3 band of Gerö,



Schmid, and von Szily¹² gave $D_3(2)$ as 6.85 x 10⁻⁶ cm⁻¹. In all the computations involving $D_v(2)$, the value was taken as 7 x 10⁻⁶ cm⁻¹. The fact that D_0 , D_2 , D_3 are all practically identical indicates that β_e in the relation $D_v = D_e + \beta_e(v+\frac{1}{2})$ is negligible, or that D_v is practically constant.

Figure 18 shows equation 13 plotted for $B_0^{*}(2)$ with \widetilde{B}_0 as 1.65 cm⁻¹ and $D_0(2)$ as 7 x 10⁻⁶ cm⁻¹. The solid line is for the combined 3-0, 2-0 infrared data and the three broken lines represent the infrared fundamental and two electronic results. Table III shows that the average Δ_2F_2 for J values of 21/2, 23/2, and 27/2 are from the 2-0 band only and for J values of 33/2 and 35/2 are from the 3-0 band only. These five points are shown in figure 18 with small horizontal lines through the circles designating the points, and all five were omitted in determining the final $B_0^{*}(2)$. Figure 18 illustrates that the 3-0, 2-0 curve matches well the infrared 1-0 curve of Gillette and Eyster and the γ 0-0, 1-0 curve of Schmid, König, and Farkas.⁹ The γ 1-0, 2-0 curve of Gerő and Schmid¹⁰ is seen to have a lesser slope.

The values of $B_0(2)$ determined from the slopes of these four curves are given in the second column of Table IV. The final B_0 values are given in column 3 of Table IV and indicate that the infrared 3-0, 2-0 value agrees as well with the electronic data as the electronic data agrees among itself.



Figure 18.

Evaluation of B_3 . The combination differences $\Delta_2 F(J) = R(J) - P(J)$ from the 3-0 data are given in Table V for both the ${}^2\Pi_{1/2}$ and the ${}^2\Pi_{3/2}$ components. Again, the numbers in parentheses indicate values computed from R lines for which the resolution was incomplete. The three combination differences for J values of 19/2, 21/2, and 25/2 are missing in the second component since amplifier noise obscured the R lines for these values (see Table I).

Figure 19 gives the graphical solution of equation 13 for the 3-0 determination of the first component of B_3 with a value of 1.54 cm⁻¹ for \widetilde{B}_3 and with $D_3(1)$ considered negligible. The solid line represents a least squares fit of points used to determine the ΔB_3 from which the final value of $B_3(1)$ was calculated as 1.6150 cm⁻¹. The dotted line represents the electronic $\in 0-3$ data of Gerö, Schmid, and von Szily¹² and also the β and γ electronic data of Schmid, König, and Farkas.⁹ The two electronic lines would be practically coincident so have not been drawn separately.

Table VI, column 1, shows a comparison of the final $B_3(1)$ values for the infrared 3-0 with the corresponding electronic values. The two electronic values agree but are appreciably higher than the 3-0 value. However, the points on the 3-0 graph show very much less scatter than either of the electronic curves (not shown here). The \in 0-3 graph shows $D_3(1)$ to be negligible for the low J values needed in this present analysis.

]+ [₽]	$\Delta_2 F_1(J)$	$\Delta_2 \mathbf{F}_2(\mathbf{J})$
2	(12.86)*	
3	(19.10)	(19.99)*
4	(25.62)	(26.70)
5	(32•23)	(33.33)
6	(38.77)	(39.97)
7	(45.17)	(46.58)
8	51.46	53.23
9	58.11	60.14
10	64.49	
11	71.00	
12	77.43	79 .94
13	84.00	
14	90.58	93.15
15	96.86	9 9.77
16	103.53	106.49
17	110.00	112.90
18	116.29	119.79
19	122.74	126.19

TABLE V

B₃ COMBINATION DIFFERENCES

*Two R components unresolved.

TABLE VI

B3(1)	B3(2)	B ₃	Source
1.6150	1.6665	1.6408	Infrared 3-0
1.6193	1.6651	1.6422	Electronic β , γ
1.6199	1.6629	1.6414	Electronic C 0-3

B3 INFRARED AND ELECTRONIC VALUES





Figure 20.

Figure 20 represents a least squares fit of [R(J)-P(J)]-4 $\widetilde{B}_3(J+\frac{1}{2})+8D_3(J+\frac{1}{2})^3$ plotted against $(J+\frac{1}{2})$ from the 3-0 data for the second component. \widetilde{B}_3 was taken as 1.60 cm⁻¹ and $D_3(2)$ as 7 x 10⁻⁶ cm⁻¹, giving the solid line. The broken lines represent the electronic data of Schmid, König, and Farkas⁹ and Gerö, Schmid, and von Szily.¹² The 3-0 infrared line is seen to have a slightly steeper slope than the two electronic lines.

The second column of Table VI gives the values for $B_3(2)$ and column 3 gives the final B_3 values. It should be noted that the 3-0 component 1 value is lower than the electronic values, but that the component 2 value is higher, so that the average or final B_3 agrees well with the final electronic B_3 .

Evaluation of B_2 . Table VII gives the combination differences for the 2-0 data from which the values of $B_2(1)$ and $B_2(2)$ were found. The parentheses show that only four values of the combination differences and therefore only four points on the curves of figures 21 and 22 involve R lines which were completely resolved. However, the line of figure 21 for the first component shows very little scatter of points after the first few. Component 2 (figure 22) shows considerable scatter and the first two points are far enough from the final curve that they were omitted in the least squares calculation of $B_2(2)$. The values used in solving for the ordinates are shown on the two graphs. The solid

J+2	$\Delta_2 \mathbb{F}_1(J)$	$\Delta_2 \mathbf{F}_2(\mathbf{J})$
2 3 4 5 6 7 8 9 10 11 12 13 14 15	$(12.81)^*$ (19.43) (25.55) (32.17) (39.38) (45.99) (52.40) (59.08) (65.74) (72.38) (78.94) (85.44) 91.96 98.43 105.16	(19.43)* (26.33) (33.23) (40.59) (47.19) (53.58) (60.36) (67.19) (73.81) (80.72) (87.26) 94.70 101.14 108.09
17	111.37	114.29

TABLE VII

B₂ COMBINATION DIFFERENCES

	_		
*Two	R	components	unresolved.

TABLE VIII

B. INFRARED	AND	ELECTRONIC	VALUES
2	-		

B2(1)	B ₂ (2)	B ₂	Source
1.6406	1.6855	1.6631	Infrared 2-0
1.6390	1.6808	1.6599	Electronic € 0-2
1.6342	1.6869	1.6606	Electronic B , Y (4 bands averaged)

.



Figure 21.



lines represent the infrared 2-0 data and the dotted lines represent the electronic \in 0-2 data of Gerö, Schmid, and von Szily.¹² The electronic β and γ data of Schmid, König, and Farkas⁹ shows so much scatter of points when plotted as in figures 21 and 22, that no corresponding lines have been inserted on the two graphs.

Table VIII shows a comparison of the $B_2(1)$, and $B_2(2)$, and B_2 values, as determined from the infrared 2-0, with the two electronic studies. The final B_2 value is slightly higher then either of the two electronic values.

Evaluation of B_e, α_e , I_e , and r_e . Figure 23 shows a plot of equation 15: $B_v = B_e - \alpha_e'(v + \frac{1}{2})$ in which B_o , B_2 , and B_3 are from the infrared 3-0 and 2-0 bands and the points B_6 through B_{13} are from the electronic β study of Jenkins, Barton, and Mulliken.¹¹ A least squares fit of these nine points, all taken with equal weight, determined B_e (the Y intercept in figure 23) as 1.7060 cm⁻¹, and α_e (the slope) as 0.01797 cm⁻¹. A separate determination was made using only the data from the present investigation with B_o given a weight of three, B_2 given a weight of one, and B_3 given a weight of three, B_2 given a weight of one more reliable than the 2-0 data. Since B_0 involved both the 3-0 and 2-0 data, it was given a weight of three. B_e determined from this infrared data was 1.7060 cm⁻¹, identical to



that determined using all nine points. The slope, however, was slightly larger, being 0.01834 cm⁻¹. The final values proposed for B_e and e are 1.7060 cm⁻¹ and 0.0180 cm⁻¹ and are shown in Table X compared with those presently accepted as taken from Gillette and Eyster.⁵ It is to be noted that the 3-0, 2-0 values are larger than the ones proposed by Gillette and Eyster. Their curve was based on the same six electronic points and two of their own infrared 1-0 points (B_0 and B_1). Since their B_0 value was slightly lower than the 3-0, 2-0 value, it would be expected that their B_e and e would be smaller.

Once B_e was known, equation 16 readily gave I_e , the equilibrium moment of inertia, and from the moment of inertia, the equilibrium distance r_e was computed. These quantities are shown in Table X along with those proposed by Gillette and Eyster. Table IX gives the B_v results for both components and the average B_v values that were used in figure 23.

Vibrational Constants

<u>3-0 band origins</u>. The combination sums R(J-1)+P(J)formed from the 3-0 data are shown in Table XI for the ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$ components. The numbers in parentheses again indicate combinations involving R lines for which the resolution was not complete. A plot of the left hand member of equation 20 against J^{2} gives the graphs shown in

TABLE :	IX
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Bo TO B13 INFRARED AND ELECTRONIC VALUES

v	B _V (1)	B _V (2)	B _v	Source
0	1.6706	1.7224	1.6965	Infrared 3-0,2-0
2	1.6406	1.6855	1.6631	Infrared 2-0
3	1.6150	1.6665	1.6408	Infrared 3-0
6	1.5649	1.6063	1.5856	Electronic $oldsymbol{eta}$
7	1.5539	1.5966	1.5753	Electronic ß
8	1.5382	1.5711	1.5547	Electronic $oldsymbol{eta}$
11	1.4744	1.5269	1.5007	Electronic /3
12	1.4639	1.4916	1.4778	Electronic $oldsymbol{eta}$
13	1.4469	1.4812	1.4641	Electronic $oldsymbol{eta}$

TABLE X

.

	Infrared 3-0, 2-0	Infrared 1-0 (Plus Electronicβ)
Be	1.7060	1.7046 cm ⁻¹
¢¢e	0.0180	0.0178 cm ⁻¹
Ie	16.404×10^{-40}	$16.423 \times 10^{-40} \text{gm cm}^2$
re	1.1503	1.1508 A

B. C. I. AND r. VALUES

J ² -1/4	$R_1(J-1)+P_1(J)$	$R_2(J-1)+P_2(J)$
2	11087.76	
6	(11087.50)*	(11086.61)*
12	(11086.98)	(11085.90)
20	(11086.21)	(11085.11)
30	(11085.27)	(11084.07)
42	(11084.21)	(11082.80)
56	(11082.77)	(11081.25)
72	11080.79	11079.29
90	11078.86	11077.42
110	11076.59	
132	11074.34	* • • •
156	11071.81	11070.28
182	11069.05	
210	11066.28	11064.31
240	11062.91	11060.93
272	11059.42	11057.42
306	11055.91	11053.31
342	11952.09	11049.62

TABLE XI

3-0 COMBINATION SUMS

*Two R components unresolved.

TABLE XII

3-0	BAND	ORIGINS	

3-0 (1)	3-0 (2)	Source
5544.28	5543.69 cm ⁻¹	Infrared 3-0
5544.21	5543.35 cm ⁻¹	Gillette, Eyster eq.6

figure 24, one for each of the two components. For the ${}^{2}\Pi_{1/2}$ component, the first five points (J² from 2.25 through 30.25) are so far from the straight line formed by the others that they were omitted in the least squares computation of the band origin (Y intercept). The fact that these few points are not regular is supported by all the previous data for the B_v quantities in which the first few points are all slightly off the straight line formed by the others. The ${}^{2}\Pi_{3/2}$ component does not show this peculiarity so all the points were included in the least squares squares determination of this band origin.

The two straight lines, when plotted together as in figure 24. should be parallel and therefore should have the same slope. It is seen that there is a gradual divergence as J^2 increases, which apparently must be attributed to experimental error. Since the data for the first component is better than that for the second, it would seem that the origin for the ${}^{2}\Pi_{1/2}$ substate is accurate, but that the line for the ${}^{2}\Pi_{3/2}$ substate has too steep a slope and that the origin for this component is too low. This interpretation was substantiated by computing the band origins from the two relations given by Gillette and Eyster⁵ as equation 6. Reference to Table XII shows that the first component band origin agrees almost exactly with the computed value, but that the second component origin is much larger than the computed origin.



Figure 24.

2-0 band origins. Table XIII gives the combination sums for the 2-0 data with the parentheses showing that only three of the sums were derived from completely resolved R lines. Figure 25 shows two graphs of equation 20 from which the band origins were determined as the Y intercepts. The two lines, as determined by a least squares fit of the points in each case, are practically parallel, although the scatter of the individual points is fairly great. For the second component, the first two points would have been far from the straight line determined by the other points so were omitted both on the graph and in the computations. Table XIV shows the band origins as determined from the infrared 2-0 data and as computed from equation 6 of Gillette and Eyster. The agreement for each component is exceptionally good.

<u>4-0 band origins</u>. Since the envelope only of the 4-0 band was obtained, it was, of course, impossible to determine the two band origins. However, the envelope of the Q branch was visible on the spectrogram and the argon emission lines on either side of it made it possible to locate the Q branch quite accurately at 7337 cm⁻¹. It will be necessary to build a longer absorption cell in order to get enough absorption to show any rotational fine structure for this band.

20	COMPINATION	SUMS
2-0	COMBINATION	DOMD

J ² -1/4	$R_1(J-1) + P_1(J)$	$R_2(J-1)+P_2(J)$
2	7448.38	****
2 6	(7447.80)*	(7447.80)'
19	(7447.77)	(7446.99)
20	(7447.11)	(7446.05)
20	(7445,98)	(7444.77)
30 4 0	(7445,23)	(7444.03)
4 6 50	(7×10^{-10})	(7443.04)
20	(7332000)	(7441.67)
72	(7 <u>44</u> 6070) (844) ⁻ 84	(7440, 29)
90		(7438,86)
110	(7440.29)	(7400000)
132	(7438.63)	
156	(7436.96)	(7400•14) (8488 80)
182	(7435.26)	(7433.32)
210	7433.42	7432.23
240	7431.11	7429.72
272	7429.11	7427.61

*Two R components unresolved.

TABLE XIV

2-0 BAND ORIGINS

2-0 (1)	2-0 (2)	Source
3724.16	3723.48 cm ⁻¹	Infrared 2-0
3724.22	3723.51 cm-1 .	Gillette, Eyster eq.6



 ω_e , $\omega_e x_e$, and $\omega_e y_e$. The term values for the anharmonic oscillator relating to the various vibrational energy levels are given by the relation:²³

 $G(\mathbf{v}) = \omega_{e} (\mathbf{v} + \frac{1}{2}) - \omega_{e} \mathbf{x}_{e} (\mathbf{v} + \frac{1}{2})^{2} + \omega_{e} \mathbf{y}_{e} (\mathbf{v} + \frac{1}{2})^{3}$ eq 22 in which ω_{e} , $\omega_{e} \mathbf{x}_{e}$, and $\omega_{e} \mathbf{y}_{e}$ are constants with the first much larger than the second and the second very much larger than the third. The difference between two such terms with a v value of zero for one gives the vibrational band origin. It can be seen that a determination of these three constants is possible only if several of the band origins are known. Gillette and Eyster, in their note-worthy study, used the electronic $\boldsymbol{\beta}$ data of Jenkins, Barton, and Mulliken¹¹ for v values of four to ten, and determined these three constants, arriving at the following relations for the components:

$$G_{1}(\mathbf{v}) = 1904.03(\mathbf{v}+\frac{1}{2})-13.97(\mathbf{v}+\frac{1}{2})^{2}-0.00120(\mathbf{v}+\frac{1}{2})^{3}$$

$$G_{2}(\mathbf{v}) = 1903.68(\mathbf{v}+\frac{1}{2})-13.97(\mathbf{v}+\frac{1}{2})^{2}-0.00120(\mathbf{v}+\frac{1}{2})^{3}$$
eq 23

Since these were the equations used to check the infrared 3-0 and 2-0 band origins, and since the agreement is very close, it would seem that the Gillette and Eyster values for ω_e , $\omega_e x_e$, and $\omega_e y_e$ are accurate.

Conclusion

During this entire study of the NO vibrational bands in the near infrared, there were no evidences of any ex-

treme perturbations to the rotational structure of the molecule. There also was no evidence of any noticeable transition from one coupling scheme to another. It is felt that the molecular constants presented here are more representative of the molecule than these previously determined from the electronic data and from the infrared fundamental investigation of Gillette and Eyster.

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