THE FIRST AND SECOND OVERTONE BANDS OF $N^{15}O$ IN THE NEAR INFRARED

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ABSTRACT

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by Sister Mary Dominic McNelis, O. P.

The 2-0 and 3-0 absorption bands of $N^{15}O$ have been observed in the near infrared at 2.7 and 1.8 microns respectively by means of a vacuum recording infrared spectrometer. A system of Edser-Butler bands, obtained with a Fabry-Perot etalon and recorded simultaneously with the absorption spectra, was used as a calibration system for this study. The records obtained were carefully analyzed and an evaluation of the molecular constants was made using MISTIC, the Michigan State University digital computer. The determination yielded the following results, where the units are in cm^{-1}, unless specified:

$$B_0 = 1.6361_2 \pm 0.00004$$

$$B_2 = 1.6028_4 \pm 0.00001$$

$$B_3 = 1.5861_2 \pm 0.00002$$

$$D_0 = (4.5 \pm 0.5) \times 10^{-6}$$

$$D_2 = (4.7 \pm 0.1) \times 10^{-6}$$

$$D_3 = (4.7 \pm 0.3) \times 10^{-6}$$

$$H_0 = (-5.8 \pm 0.6) \times 10^{-10}$$

$$H_2 = (-4.9 \pm 0.1) \times 10^{-10}$$

$$B_e = 1.6444_7 \pm 0.00004$$

$$\alpha_e = -0.0166_7 \pm 0.00004$$

$$D_e = (4.4 \pm 0.4) \times 10^{-6}$$

$$I_e = 17.01_6 \times 10^{-40} \text{ gm-cm}^2$$

$$r_e = (1.150_6 \pm .0005) \times 10^{-8} \text{ cm.}$$

$$^2\pi_{1/2}: \omega_e = 1870.07_5 \pm 0.002$$
$$\omega_e x_e = 13.52_9 \pm 0.002$$
$$^2\pi_{3/2}: \omega_e = 1869.87_4 \pm 0.001$$
$$\omega_e x_e = 13.53_2 \pm 0.001$$

These constants were compared with the molecular parameters of $N^{14}O$ by means of an isotope calculation and found to be in good agreement.

To further examine their significance, the $N^{15}O$ constants above were compared with those obtained by Fletcher and Begun for the fundamental of $N^{15}O$ and those obtained from microwave data of Gallagher and Johnson. The agreement was found to be quite good.

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By

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INTRODUCTION

Nitric Oxide is a diatomic molecule which has been of considerable interest in spectroscopy for some time. It is the only stable diatomic molecule with an unpaired electron having both non-zero spin and orbital angular momentum and a normal $^2\pi$ ground state. The two substates of the ground state, designated as $^2\pi_{1/2}$ and $^2\pi_{3/2}$, are separated by only 122.14 cm^{-1} [1] and for this reason are both appreciably populated at room temperature.

$N^{14}O$ has been quite thoroughly studied and a history of the investigations made to 1953 is presented by N. L. Nichols [2]. W. H. Fletcher and G. M. Begun [3] also give a resume of the more recent experimental work done on $N^{14}O$. They list the first high resolution observation of the fundamental made simultaneously by Neilsen and Gordy [4] and Gillette and Eyster [5] in 1939, Nichols, Hause and Noble's [6] study of the first and second overtones in 1955, the microwave analysis done by Burrus and Gordy [7] in 1953 and Gallagher, Bedard and Johnson [8] in 1954, and Shaw's [9] re-examination of the fundamental in 1956.

In 1955 Gallagher, King and Johnson [10] reported preliminary results on the microwave spectrum of $N^{15}O$. Coupling this information with the microwave studies [7, 8] done on $N^{14}O$, Gallagher and Johnson [11] in 1956 presented a comparison of the microwave observations of these two isotopes along with a completed list of all the molecular and nuclear parameters then determined. Fletcher and Begun's [3] work in 1957 was an analysis of the fundamental of $N^{15}O$ made with a grating spectrometer.

The first and second overtone bands of $N^{15}O$ analyzed here were obtained with a vacuum recording infrared spectrometer, the bands occurring at 2.7 and 1.8μ respectively. The rotational and vibrational constants of the molecule were determined and as an additional check on their accuracy, these constants were compared with the molecular constants [12] of $N^{14}O$ by means of an isotope calculation.

THEORY

Angular Momentum Coupling Cases. In a diatomic molecule the electrons move in a field axially symmetric about the internuclear axis. As a result only the projection of the orbital angular momentum on the internuclear axis is constant, i.e., L, the total orbital angular momentum precesses about the internuclear axis with a constant component designated as Λ. The electronic states of diatomic molecules are classified according to Λ. Thus, in the case of $N^{15}O$ where $\Lambda = 1$, it is a π state and because Λ can be ± 1, the π state is doubly degenerate.

The orbital motion of the electrons causes an internal magnetic field in the direction of the internuclear axis which in turn causes a precession of S, the resultant of the spins of the individual electrons, about the field direction. The projection of S on the internuclear axis is designated as Σ which for $N^{15}O$, because of the odd electron, may be $\pm 1/2$. The total angular momentum of electronic origin along the internuclear axis is denoted by Ω where

$$\Omega = |\Lambda + \Sigma| \tag{1}$$

Because Λ and Σ are both along the internuclear axis, their sum may be taken directly. For each value of Λ there are $(2S+1)$ possible Σ values, $(2S+1)$ being the multiplicity. For $N^{15}O$ the multiplicity is 2, and Ω may be 1/2 or 3/2. Consequently, the substates are designated as $^2\pi_{1/2}$ and $^2\pi_{3/2}$, the former being lower in energy.

If one next considers the angular momentum of nuclear rotation as well as the orbital and spin angular momenta of the electrons, several possible modes of coupling are possible--all of which are treated in detail by Hund [13]. In case "a", Hund assumes that the total electronic momentum is strongly coupled to the internuclear axis and that the interaction of nuclear rotation with the electronic motion is weak. In terms of Figure 1-A, Λ and Σ are strongly coupled to form Ω which in turn is weakly coupled with N to form J, a vector fixed in space which is the resultant of the different momenta neglecting nuclear spin. In case "b", the spin S is only weakly coupled to the internuclear axis. Λ and N are coupled directly to form K, the total angular momentum apart from spin. K and S then form the resultant J. See Figure 1-B. The molecule NO exhibits a coupling which is intermediate between case "a" and case "b", being just slightly removed from case "a". We have evidence of this because the doublet separation is large (122.14 cm^{-1}) compared to the rotational constant (~ 2 cm^{-1}). As rotational speed increases, rotational velocity becomes comparable to the precessional velocity of S and eventually the molecular rotation dominates. S then uncouples from the molecular axis and case "b" is approached.

Energy Relations. The case "a" coupling described above is entirely similar to that of the symmetric top whose energy levels to a first approximation are given by:

$$F(J) = BJ(J + 1) + (A - B)\Omega^2 \tag{2}$$

Here $B = \dfrac{h}{8\pi^2 c I_B}$ and $A = \dfrac{h}{8\pi^2 c I_A}$.

I_B is the moment of inertia of the molecule about an axis perpendicular to the internuclear axis and is much larger than I_A, the moment of inertia of the electrons about the internuclear axis.

If this simple case is extended to that of a non-rigid, vibrating symmetric top, the rotational term values then become

$$F_v(J) = B_v J(J + 1) + (A - B_v)\Omega^2 - D_v J^2(J + 1)^2 + \dots \tag{3}$$

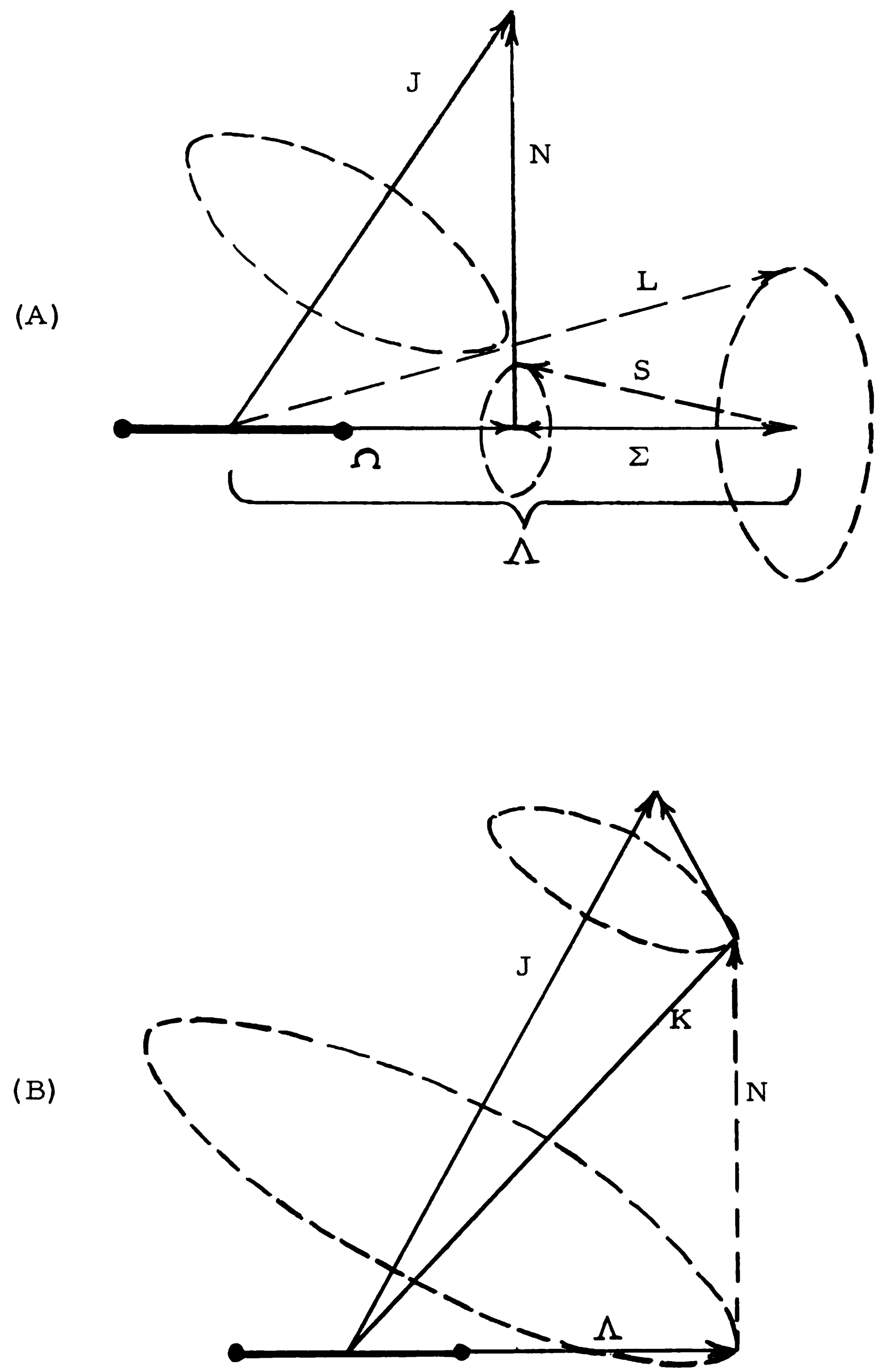

FIGURE I. HUND'S COUPLING CASES

The term D accounts for the influence of the centrifugal force and higher order correction terms may be added as needed. The subscripts on the rotational constants indicate that effective values of B and D must be used which show the slight dependence of these constants on the vibrational level. For a given vibrational level of a given electronic state, the term in Ω^2 is constant and can be neglected in the computation of rotational transitions if the band origin is chosen properly.

Equation (3) is essentially that used in this analysis of $N^{15}O$. It was mentioned above, however, that $N^{15}O$ is only close to case "a" actually being intermediate between cases "a" and "b".

Hill and Van Vleck [14] derived a general expression for any magnitude of coupling between S and Λ. This relation is given below along with the centrifugal distortion term arrived at by Almy and Horsfall [11].

$$E = B_v[(J + 1/2)^2 - \Lambda^2] \pm 1/2\, B_v[\lambda \Lambda^2(\lambda - 4) + 4(J + 1/2)^2]^{1/2}$$
$$- D_v[J^2(J + 1)^2 - J(J + 1) + 13/16] \qquad (4)$$

where $\lambda = \dfrac{A}{B_v}$, the upper sign refers to the $^2\pi_{3/2}$ state, and the lower sign to the $^2\pi_{1/2}$ state.

When spin uncoupling is small, i.e., $\lambda >> 1$ as it is in the case of $N^{15}O$ where $\lambda \approx 75$, the radical may be expanded and an equation of the form

$$E = (B_v')_{eff}(J + 1/2)^2 - (D_v)(J + 1/2)^4 + \text{constant} \qquad (5)$$

is obtained, where

$$(B_v')_{eff} = B_v\left(1 \pm \frac{B_v}{[A\Lambda^2(A - 4B_v)]^{1/2}}\right) + D_v \qquad (6)$$

$$D_v = D_v \pm \frac{B_v^4}{[A\Lambda^2(A - 4B_v)]^2} \qquad (7)$$

$$\text{constant} = -B_v \Lambda^2 \pm 1/2[A\Lambda^2(A - 4B_v)]^{1/2} - D_v + A\Lambda\Sigma$$
$$+ B_v[L(L + 1) - \Lambda^2] + B_v[S(S + 1) - \Sigma^2] \qquad (8)$$

If to these effects of spin uncoupling, one also takes account of l uncoupling, an additional term is added to the $(B_v')_{eff}$, namely:

$$-4 \sum_{\substack{\text{all } \Sigma \\ \text{states}}} \frac{|\pi| BL_{x'} |\Sigma|^2}{\nu\,(\pi \longrightarrow \Sigma)} \tag{9}$$

The value listed by Gallagher and Johnson [11] for this term is 0.71 Mc/sec. It is now evident that Equations (3) and (5) are essentially the same; $(J + 1/2)^2$ and $J(J + 1)$ differing by only 1/4 which is accounted for in the constant term. Thus we see that when the spin uncoupling is small, $\lambda >> 1$, the general equation for the energy levels in the intermediate coupling case may be represented by the symmetric top form where the B's and D's are interpreted as B_{eff} and D_{eff}.

Equation (3) was therefore used in the form:

$$F_v(J) = B_v J(J + 1) - D_v J^2(J + 1)^2 \tag{10}$$

for the analysis of the 3-0 band and in the form

$$F_v(J) = B_v J(J + 1) - D_v J^2(J + 1)^2 + H_v J^3(J + 1)^3 \tag{11}$$

for the 2-0 band where the higher order term was found to be significant. These bands are rotation-vibration bands of a single electronic state. For the 2-0 band or first overtone, the vibrational transition occurs between the zero vibrational level, v = 0, and the second vibrational level, v = 2. For the 3-0 band or second overtone, the transition occurs between v = 0 and v = 3. These vibrational transitions show a fine structure due to the rotation of the molecule and therefore the bands are called rotation-vibration bands.

The anharmonic approximation for the vibration terms is given by

$$G(v) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \omega_e y_e(v + 1/2)^3 + \ldots \tag{12}$$

Therefore a rotation-vibration term T, is:

$$T = G(v) + F_v(J) \tag{13}$$

and a rotation-vibration transition is given by:

$$\nu = G'(v) - G''(v) + F'_v(J) - F''_v(J) \tag{14}$$

where (') refers to the upper state and ('') refers to the lower state. If G'(v) - G''(v) be represented as ν_0, the band origin, then by a substitution in Equation (14):

$$\nu = \nu_0 + F'_v(J) - F''_v(J) \tag{15}$$

Band Branches. The spectrum of $N^{15}O$ consists of two almost superimposed bands each having three branches called P, Q, and R. When $\Lambda = 1$, as it does for NO, the allowed transitions must follow the selection rule $\Delta J = 0, \pm 1$. The P branch consists of those lines for which $\Delta J = -1$, the Q branch those for which $\Delta J = 0$, and the R branch those for which $\Delta J = +1$. See Figure 2. It will be noted that the line designation corresponds to the lower state J value. When $\Lambda = 0$, (the Σ state) the selection rule becomes $\Delta J = \pm 1$, and therefore no Q branch results. This is the case with most diatomic molecules.

For P and R branches the frequencies in cm^{-1} of the transitions may be represented by

$$P(J) = \nu_0 + F'_v(J - 1) - F''_v(J) \tag{16}$$

$$R(J) = \nu_0 + F'_v(J + 1) - F''_v(J) \tag{17}$$

respectively. These may be written collectively as

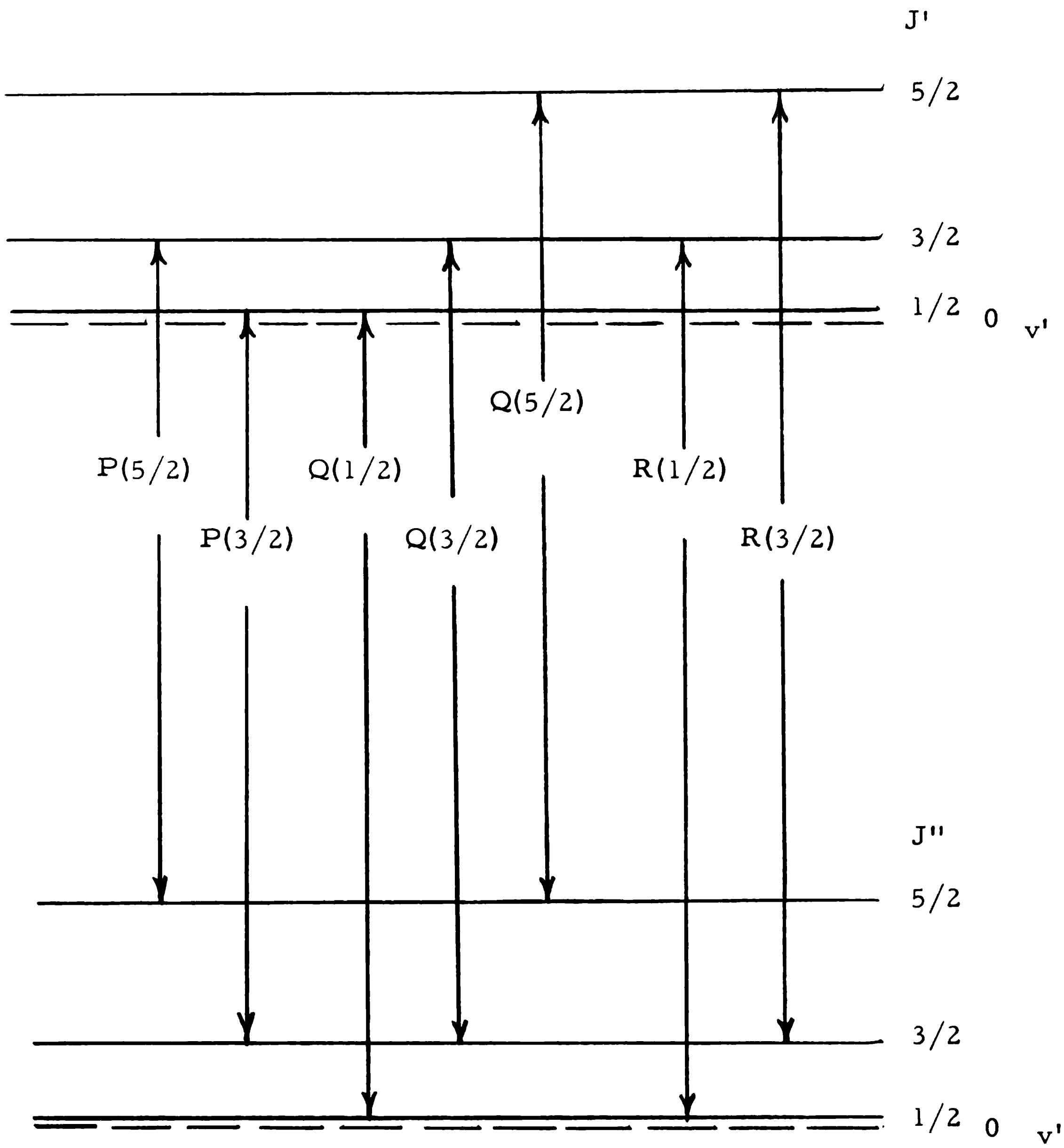

FIGURE 2. FORMATION OF P, Q, R BRANCHES

$$\nu_{P,R} = \nu_0 + (B'_v + B''_v)m + (B'_v - B''_v - D'_v + D''_v)m^2$$
$$+ (H'_v + H''_v - 2D'_v - 2D''_v)m^3 + (3H'_v - 3H''_v - D'_v + D''_v)m^4$$
$$+ 3(H'_v + H''_v)m^5 + (H'_v - H''_v)m^6 \qquad (18)$$

after appropriate substitutions from Equation (10) or (11) are made for $F'_v(J)$ and $F''_v(J)$. To use the single relation, (-J) must be substituted for m to obtain P branch lines, and (J + 1) to obtain R branch lines. For Q branch lines:

$$\nu_Q = \nu_0 + (B'_v - B''_v)J + (B'_v - B''_v)J^2 \qquad (19)$$

and from this relation, using the band origin and the determined B values, the frequencies of the Q branch lines were calculated.

Molecular Constants and Isotope Effect. The effective rotational constants, B''_v, D''_v, H''_v, B'_v, D'_v, and H'_v, along with ν_0, the band origin, were obtained from a least squares determination following methods suggested by Rank [15]. This method will be explained in the section labeled Data Analysis.

Using these effective constants and the relations given above in Equations (6), (7), and (9), the actual rotational constants B_v and D_v were obtained. H_v was evaluated by averaging the two effective H values obtained experimentally. In Equation (6) for example, $a(B''_v)_{eff}$ was substituted for the ground state of each of the substates of one band. When combined the result is immediately obtained:

$$B_v = \frac{(B''_v)_1 + (B''_v)_2}{2} - D_v - 0.71 \text{ Mc/sec} \qquad (20)$$

Next by plotting the B_v values versus (v + 1/2) the equilibrium $B(B_e)$ was determined as the intercept, and αe determined as the slope of the straight line obtained. αe is a measure of the change in B_v with changes in vibration, i.e.,

$$B_v = B_e - \alpha_e(v + 1/2) \tag{21}$$

B_e is given by

$$B_e = \frac{h}{8\pi^2 c I_e} \tag{22}$$

where $I_e = \mu r_e^2$ is the moment of inertia for the equilibrium separation of the atom, r_e is the equilibrium separation and μ is the reduced mass of NO $(= \frac{m_1 m_2}{m_1 + m_2})$. By an analogous method D_e can be determined and also β which is a measure of the change in D_e as the vibration changes:

$$D_v = D_e + \beta (v + 1/2) \tag{23}$$

The vibrational anharmonic constants given above in Equation (12) were determined from a knowledge of the band origins by means of the following relations:

$$\nu_{3-0} = G(3) - G(0) \tag{24}$$

$$\nu_{2-0} = G(2) - G(0) \tag{25}$$

When isotopic species are involved, it is usual to relate their constants in terms of a factor ρ which may be defined as follows:

$$\rho = \sqrt{\frac{\mu}{\mu^i}} \tag{26}$$

where the heavier isotope, distinguished by the superscript i, has the smaller frequency. It can be shown from Equation (12) that to a first approximation the vibrational term may be written as

$$G(v) = \omega_e(v + 1/2) \tag{27}$$

for the "ordinary" molecule, and one may also write

$$G^i(v) = \omega_e^i(v + 1/2) \tag{28}$$

for the heavier molecule. This assumes the vibrations are harmonic and it follows that

$$\omega_e^i = \rho\,\omega_e \qquad (29)$$

By similar calculations the relation between the higher order vibrational constants, $\omega_e x_e$ and $\omega_e y_e$, for the "ordinary" molecule and their counterparts for the isotope are found to be:

$$\omega_e^i x_e^i = \rho^2 \omega_e x_e \qquad (30)$$

$$\omega_e^i y_e^i = \rho^3 \omega_e y_e \qquad (31)$$

The rotational constant B was defined in Equation (22). This equation may also be written as

$$B_e = \frac{h}{8\pi^2 c\mu r_e^2} \qquad (32)$$

by substitution of the value of I_e. For the heavier molecule this becomes

$$B_e^i = \frac{h}{8\pi^2 c\mu^i r_e^2} \qquad (33)$$

However, from Equation (26) μ^i equals $\frac{\mu}{\rho^2}$ and therefore Equation (33) may be written as:

$$B_e^i = \frac{\rho^2 h}{8\pi^2 c\mu r_e^2} = \rho^2 B_e \qquad (34)$$

Similarly:

$$\alpha_e^i = \rho^3 \alpha_e \qquad (35)$$

and

$$D_e^i = \rho^4 D_e \qquad (36)$$

By means of these relations between the constants of the two isotopes the rotational and vibrational constants of $N^{15}O$ were compared with those of $N^{14}O$.

EXPERIMENTAL PROCEDURES

The first and second overtone bands of $N^{15}O$ analyzed here were obtained by Professor T. H. Edwards and Professor C. Ḋ. Hause with a vacuum recording infrared spectrometer. The spectrometer was equipped with a Bausch and Lomb precision grating in a Littrow mounting having 600 grooves per mm and a 6" x 8" ruled surface.

The source of radiation was a 300-watt Zirconium arc, and the detector used was a PbS type P. The $N^{15}O$ gas was placed in a Multiple Traverse Cell which was designed by T. H. Edwards [16]. For both the 2-0 band and the 3-0 band the path length of the radiation in the cell was eight meters. The pressure maintained in the cell was 3 cm for the 2-0 band and 15 cm for the 3-0 band.

Calibration of the absorption bands was accomplished by means of Edser-Butler bands. These bands were produced by visible radiation in higher orders traversing the monochromator and a 3 mm Fabry-Perot etalon. Their maxima were detected by a 1P21 photo-multiplier and phase sensitive amplifier. The Edser-Butler bands and the spectra were recorded simultaneously with a Leeds and Northrup two pen recorder. Neon and Argon lines were inserted and/or superimposed in the spectra as standard lines.

DATA ANALYSIS

Observed Spectra and the Fringe System. The observed absorption spectra of the 2-0 and the 3-0 bands of $N^{15}O$ at 2.7 and 1.8 μ respectively are shown in Figure 3. Because B' is less than B'', the bands degrade toward low frequencies. This is seen as a spreading of the lines in the P branch and a drawing together of the lines in the R branch. Since the selection rule $\Delta J = 0$ is allowed and Ω may be 1/2 or 3/2, the lowest J value for the $^2\pi_{1/2}$ state is J = 1/2 and for the $^2\pi_{3/2}$ state is J = 3/2. This then means that the P_1 and P_2 branches start with $P_1(3/2)$ and $P_2(5/2)$, respectively, and the R_1 and R_2 branches start with $R_1(1/2)$ and $R_2(3/2)$ respectively. The subscript 1 denotes the $^2\pi_{1/2}$ state and subscript 2 denotes the $^2\pi_{3/2}$ state. Because the separation of the substates is small the Q branches almost coincide, the P and R branches spreading and overlapping as indicated above. No transitions between substates are observed so the stronger P and R lines are a result of the $^2\pi_{1/2}$ - $^2\pi_{1/2}$ transition and the weaker lines of these branches from the $^2\pi_{3/2}$ - $^2\pi_{3/2}$ transition.

As can be noted in Figure 3-A, the high J region of the R branch of the 2-0 band is somewhat overlapped by the 101 band of the linear polyatomic molecule CO_2. The presence of this band did not hinder the identification of the various components of the $N^{15}O$ spectrum, but it did render some of the lines useless in the determination of the molecular constants. The lines not used and the reasons for their disregard are given in Table I. The P_1 and P_2 branch lines were identified to J = 53/2, and the R_1 and R_2 branch lines to J = 55/2. Only two of the Q_1 branch lines were observed and identified: J = 1/2 and J = 5/2. The Q_2 branch is particularly well resolved, the lines J = 3/2 to J = 27/2 being identified and measured. The R_2 branch lines are well resolved for J = 3/2 and 5/2,

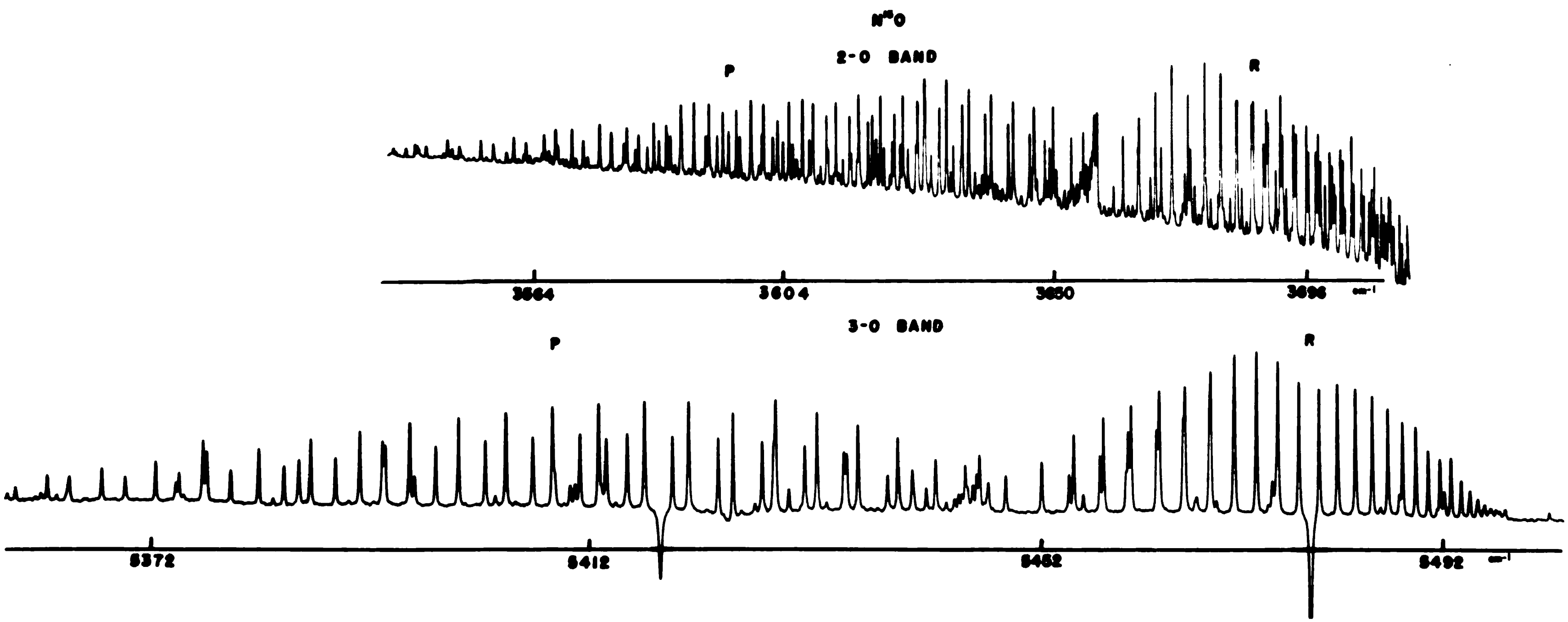

FIGURE 3. 2-0 BAND AND 3-0 BAND OF $N^{15}O$

Table I. Lines deleted from the Overtone Bands

Line	Reason*	Line	Reason	Line	Reason
		2-0 Band			
$P_1(15/2)$	1	$R_1(11/2)$	3	$P_2(51/2)$	2
$P_1(43/2)$	1	$R_1(55/2)$	2	$P_2(53/2)$	2
$P_1(47/2)$	1	$P_2(9/2)$	1	$R_2(7/2)$	3
$P_1(51/2)$	2	$P_2(11/2)$	1	$R_2(9/2)$	3
$P_1(53/2)$	2	$P_2(13/2)$	1	$R_2(11/2)$	3
$R_1(7/2)$	3	$P_2(35/2)$	1	$R_2(37/2)$	1
$R_1(9/2)$	3	$P_2(45/2)$	1	$R_2(55/2)$	2
		3-0 Band			
$P_1(11/2)$	1	$R_1(15/2)$	3	$R_1(45/2)$	2
$P_1(17/2)$	1	$R_1(17/2)$	3	$R_1(47/2)$	2
$P_1(41/2)$	2	$R_1(19/2)$	3	$R_1(49/2)$	2
$P_1(43/2)$	2	$R_1(35/2)$	1	$P_2(27/2)$	1
$P_1(45/2)$	2	$R_1(41/2)$	1	$P_2(37/2)$-$P_2(47/2)$	2
$P_1(47/2)$	2	$R_1(43/2)$	2	$R_2(15/2)$-$R_2(49/2)$	3

*Reasons:
1. Overlapped or distorted by an impurity.
2. Identified, but not well enough resolved for measurement.
3. Overlapped by component of the other substate.

but as J increases the components of the two R branches draw closer together so that at $J = 7/2$ the two are not resolved. The second component appears again at $J = 13/2$ but is then on the other side of the R_1 branch lines.

The 3-0 band appearing in Figure 3 was overlapped by H_2O lines and the effect was comparable to the effect of the CO_2 lines on the 2-0 band. Here the P_1 and P_2 branch lines were identified through $J = 47/2$, and the R branches through $J = 49/2$. Again the resolution of the Q_2 branch was better than the resolution of the Q_1 branch. In the Q_1 branch only the $J = 1/2$ to $J = 5/2$ lines were identified whereas in the Q_2 branch, lines for $J = 3/2$ to $J = 13/2$ were measured. The R_1 and R_2 branches in this band are fairly well resolved to $J = 13/2$. From this point to the end of the R branch the two components are overlapped and no indication of the R_2 lines appearing on the other side of the R_1 lines is in evidence.

In order to determine the frequencies of these observed spectral lines a set of calibration fringes obtained by means of a Fabry-Perot etalon was employed. The construction of this system is described in detail by Van Horne [17]. The etalon follows the exit slit of the monochromator and is illuminated with higher order visible radiation. Fringe maxima occur at those wave lengths for which:

$$2d = n_0\lambda_0 \tag{37}$$

In wave numbers this relation becomes

$$n_0 = 2d\,\nu_0 \tag{38}$$

where n_0 may be an arbitrary number assigned to the first fringe, the fringe corresponding to a definite wave number ν_0. If the fringes are numbered consecutively we may represent any later fringe by:

$$n_0 + n = 2d\,\nu_0 + n = 2d\,\nu_n \tag{39}$$

By subtracting Equations (38) and (39) a linear relation is obtained between the wave number of a fringe and the number of the fringe.

$$\nu_n = \nu_0 + \frac{n}{2d} \tag{40}$$

Although Figure 3 shows only the overtone bands, the charts actually measured were a simultaneous record of the overtone band and the fringe system. A series of Neon and Argon lines whose frequencies are well established were inserted at the proper angle of the grating rotation as a means of calibration.

A least squares fit was made based on Equation (40) using the fringe number, n, assigned to each standard and the corresponding known frequency of the Neon or Argon line. The lines used for this calibration appear in Table II. The slope of the straight line obtained is $\frac{1}{2d}$ where d is the etalon spacing. A 3 mm spacer was used and therefore the spacing between adjacent fringes was approximately 1.6 cm^{-1}. The slopes actually obtained for the 2-0 and 3-0 bands were 0.3215 cm^{-1} and 0.4019 cm^{-1} respectively. These correspond to fifth order fringes for the first overtone band and 4th order fringes for the 2nd overtone band. The intercepts obtained were $\nu_0 = 3523.848$ cm^{-1} and $\nu_0 = 5308.361$ cm^{-1} respectively.

By use of Equation (40) and the values for ν_0 and $\frac{1}{2d}$ given above, the frequency of each observed spectral line was determined. The measured fringe number which corresponds to an absorption line was substituted for n and ν_n was then evaluated. The observed frequencies thus determined are listed in Tables III and IV.

Determination of B_V, D_V, H_V and ν_0 for the 2-0 Band. The wave numbers thus determined for the 2-0 band were fit to a set of least mean squares equations based on Equation (18). This equation is essentially of the same form as the first equation in the following block:

Table II. Argon and Neon Standards

Gas	Wavelength (Å)	Vacuum Wave No. (cm^{-1})	Order	$\frac{\text{Vac. Wave. No.}}{\text{Order}}$ (cm^{-1})
		2-0 Band		
Neon	7032.413	14215.951	4	3553.988
Neon	6929.467	14427.145	4	3606.786
Argon	13718.576	7287.394	2	3643.696
Argon	13622.658	7338.705	2	3669.352
Argon	13504.190	7403.085	2	3701.542
Argon	13367.111	7479.003	2	3739.502
		3-0 Band		
Neon	6266.495	15953.472	3	5317.824
Neon	6143.062	16274.024	3	5424.675
Argon	9122.966	10958.340	2	5479.170
Neon	6029.997	16579.166	3	5526.388

Table III. Calculated and Observed Frequencies for the 2-0 Band

J	Wt.	Calc. ν(cm^{-1})	Obs. ν(cm^{-1})	Calc.-Obs. (cm^{-1})
		$^2\pi_{1/2}$ State, P Branch		
1.5	1	3654.111	3654.112	-.001
2.5	2/3	3650.786	3650.784	+.002
3.5	2/3	3647.399	3647.399	.000
4.5	1	3643.942	3643.943	-.001
5.5	1	3640.423	3640.425	-.002
6.5	1	3636.838	3636.839	-.001
8.5	1	3629.474	3629.475	-.001
9.5	1	3625.695	3625.695	.000
10.5	1	3621.850	3621.850	.000
11.5	1	3617.941	3617.944	-.003
12.5	1	3613.966	3613.954	+.012
13.5	1	3609.926	3609.929	-.003
14.5	1	3605.821	3605.827	-.006
15.5	1	3601.652	3601.650	+.002
16.5	1	3597.417	3597.410	+.007
17.5	1	3593.117	3593.123	-.006
18.5	1	3588.753	3588.752	+.001
19.5	1	3584.324	3584.328	-.004
20.5	1	3579.831	3579.831	.000
22.5	1	3570.652	3570.649	+.003
24.5	1	3561.219	3561.220	-.001
		$^2\pi_{1/2}$ State, R Branch		
0.5	2/3	3663.696	3663.699	-.003
1.5	1	3666.760	3666.755	+.005
2.5	1	3669.760	3669.754	+.006
6.5	1	3681.110	3681.120	-.010
7.5	1	3683.784	3683.789	-.005
8.5	1	3686.392	3686.392	.000
9.5	1	3688.936	3688.932	+.004
10.5	1/3	3691.413	3691.400	+.013
11.5	1	3693.824	3693.825	-.001
12.5	1	3696.170	3696.164	+.006
13.5	1	3698.450	3698.451	-.001
14.5	1	3700.662	3700.664	-.002

Continued

Table III - Continued

J	Wt.	Calc. ν (cm^{-1})	Obs. ν (cm^{-1})	Calc.-Obs. (cm^{-1})
		$^2\pi_{1/2}$ State, R Branch		
15.5	1	3702.809	3702.814	-.005
16.5	2/3	3704.889	3704.888	+.001
17.5	1	3706.901	3706.893	+.008
18.5	1	3708.847	3708.853	-.006
19.5	1	3710.725	3710.723	+.002
20.5	1	3712.536	3712.538	-.002
21.5	1	3714.278	3714.280	-.002
22.5	1	3715.953	3715.960	-.007
23.5	1	3717.559	3717.552	+.007
24.5	2/3	3719.097	3719.088	+.009
25.5	1	3720.566	3720.569	-.003
26.5	1	3721.966	3721.967	-.001
		$^2\pi_{3/2}$ State, P Branch		
2.5	1	3650.137	3650.139	-.002
3.5	1	3646.650	3646.657	-.007
7.5	1	3632.030	3632.031	-.001
8.5	2/3	3628.208	3628.214	-.006
9.5	1	3624.320	3624.318	+.002
10.5	1	3620.365	3620.366	-.001
11.5	1	3616.345	3616.327	+.018
12.5	1	3612.259	3612.264	-.005
13.5	2/3	3608.107	3608.095	+.012
14.5	1	3603.891	3603.897	-.006
15.5	2/3	3599.609	3599.611	-.002
16.5	1	3595.262	3595.273	-.011
18.5	1	3586.376	3586.375	+.001
19,5	1	3581.837	3581.835	+.002
20.5	1	3577.233	3577.231	+.002
21.5	1	3572.567	3572.566	+.001
23.5	1	3563.044	3563.044	.000
24.5	2/3	3558.188	3558.188	.000

Table III - Continued

J	Wt.	Calc. ν(cm^{-1})	Obs. ν(cm^{-1})	Calc.-Obs. (cm^{-1})
		$^2\pi_{3/2}$ State, R Branch		
1.5	1	3666.550	3666.548	+.002
2.5	2/3	3669.628	3669.628	.000
6.5	1	3681.246	3681.230	+.016
7.5	1	3683.977	3683.978	-.001
8.5	1	3686.637	3686.655	-.018
9.5	1	3689.228	3689.226	+.002
10.5	1	3691.749	3691.744	+.005
11.5	2/3	3694.199	3694.196	+.003
12.5	1	3696.579	3696.578	+.001
13.5	1	3698.888	3698.888	.000
14.5	1	3701.126	3701.119	+.007
15.5	2/3	3703.293	3703.319	-.026
16.5	1	3705.390	3705.390	.000
17.5	1	3707.415	3707.412	+.003
19.5	1	3711.252	3711.246	+.006
20.5	1	3713.064	3713.065	-.001
21.5	1	3714.804	3714.809	-.005
22.5	1	3716.472	3716.468	+.004
23.5	1	3718.070	3718.065	+.005
24.5	1	3719.596	3719.595	+.001
25.5	1	3721.050	3721.059	-.009
26.5	1	3722.433	3722.429	+.004

Table IV. Calculated and Observed Frequencies for the 3-0 Band

J	Wt.	Calc. ν (cm^{-1})	Obs. ν (cm^{-1})	Calc.-Obs. (cm^{-1})
		$^2\pi_{1/2}$ State, P Branch		
1.5	2/3	5443.000	5443.000	.000
2.5	1	5439.627	5439.638	-.011
3.5	1	5436.156	5436.157	-.001
4.5	1	5432.588	5432.594	-.006
6.5	1	5425.160	5425.163	-.003
7.5	1	5421.300	5421.306	-.006
9.5	1	5413.285	5413.281	+.004
10.5	2/3	5409.131	5409.117	+.014
11.5	1	5404.879	5404.869	+.010
12.5	1	5400.528	5400.519	+.009
13.5	1	5396.079	5396.081	-.002
14.5	1	5391.530	5391.539	-.009
15.5	1	5386.883	5386.878	+.005
16.5	1	5382.136	5382.138	-.002
17.5	1	5377.290	5377.303	-.013
18.5	2/3	5372.343	5372.362	-.019
19.5	2/3	5367.296	5367.320	-.024
		$^2\pi_{1/2}$ State, R Branch		
0.5	1	5452.536	5452.536	+.001
1.5	1	5455.520	5455.524	-.004
2.5	1	5458.406	5458.409	-.003
3.5	1	5461.196	5461.191	+.005
4.5	1	5463.887	5463.891	-.004
5.5	1	5466.481	5466.467	+.014
6.5	2/3	5468.977	5468.975	+.002
10.5	1	5477.980	5477.976	+.004
11.5	1	5479.984	5479.974	+.010
12.5	1	5481.890	5481.893	-.003
13.5	1	5483.695	5483.701	-.006
14.5	1	5485.402	5485.394	+.008
15.5	1	5487.008	5487.015	-.007
16.5	1	5488.514	5488.509	+.005
18.5	1	5491.224	5491.215	+.009
19.5	2/3	5492.427	5492.408	+.019

Continued

Table IV - Continued

J	Wt.	Calc. ν (cm^{-1})	Obs. ν (cm^{-1})	Calc. - Obs. (cm^{-1})
		$^2\pi_{3/2}$ State, P Branch		
2.5	1/3	5438.756	5438.756	.000
3.5	1/3	5435.182	5435.185	-.003
4.5	1	5431.508	5431.510	-.002
5.5	1	5427.731	5427.733	-.002
6.5	1	5423.853	5423.853	.000
7.5	1	5419.874	5419.874	.000
8.5	1	5415.794	5415.782	+.012
9.5	1	5411.613	5411.611	+.002
10.5	1	5407.332	5407.327	+.005
11.5	1	5402.952	5402.957	-.005
12.5	1	5398.471	5398.478	-.007
14.5	1	5389.214	5389.208	+.006
15.5	1	5384.437	5384.436	+.001
16.5	2/3	5379.562	5379.571	-.009
17.5	1/3	5374.590	5374.583	+.007
		$^2\pi_{3/2}$ State, R Branch		
1.5	1/3	5455.083	5455.075	+.008
2.5	2/3	5458.040	5458.033	+.007
3.5	2/3	5460.893	5460.895	-.002
4.5	2/3	5463.643	5463.656	-.013
5.5	2/3	5466.289	5466.286	+.003
6.5	1/3	5468.831	5468.845	-.014

$$a n + b\Sigma x_i + c\Sigma x_i^2 + d\Sigma x_i^3 + e\Sigma x_i^4 + f\Sigma x_i^5 + g\Sigma x_i^6 = \Sigma y_i$$

$$a\Sigma x_i + b\Sigma x_i^2 + c\Sigma x_i^3 + d\Sigma x_i^4 + e\Sigma x_i^5 + f\Sigma x_i^6 + g\Sigma x_i^7 = \Sigma x_i y_i$$

$$\vdots$$

$$a\Sigma x_i^6 + b\Sigma x_i^7 + c\Sigma x_i^8 + d\Sigma x_i^9 + e\Sigma x_i^{10} + f\Sigma x_i^{11} + g\Sigma x_i^{12} = x_i^6 y_i \qquad (41)$$

This set was evaluated on the Michigan State University digital computer MISTIC. The program used was one entitled "Dalcevac" and was written by Mr. John Boyd. Actually in the use of this program the basic Equation (18) was rewritten as

$$\nu = \nu_0 + B'_v(m + m^2) + B''_v(m - m^2) + D'_v(-m^2 - 2m^3 - m^4)$$
$$+ D''_v(m^2 - 2m^3 + m^4) + H'_v(m^3 + 3m^4 + 3m^5 + m^6)$$
$$+ H''_v(m^3 - 3m^4 + 3m^5 - m^6) \qquad . \qquad (42)$$

in order to obtain the desired constants directly. For the 2-0 band, $^2\pi_{1/2}$ state, forty-five lines were used; and for the $^2\pi_{3/2}$ state, forty lines were used. If the relation had been left in the form of Equation (18), the constants would have been composite constants, i.e., $a = \nu_0$; $b = (B' + B'')$; $c = (B' - B'' - D' + D'')$; etc. The values of the molecular constants found by this means for the 2-0 band are listed in Table V. This table also contains the standard deviation for each constant as was determined in the "Dalcevac" program. The subscripts 01 and 21 refer to the zero and second vibrational levels of the first substate and the 02 and 22 refer to the same vibrational levels of the second substate.

The constants evaluated by the method above were used in Equation (18) to calculate the frequency in wave numbers of each observed line. These calculated values are given in Table III where they are compared

Table V. Effective Rotational Constants for $N^{15}O$*

$B_{01} = 1.6136_5 \pm 0.00003$	$B_{02} = 1.6585_6 \pm 0.00004$
$B_{21} = 1.5811_9 \pm 0.00001$	$B_{22} = 1.6244_4 \pm 0.00001$
$B_{31} = 1.5650_0 \pm 0.00001$	$B_{32} = 1.6071_8 \pm 0.00002$
$D_{01} = (2.4 \pm 0.8) \times 10^{-7}$	$D_{02} = (8.8 \pm 0.4) \times 10^{-6}$
$D_{21} = (6.5 \pm 0.2) \times 10^{-7}$	$D_{22} = (8.7 \pm 0.1) \times 10^{-6}$
$D_{31} = (1.1 \pm 0.1) \times 10^{-6}$	$D_{32} = (8.3 \pm 0.3) \times 10^{-6}$
$H_{01} = (-1.56 \pm 0.01) \times 10^{-9}$	$H_{02} = (3.9 \pm 0.6) \times 10^{-10}$
$H_{21} = (-1.4 \pm 0.3) \times 10^{-9}$	$H_{22} = (4.2 \pm 0.1) \times 10^{-10}$

$^2\pi_{1/2}: \nu_{2-0} = 3658.97_6 \pm 0.001$

$\nu_{3-0} = 5447.87_7 \pm 0.002$

$^2\pi_{3/2}: \nu_{2-0} = 3658.55_6 \pm 0.001$

$\nu_{3-0} = 5447.24_0 \pm 0.001$

*All constants are given in cm^{-1}.

to the observed values. Only two lines in the first substate and five lines in the second substate show a variation greater than 0.010 cm^{-1}.

The lines used for the determination of the constants were weighted on a basis of 1, 2/3, and 1/3. The magnitude of weighting was determined by the amount of the distortion or disturbance of a particular line. The weight given each line is also tabulated in Table III.

The effective B values, B_{01}, B_{02}, B_{21}, and B_{22}, listed in Table V were used in relation (20) to obtain the actual rotational constants B_0 and B_2. The actual values of D_0, D_2, H_0, and H_2 were evaluated by averaging the effective D's and H's. These actual rotational constants are collected in Table VI.

Determination of B_V, D_V and ν_0 for the 3-0 Band. Only thirty-three lines of the first substate of the 3-0 band and twenty-one lines of the second substate were usable so the following method was employed in the evaluation of the parameters of this band. The 2-0 and 3-0 bands of the same electronic state have their ground states in common, so the ground state constants of the 2-0 band were accepted and used as the ground state constants of the 3-0 band. This, then, left only four constants to be obtained from the data: B'_V, D'_V, H'_V, and ν_0, rather than the seven required from the more numerous data of the 2-0 band. When this computation was carried out, it became obvious from the standard deviations that the H'_V evaluated was not significant so the determination was repeated using the B''_V and D''_V from the ground state of the first overtone and requiring just three constants from the data, namely, B'_V, D'_V, and ν_0. The program "Dalcevac" was again used and the equation being fit was a modification of Equation (18) with the H's deleted. The actual form used in the analysis was

$$\nu' = \nu_0 + B'_V(m + m^2) + D'_V(-m^2 - 2m^3 - m^4) \qquad (43)$$

where

$$\nu' = \nu - B''(m - m^2) - D''(m^2 - 2m^3 + m^4)$$

The constants thus obtained and their standard deviations are listed in Table V with those obtained from the 2-0 band. The subscripts 01 and 31 refer to the zero and third vibrational levels of the first substate and 02 and 32 refer to the same vibrational levels of the second substate. These effective constants were substituted in the modified form of Equation (18) and the line frequencies in wave numbers were calculated. A comparison of the observed and calculated frequencies of the spectral lines of the 3-0 band is made in Table IV. Here seven lines of the first substate differ from the observed values by slightly more than 0.010 cm^{-1}. The method of using weights described above was also employed, and the weights are given in Table IV. The actual B_3 value was obtained by using B_{31} and B_{32} in Equation (20). D_3 was evaluated by a numerical averaging of D_{31} and D_{32}. These actual rotational constants are listed in Table VI with those obtained from the 2-0 band.

Determination of B_e, α_e, I_e and r_e. The values for B_0, B_2, and B_3 as listed in Table VI were plotted versus $(v + 1/2)$ following the relation given in Equation (21) to obtain the intercept, B_e, and the slope α_e. See Figure 4. The values obtained were $B_e = 1.64447$ cm^{-1} and $\alpha_e = 0.0167$ cm^{-1}. The values were checked by a least squares calculation.

By use of Equation (22) and the value of B_e given above, the equilibrium moment of inertia, I_e was calculated and found to be 17.016 x 10^{-40} gm-cm^2. This constant was then used with the reduced mass, μ, equal to 7.743235 amu [18] to compute r_e, the equilibrium separation of the atoms. The value obtained for r_e was 1.1506 x 10^{-8} cm.

It can be noted from Table VI that the value for D_3 seems somewhat in error in relation to D_0 and D_2. These latter constants were obtained along with values for H_0 and H_2 whereas D_3 was obtained without this higher order correction constant. Because of this it was felt that

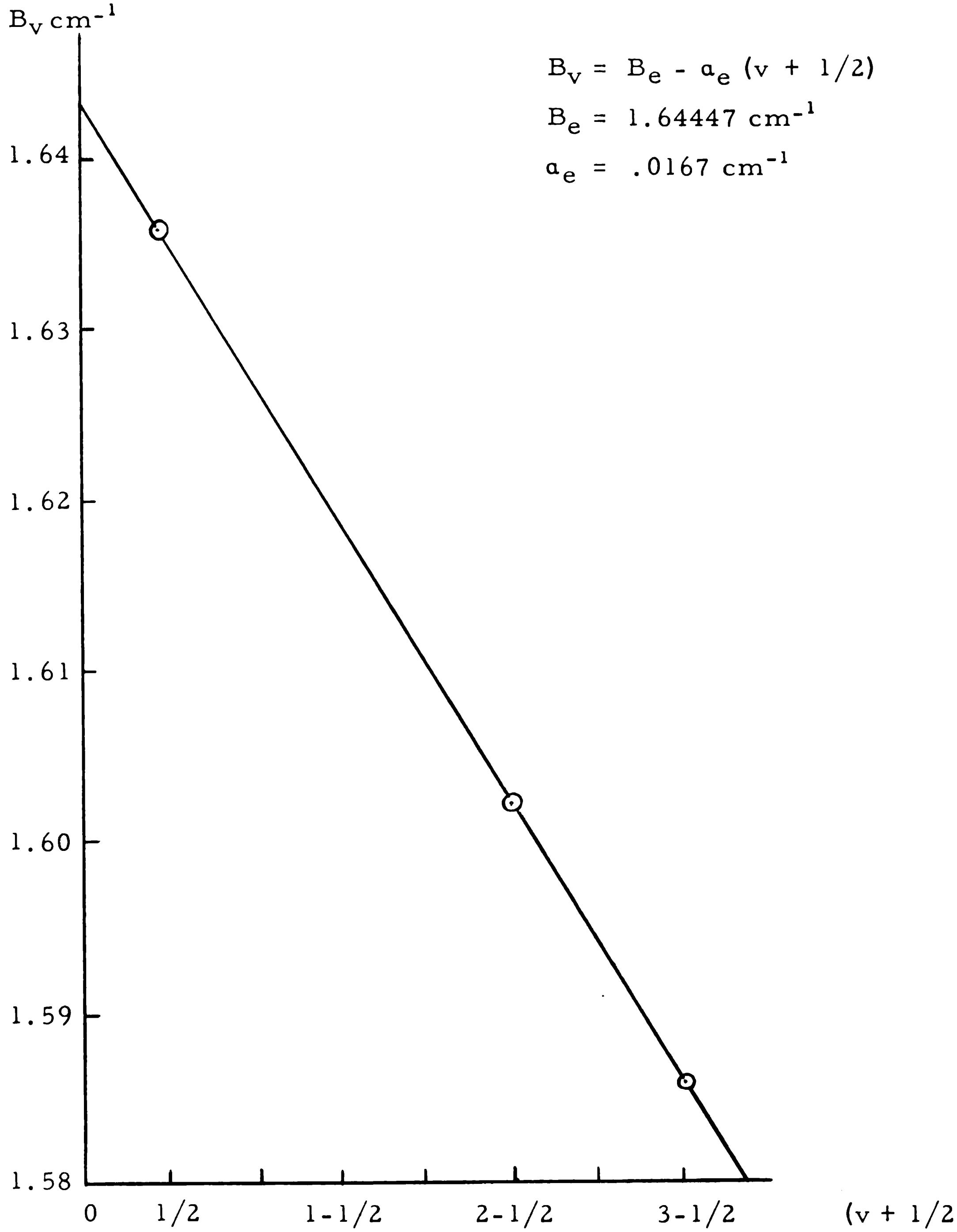

FIGURE 4. GRAPHICAL DETERMINATION OF B_e AND α_e

D_0 and D_2 were more reliable constants and consequently the value of D_e quoted in Table VI is a result of a computation using these two alone.

Calculation of the Q Branch. It was stated in the theory that Q branch lines can be calculated by use of Equation (19) and the constants B and ν_0, already determined. This was done for each band and the results of these calculations are given in Table VII. For the 2-0 band the lines $Q_1(5/2)$ and $Q_2(15/2)$ were not measured or calculated although they could be identified. $Q_1(5/2)$ is not well resolved and $Q_2(15/2)$ is overlapped by an impurity making it much too intense. In the case of the 3-0 band, the lines $Q_1(3/2)$, $Q_2(11/2)$, and $Q_2(13/2)$ although identifiable were not well enough resolved for measurement. The differences between the observed and calculated values are stated in Table VII where it can be seen that the accuracy here is comparable to that of the P and R branches.

Determination of the Vibrational Constants, ω_e and $\omega_e x_e$. The band origins as given in Table V were used in Equations (24) and (25) to evaluate the anharmonic vibrational constants, ω_e and $\omega_e x_e$. After appropriate substitutions for G(3), G(2), and G(0), the relations used for each substate were:

$$\nu_{3-0} = 3\omega_e - 12\omega_e x_e \qquad (44)$$

$$\nu_{2-0} = 2\omega_e - 6\omega_e x_e \qquad (45)$$

The constants evaluated by the simultaneous solution of these two equations are given in Table VI.

Table VI. Rotational and Vibrational Constants for $N^{15}O$.*

$B_0 = 1.6361_2 \pm 0.00004$

$B_2 = 1.6028_4 \pm 0.00001$

$B_3 = 1.5861_2 \pm 0.00002$

$D_0 = (4.5 \pm 0.4) \times 10^{-6}$

$D_2 = (4.7 \pm 0.1) \times 10^{-6}$

$D_3 = (4.7 \pm 0.3) \times 10^{-6}$

$H_0 = (-5.8 \pm 0.6) \times 10^{-10}$

$H_2 = (-4.9 \pm 0.1) \times 10^{-10}$

$B_e = 1.6444_7 \pm 0.00004$

$\alpha_e = -0.0166_7 \pm 0.00004$

$D_e = (4.4 \pm 0.4) \times 10^{-6}$

$I_e = 17.01_6 \times 10^{-40}$ gm-cm^2

$r_e = (1.150_6 \pm .0005) \times 10^{-8}$ cm

$^2\pi_{1/2}: \omega_e = 1870.07_5 \pm 0.002$

$\omega_e x_e = 13.52_9 \pm 0.002$

$^2\pi_{3/2}: \omega_e = 1869.87_4 \pm 0.001$

$\omega_e x_e = 13.53_2 \pm 0.001$

*All constants are in cm^{-1} except in cases where the appropriate units are specified.

Table VII. Calculated and Observed Q Branch Lines.

Line	Calc.(cm^{-1})	Obs.(cm^{-1})	Calc.-Obs.(cm^{-1})
		2-0 Band	
$Q_1(1/2)$	3658.952	3658.943	+.009
$Q_2(3/2)$	3658.429	3658.439	-.010
$Q_2(5/2)$	3658.259	3658.257	+.002
$Q_2(7/2)$	3658.020	3658.026	-.006
$Q_2(9/2)$	3657.713	3657.719	-.006
$Q_2(11/2)$	3657.337	3657.329	+.008
$Q_2(13/2)$	3656.894	3656.883	+.011
$Q_2(17/2)$	3655.802	3655.793	+.009
$Q_2(19/2)$	3655.154	3655.155	-.001
$Q_2(21/2)$	3654.437	3654.428	+.009
$Q_2(23/2)$	3653.653	3653.653	.000
$Q_2(25/2)$	3652.800	3652.808	-.008
$Q_2(27/2)$	3651.878	3651.880	-.002
		3-0 Band	
$Q_1(1/2)$	5447.841	5447.842	-.001
$Q_1(5/2)$	5447.451	5447.446	+.005
$Q_2(3/2)$	5447.047	5447.053	-.006
$Q_2(5/2)$	5446.790	5446.792	-.002
$Q_2(7/2)$	5446.431	5446.425	+.006
$Q_2(9/2)$	5445.969	5445.971	-.002

COMPARISON OF $N^{15}O$ WITH OTHER WORK

To check on the accuracy of the rotational and vibrational constants determined for $N^{15}O$ several comparisons were made, the first of which was the isotope calculation.

Hause and Olman [12] have re-evaluated the molecular constants of the 2-0 band of $N^{14}O$ and these were used as a basis for comparison with the $N^{15}O$ constants determined here. The $N^{14}O$ constants from this computation that were used are $B_e = 1.70477\ cm^{-1}$, $\alpha_e = .0173\ cm^{-1}$, and the band origins for each substate; namely, $\nu_0 = 3724.100\ cm^{-1}$ for $^2\pi_{1/2}$ state and $\nu_0 = 3723.676\ cm^{-1}$ for the $^2\pi_{3/2}$ state. In order to calculate ω_e and $\omega_e x_e$ for $N^{14}O$, another set of band origins was needed so those obtained by Van Horne [17] for the 3-0 band were employed. Equations (44) and (45) were then used as described above to evaluate ω_e and $\omega_e x_e$ for $N^{14}O$. The reduced mass μ, for $N^{14}O$ was taken to be 7.4688067 amu and for $N^{15}O$, μ^i was taken as 7.7432348 amu. According to Equation (26) then, ρ equals 0.9821196 and this was the value used in Equations (29), (30), (34), and (35) to calculate the $N^{15}O$ constants on the basis of $N^{14}O$. The results are given in Table VIII.

As can be seen from this table the agreement is particularly good for the vibrational constants ω_e and $\omega_e x_e$. The values of B_e are only in fair agreement differing by $0.00012\ cm^{-1}$. It is felt that the presently evaluated $N^{15}O$ constants are correct to six significant digits whereas this variation occurs in the fifth place. Perhaps this is due to the fact that the B_e of $N^{15}O$ was determined on the basis of three B values while the B_e of $N^{14}O$ was found using only two.

As a second check, a comparison was made with the constants given by Fletcher and Begun [3], and Gallagher and Johnson [11]. These values are listed in Table VIII.

Table VIII. Comparison of $N^{15}O$ Constants

	$N^{14}O$ [12]	$N^{15}O$ (Isotope Calc.)	$N^{15}O$ (Present Evaluation)
		Isotope Comparison	
B_e	1.7047_7	1.6443_5	1.6444_7
α_e	0.017_3	0.016_4	0.016_7
$\omega_e(1)$	1904.0_9	1870.0_4	1870.07_5
$\omega_e x_e(1)$	14.0_1	13.5_2	13.52_9
$\omega_e(2)$	1903.9_2	1869.8_8	1896.87_4
$\omega_e x_e(2)$	14.0_3	13.5_3	13.53_2

Comparison with Other Studies

	Present Evaluation	Gallagher and Johnson	Fletcher and Begun
B_e	1.6444_7	1.6445_0	1.644_6
α_e	0.016_7	0.017_1	0.017_0
I_e	$17.01_6 \times 10^{-40}$ gcm^2	$17.01_9 \times 10^{-40}$ gcm^2	---
r_e	1.150_6 Å	1.150_8 Å	---
$\omega_e(1)$	1870.07_5	---	1869.9_8
$\omega_e(2)$	1869.87_4	---	1869.6_4
$\omega_e x_e(1)$	13.52_9	---	13.4_7
B_0	1.6361_2	1.6358_4	---
D_0	4.5×10^{-6}	4.6×10^{-6}	---
r_0		1.153_9 Å	---

*All constants are given in cm^{-1} except in cases where the appropriate units are specified.

The equilibrium B seems to be in better agreement with the microwave value obtained by Gallagher and Johnson than with the infrared value obtained by Fletcher and Begun. The differences are 0.00003 cm^{-1} and 0.0001 cm^{-1} respectively. The α_e values are fairly comparable, but the value obtained here is slightly lower than either of the values quoted for comparison. Fletcher and Begun state in their paper that the experimental value they obtained for α_e was 0.0166 cm^{-1} but because it was based only on the fundamental they felt the value 0.0170 cm^{-1} obtained by the isotopic relation was more reliable. The experimental value of α_e in this paper is in closer agreement with their experimental value than with the value they actually quoted.

It will also be noted that the values of I_e and r_e given by Gallagher and Johnson are in excellent agreement with those given here. As would be expected, I_e for $N^{15}O$ is slightly larger than I_e for $N^{14}O$. The value listed for $N^{14}O$ by Van Horne [17] is 16.422×10^{-40} gm. cm^2. The variation between the r_e value given here and that of $N^{14}O$ by Van Horne, 1.15096×10^{-8} cm, is within experimental error.

SUMMARY AND CONCLUSION

It is felt that the data obtained from the records of the two overtone bands of $N^{15}O$ was quite good. In previous work done on these bands in this laboratory the resolution was not as high as it is now with the revised optical system. The computer analysis to determine the constants also gave a measure of their accuracy and it is not probable that a more refined set of constants can be obtained without a higher resolution instrument.

It would be of considerable interest to observe the fundamental of $N^{15}O$ under the resolution available here in the infrared and re-evaluate the rotation-vibration constants of the band.

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