

Infrared Spectra and Molecular Constants of N^{14}O_2 and N^{15}O_2 *†

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The infrared spectra of N^{14}O_2 and N^{15}O_2 were observed under high dispersion with gas pressures up to 15 cm of N^{14}O_2 and 4 cm of N^{15}O_2 in a 20-meter absorption cell. Ten bands of N^{14}O_2 , eight with well-resolved rotation lines; and nine bands of N^{15}O_2 , seven with well-resolved rotation lines, were observed. The band centers of these bands were determined, from which all the ω_i and x_{ij} were calculated. By making use of the very good assumption that the potential constants are the same for isotopic molecules, the four force constants in the most general quadratic potential function were found to be $f_d = 10.927 \pm 0.065$, $f_a = 1.125 \pm 0.003$, $f_{da} = 2.038 \pm 0.065$, and $f_{aa} = 0.390 \pm 0.20$ (all in millidynes/A).

The following ground state rotational constants were obtained from the rotational structures of the observed bands using symmetric top combination relations: for N^{14}O_2 , $A = 8.003$, $B = 0.434$, $C = 0.412$; and for N^{15}O_2 , $A = 7.642$, $B = 0.434$, $C = 0.410$ (all in cm^{-1}). Theoretical spectra calculated for type A and type B bands by substituting these rotational constants into the asymmetric top equations gave excellent agreement when compared with the observed spectra. The partition function ratio for N^{15}O_2 to N^{14}O_2 is found to be 1.1080 at 25°C.

I. INTRODUCTION

Investigations of the infrared spectrum of NO_2 have been carried out over a span of fifty years by a large number of workers.¹ Because NO_2 is contaminated at room temperature by the dimer, N_2O_4 , and because for the most part the spectra were observed under low dispersion, considerable confusion resulted in

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¹ The reader is referred to the bibliography in Herzberg (1) for papers on NO_2 up through 1945.

identification of the bands with the appropriate molecule. The principal uncertainty was with regard to the band center of $\tilde{\nu}_1$. Up to the present the only grating work has been by Sutherland (1), Sutherland and Penney (1) and by Moore (2). However, only Moore was able to resolve any rotational structure and his work did not include any of the fundamental bands. The band center of $\tilde{\nu}_3$ was, therefore, not known from an actual band analysis, and various estimates of the band center of $\tilde{\nu}_1$ were obtained from prism data, ultraviolet spectra by Harris, Benedict, and King (1), and from combination bands observed by Moore. Indeed, neither $\tilde{\nu}_1$ nor $\tilde{\nu}_2$ were observed in the infrared until 1949 when Wilson and Badger (3) observed them with a prism. Recent prism and grating work, respectively, by Brown and Wilson (4) and by Keller and Nielsen (5) has fixed the band center of $\tilde{\nu}_2$ definitely at 749.8 cm^{-1} . The nonlinear character of NO_2 was suggested in 1935 by Sutherland and Penney (1) with the report of the observation of $2\tilde{\nu}_3$, and verified by the electron diffraction experiments of Maxwell and Mosley (1).

Nine bands from 1.4μ to 3.4μ observed with a grating by Moore (2) provided data from which the vibrational and rotational constants were determined. Weston (6) combined the results of Moore with his own prism observations on N^{16}O_2 and calculated the force constants for NO_2 .

Recently, Bird (7) has investigated the microwave spectrum of NO_2 and established the rotational constants of N^{14}O_2 as $(A'' - \bar{B}'') = 7.567\text{ cm}^{-1}$, and $\bar{B}'' = (B'' + C'')/2 = 0.4216\text{ cm}^{-1}$. The structural parameters from this work are $r(\text{N—O}) = 1.197\text{ \AA}$, and the O—N—O angle $= 134^\circ 15'$.

Considering the uncertainties in the fundamental vibrational frequencies of N^{14}O_2 and the small amount of existing data on N^{16}O_2 , it appeared to be worth while to make a grating study of the fundamental bands, and as many overtone and combination bands as possible with a view to clearing up any uncertainties and calculating the force constants accurately.

II. EXPERIMENTAL DETAILS

The observations and measurements covering the spectral region 1.7μ – 15.0μ on the bands in the NO_2 molecule were made using The University of Tennessee prism-grating infrared spectrometer designed and described by Nielsen (8). Four gratings were required to cover the spectral range encountered in this investigation. These gratings consisted of a 1200 lines-per-inch original ruled at the University of Michigan and three Bausch and Lomb replicas of 4500, 7500, and 15,000 lines-per-inch. Three detectors were used in conjunction with these gratings. A Golay pneumatic detector (9) was used with the 1200, 4500, and 7500 lines-per-inch gratings for wavelengths longer than 3μ , and a lead sulfide photoconducting cell was used with the 15,000 lines-per-inch grating for wavelengths less than 3μ . A lead telluride photoconducting system was used for one band, the 2900-cm^{-1} band of N^{14}O_2 .

Three sample cells were used to vary the absorption path length from 10 cm to 20 meters. The 20-meter path length was achieved through the use of a 60-cm White type (10) multiple reflection cell. The mirrors in this cell were adjusted for 32 traversals through the sample. A 10-cm fluorothene cell equipped with NaCl windows was used for the bands with strong absorption. Since NO₂ polymerizes to N₂O₄ to a considerable extent at room temperature, it was necessary for the sample to be heated to 150–200°C to ensure that bands observed were caused by NO₂ and not by N₂O₄. This was accomplished with a 26-cm monel cell equipped with heating coils. This cell was fitted with AgCl windows to withstand the high temperatures used. Pressures of NO₂–N₂O₄ in the absorption cells were measured by the use of a Booth-Kromer gauge, which consists essentially of a flexible diaphragm to separate the highly reactive NO₂ from the mercury in the manometer. A simple electronic device indicates the existence of equal pressures on both sides of the diaphragm.

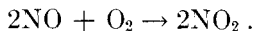
Collected in columns 1 and 2 of Table I are the assignments and band centers of all the bands observed in this investigation. The band centers have been determined from combination relations discussed in later sections. Some overlap occurs with regions measured by Moore.

The sample of N¹⁴O₂ used in this investigation was procured from the Matheson Company and purified by repeated fractional distillation from a dry ice-acetone bath until a crystalline white solid was obtained. Water was removed from the sample by passing the gas through a CaSO₄ drying tube. Much N¹⁴O₂ was lost through this method of drying because CaSO₄ absorbs NO₂ quite readily. Therefore, extreme precautions were taken in preparing the much more expensive N¹⁵O₂ to ensure that the gas was dry. This was accomplished by first preparing NO from which the water can easily be frozen out, in contrast to NO₂, whose 11°C freezing temperature necessitates some other means of H₂O removal.

The sample of N¹⁵O₂ was prepared from 99 percent isotopically enriched HNO₃ through the reactions



and



The excess SO₂ in the first reaction was removed by vigorous shaking in a 10-percent KOH solution. The NO was passed through a solid ether-ether freezing bath to remove water and any SO₂ that remained. The NO was then allowed to react with dry oxygen to form NO₂. Finally the reaction vessel was completely encased with dry ice to freeze the NO₂ and any excess oxygen in the final reaction was pumped out of the flask.

TABLE I
ROTATIONAL CONSTANTS DETERMINED FROM ANALYSES OF OBSERVED BANDS (cm⁻¹)

Type A bands							
Assignment	$\tilde{\nu}_0$	E''	B'	ΔB	$D_J'' (\times 10^6)$	$D_J' (\times 10^6)$	
$N^{14}O_2$	$\tilde{\nu}_3$	1617.75	0.422	0.420	-0.003	0.95	2.1
	$\tilde{\nu}_1 + \tilde{\nu}_3$	2907.42	0.425	0.420	-0.005	6.7	7.9
	$2\tilde{\nu}_1 + \tilde{\nu}_3$	4179.97	0.422	0.414	-0.008	3.0	3.0
	$3\tilde{\nu}_1 + \tilde{\nu}_3$	5437.55					
	$3\tilde{\nu}_3$	4752.45	0.425	0.419	-0.007	4.4	4.6
	$\tilde{\nu}_1 + 3\tilde{\nu}_3$	5981.92					
$N^{15}O_2$	$\tilde{\nu}_3$	1580.32	0.421	0.419	-0.002	1.5	1.8
	$\tilde{\nu}_1 + \tilde{\nu}_3$	2860.20	0.422	0.416	-0.005	7.8	7.0
	$2\tilde{\nu}_1 + \tilde{\nu}_3$	4120.20	0.425	0.419	-0.007	3.5	3.5
	$3\tilde{\nu}_1 + \tilde{\nu}_3$	5368.95					
	$3\tilde{\nu}_3$	4653.60	0.422	0.415	-0.006	(17?)	(17?)
	$\tilde{\nu}_1 + 3\tilde{\nu}_3$	5875.92					
Type B bands							
Assignment	$\tilde{\nu}_0$	$A'' - B''$	$A' - B'$	$\Delta(A - B)$	$D_K'' (\times 10^6)$	$D_K' (\times 10^6)$	
$N^{14}O_2$	$\tilde{\nu}_1$	1318	8.12	8.03			
		(1319.7) ^a					
	$\tilde{\nu}_2$	749.8	7.58	7.92	0.34	2.41	2.67
	$2\tilde{\nu}_2 - \tilde{\nu}_2$	748.6	7.91	8.30	0.39	2.36	3.01
	$2\tilde{\nu}_3$	3199	8.13	8.10			
$N^{15}O_2$	$\tilde{\nu}_1$	1306	7.48	7.42			
		(1306.5) ^a					
	$\tilde{\nu}_2$	740.15	7.22	7.55	0.32	4.7	5.2
	$2\tilde{\nu} - \tilde{\nu}_2$	739.55	7.56	7.94	0.34	5.4	6.7

^a From vibrational analysis.

III. ANALYSIS OF THE EXPERIMENTAL DATA

TYPE B BANDS (TABLE I)

$\bar{\nu}_1$.

The symmetric stretching vibration, $\bar{\nu}_1$, shown in Fig. 1 for $N^{14}O_2$ and $N^{15}O_2$ presented the most serious difficulty with regard to experiment and analysis. As may be seen from the background curve at the bottom of Fig. 1, the R branch overlaps the intense atmospheric water vapor band. Attempts to dry out the instrument were, however, sufficiently successful to make it possible to identify the NO_2 Q branches quite accurately. The Q branches appear to fade out below

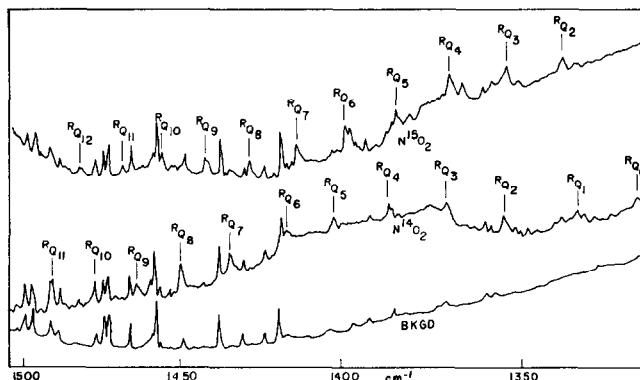


FIG. 1. The $\bar{\nu}_1$ vibration-rotation bands of $N^{14}O_2$ and $N^{15}O_2$.

1325 cm^{-1} and none of the attempts made to observe lines below 1300 cm^{-1} were successful, though conditions were varied in these attempts. It was necessary to operate the cell at over 200°C to reduce the N_2O_4 absorption by dissociation of the dimer into NO_2 .

Two widely different choices are possible for the band center of $\bar{\nu}_1$: The first, and least attractive, of these is 1412.0 cm^{-1} for $N^{14}O_2$ and 1393.5 cm^{-1} for $N^{15}O_2$. Such a choice does indeed put the band center half-way between two strong Q branches as predicted for a symmetric top. However, the width of the band would be only about 150 cm^{-1} with 12 observed lines, whereas $\bar{\nu}_2$ extends over 326 cm^{-1} with 22 observed lines.

The second possible choice, 1319.7 cm^{-1} for $N^{14}O_2$, is given by vibrational analysis of the observed bands $\bar{\nu}_3$, $\bar{\nu}_1 + \bar{\nu}_3$, and $2\bar{\nu}_1 + \bar{\nu}_3$. As the lowest wave number line observed for $N^{14}O_2$ was 1325.46 cm^{-1} this line would then have to be assigned as RQ_0 . The implication of this is that the PQ lines were not observed. The observed Q branches can be represented by the relation

$$\bar{\nu} = \bar{\nu}_0 + \Delta(A - B)/4 + [(A' - B') + (A'' - B'')]m + \Delta(A - B)m^2, \quad (1)$$

where $m = \pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}, \dots$. Analyses of the bands for $N^{14}O_2$ and $N^{15}O_2$ were performed by plotting $(\bar{\nu} - \bar{\nu}_0)/m$ versus m . A study of Fig. 2, in which the Q branch wave numbers have been plotted versus a running number shows that a band center choice of 1318 cm^{-1} falls half-way between the lowest wave number line and the position of the next line predicted by the curve. Asymmetric top theory predicts a minimum intensity at the band center. Such a choice is also in agreement with the value computed by Moore from combination bands alone, and with the value suggested by Harris, King, Benedict, and Pearse. The band center choice of 1319.7 cm^{-1} for $N^{14}O_2$ is, therefore, made. Reference to Table I indicates that there appears to be a discrepancy as regards the value of $(A'' -$

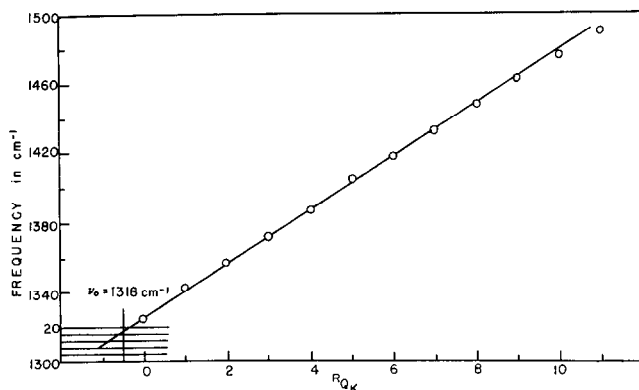


FIG. 2. Plot of the wave numbers of the observed Q branches of $\tilde{\nu}_1(\text{N}^{14}\text{O}_2)$ versus a running number (K).

$B'' = 8.12 \text{ cm}^{-1}$ obtained from $\tilde{\nu}_1$ compared with $(A'' - B'') = 7.58 \text{ cm}^{-1}$ obtained from $\tilde{\nu}_2$ for N^{14}O_2 . In N^{15}O_2 the agreement appears to be somewhat better. The analysis of $\tilde{\nu}_2$ was carried out using lines which were well-distributed on both sides of the band center, while for $\tilde{\nu}_1$ this could not be done because the PQ lines were not observed. It is therefore likely that $(A'' - B'')$, and consequently also the band center, cannot be determined from rotational analysis of $\tilde{\nu}_1$ to better than 0.5 cm^{-1} . Analysis of $\tilde{\nu}_2$ using only the RQ lines gave an $(A'' - B'')$ value of 7.85 cm^{-1} which is 0.27 cm^{-1} larger than 7.58 cm^{-1} obtained from the whole band.

$\tilde{\nu}_2$.

A detailed account of the symmetric bending mode $\tilde{\nu}_2$ of N^{14}O_2 is not included here because a study of this band has recently been published by Keller and Nielsen (5) from this laboratory. However, $\tilde{\nu}_2$ for N^{15}O_2 , shown in Fig. 3, was thoroughly investigated at temperatures of 115°C , 157°C , and 210°C which virtually eliminated dimer absorption. As in N^{14}O_2 the central four lines were not used in the analysis because the deviation from the symmetric top equation is too large for these low K values.

$2\tilde{\nu}_2 - \tilde{\nu}_2$.

The difference band $2\tilde{\nu}_2 - \tilde{\nu}_2$ has recently been reported by Keller and Nielsen (11) and is, therefore, not given in detail here. The lines of the difference band for N^{15}O_2 are clearly visible between the intense Q branches of $\tilde{\nu}_2$ in Fig. 3. The band center was determined from analysis and is listed in Table I.

$2\tilde{\nu}_3$.

Eleven weak Q lines of a perpendicular type band were observed in the 20-meter absorption cell at a pressure of 11 cm of N^{14}O_2 . These lines agree sub-

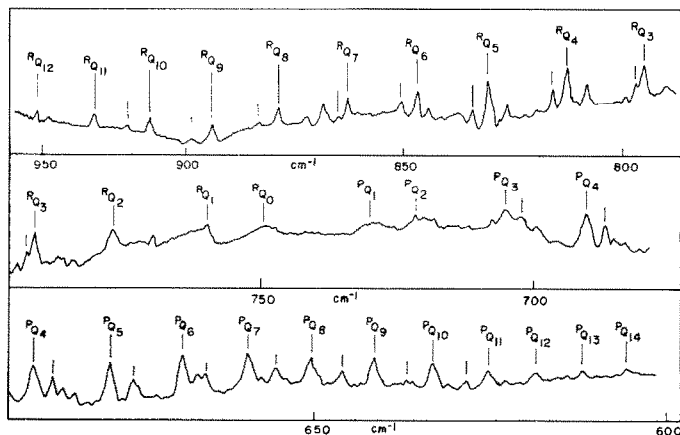


FIG. 3. The $\bar{\nu}_2$ and $2\bar{\nu}_2 - \bar{\nu}_2$ vibration-rotation bands of N¹⁵O₂.

stantially with those ascribed to $2\bar{\nu}_3$ by Moore. Rotational constants listed in Table I were found from plots of $(\nu - \nu_0)/m$ versus m [Eq. (1)]. It should be noted that for $2\bar{\nu}_3$ as for $\bar{\nu}_1$ only two lines of the PQ series could be measured and the analysis was therefore carried out essentially with RQ lines. As in the case of $\bar{\nu}_1$, the $(A'' - B'') = 8.13 \text{ cm}^{-1}$ appeared to be about 0.5 cm^{-1} larger than for $\bar{\nu}_2$. Perhaps also in this case the $(A'' - B'')$ cannot be determined to better than 0.5 cm^{-1} in this way.

$2\bar{\nu}_3$ was not observable in N¹⁵O₂ with the available gas, 4-cm pressure in the 20-meter cell.

TYPE A BANDS (TABLE I)

$\bar{\nu}_3$.

The antisymmetric stretching mode $\bar{\nu}_3$ (Figs. 4 and 5) caused much experimental concern because of the irregular appearance of its P branch. It was first believed that this was caused by the strong water vapor background in which this band appears, but careful drying of the sample and spectrometer offered convincing proof that the irregularities are real and are probably caused by the asymmetry of the molecule. Determination of the band center proved a fairly

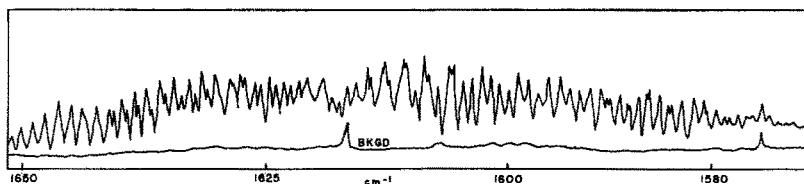
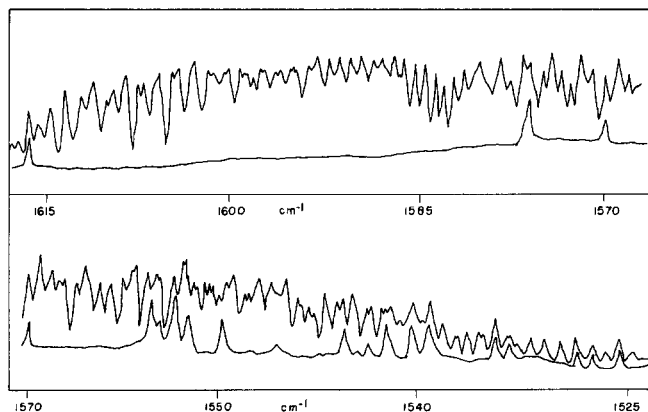


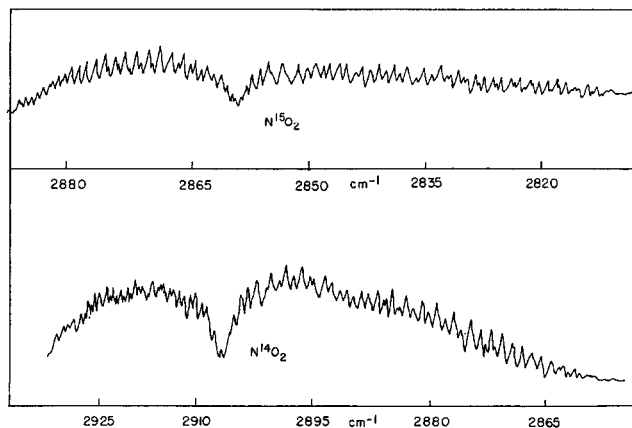
FIG. 4. The $\bar{\nu}_3$ vibration-rotation band of N¹⁴O₂.

FIG. 5. The $\tilde{\nu}_3$ vibration-rotation band of $N^{15}O_2$.

difficult task. It was accomplished by performing rotational analyses on several tentative assignments. It was noted that the ΔB value remained fairly constant irrespective of the assignment used. Therefore, this ΔB value, together with B'' and $A'' - B''$ from Bird's (7) results were used to calculate a theoretical spectrum. A comparison of this theoretical spectrum with the experimental spectrum then made the assignment of lines fairly easy and certain. The rotational constants and band center given in Table I were obtained from this final assignment.

$$\tilde{\nu}_1 + \tilde{\nu}_3, 2\tilde{\nu}_1 + \tilde{\nu}_3, 3\tilde{\nu}_3.$$

The combination band $\tilde{\nu}_1 + \tilde{\nu}_3$ (Fig. 6), as well as $2\tilde{\nu}_1 + \tilde{\nu}_3$ and $3\tilde{\nu}_3$ presented no real difficulty either experimentally or in analysis. These bands show most

FIG. 6. The $\tilde{\nu}_1 + \tilde{\nu}_3$ vibration-rotation bands of $N^{14}O_2$ and $N^{15}O_2$.

clearly the expected structure of the parallel bands of NO₂—i.e., intensity alternation in the *P* branch, merging of adjacent lines in the *R* branch, and a very weak *P* branch. The intensity alternation is produced by different statistical weights and occurs also in the *R* branch, but it is not easily observable there because of the pair-wise merging of the even and odd *J* lines.

$$3\bar{\nu}_1 + \bar{\nu}_3, \bar{\nu}_1 + 3\bar{\nu}_3.$$

Two very weak bands were found at 5437 and 5982 cm⁻¹ for N¹⁴O₂ which were ascribed to $3\bar{\nu}_1 + \bar{\nu}_3$ and $\bar{\nu}_1 + 3\bar{\nu}_3$, respectively. The 20-meter path length and 15-cm gas pressure required to observe these bands made it necessary to use slits as wide as 1.2 cm⁻¹. Therefore, these bands were not resolved.

These two bands were observed with the same path length but with only 4 cm of N¹⁵O₂, which was all the gas available. All of these bands showed definite band heads which made a check on the measured band centers possible.

The location of the band centers can be calculated from the equation

$$\bar{\nu} = \bar{\nu}_0 + (B' + B'')m + (B' - B'')m^2, \quad (2)$$

where $m = J + 1$ for the *R* branch, and $m = -J$ for the *P* branch.

A band head is expected when $d\bar{\nu}/dm = 0$ or when $m = -(B' + B'')/2(B' - B'')$. Substituting this value of m into Eq. (2) gives

$$\bar{\nu}_{b.h.} - \bar{\nu}_0 = -(B' + B'')^2/4(B' - B''). \quad (3)$$

For $\bar{\nu}_1 + 3\bar{\nu}_3$, the calculated value $\bar{\nu}_{b.h.} - \bar{\nu}_0 = -(0.411 + 0.422)^2/4(-0.0112) = 15.5$ cm⁻¹ compares favorably with the experimental values of 17.4 and 15.2 cm⁻¹ for N¹⁴O₂ and N¹⁵O₂, respectively.

Complexity of $3\bar{\nu}_3$ and $\bar{\nu}_1 + 3\bar{\nu}_3$ Regions.

Two anomalous regions, $3\bar{\nu}_3$ and $\bar{\nu}_1 + 3\bar{\nu}_3$, occur in the spectra where *A* type bands are apparently overlaid by *B* type structure. The spacing of the *Q* branches in these bands suggests that the observed lines belong to the *R* branches of type *B* vibration-rotation bands whose *P* branches cannot be seen, in analogy with the observations of the $\bar{\nu}_1$ bands. Therefore these *B* type bands have been tentatively assigned to $2\bar{\nu}_2 + 2\bar{\nu}_3$ and $\bar{\nu}_1 + 2\bar{\nu}_2 + 2\bar{\nu}_3$. The band centers calculated from the vibrational constants are: $2\bar{\nu}_2 + 2\bar{\nu}_3 = 4689$ cm⁻¹ and $\bar{\nu}_1 + 2\bar{\nu}_2 + 2\bar{\nu}_3 = 5933$ cm⁻¹ for N¹⁴O₂; $2\bar{\nu}_2 + 2\bar{\nu}_3 = 4601$ cm⁻¹ and $\bar{\nu}_1 + 2\bar{\nu}_2 + 2\bar{\nu}_3 = 5833$ cm⁻¹ for N¹⁵O₂.

IV. ROTATIONAL CONSTANTS

The rotational constants derived from combination relations applied to all the bands are summarized in Table I.

For plane molecules, $I_C = I_A + I_B$, which holds rigorously only for the equilib-

TABLE II
 ROTATIONAL CONSTANTS (cm^{-1})

Constant	$\text{N}^{14}\text{O}_2^{\text{a}}$	$\text{N}^{14}\text{O}_2^{\text{b}}$	$\text{N}^{15}\text{O}_2^{\text{b}}$
A''	7.982	8.003	7.642
B''	0.4331	0.434	0.434
C''	0.4108	0.412	0.410
α_1^B	—	-0.0028	-0.0026
α_3^B	—	-0.0024	-0.0021
α_2^A	—	0.36	0.33

^a Bird's microwave results.^b Present work.

rium moment of inertia, but with very good approximation for the ground state moments of inertia. Therefore, if A is known from perpendicular bands, B and C can be obtained separately from $\bar{B} = (B + C)/2$. The following relations are easily found:

$$B = -(A - \bar{B}) + (A^2 + \bar{B}^2)^{1/2}, \quad (4)$$

$$C = (A + \bar{B}) - (A^2 + \bar{B}^2)^{1/2}. \quad (5)$$

From the constants listed in Table I, we obtain the average values: for N^{14}O_2

$$A'' = 8.003 \text{ cm}^{-1}$$

$$\bar{B}'' = 0.423 \text{ cm}^{-1};$$

and for N^{15}O_2

$$A'' = 7.642 \text{ cm}^{-1}$$

$$\bar{B}'' = 0.422 \text{ cm}^{-1}.$$

The results obtained by substituting these values into Eqs. (4) and (5) are summarized in Table II.

The rotational constants α_i were calculated by substituting the measured ΔB values into the equation

$$\Delta B = B'' - B' = \sum_{i=1}^3 \alpha_i^B (v_i' - v_i''). \quad (6)$$

V. VIBRATIONAL CONSTANTS

The vibrational constants which best fit the observed band centers of N^{14}O_2 and N^{15}O_2 and also the relationship $x_{ij}'/x_{ij} = \omega_i'\omega_j'/\omega_i\omega_j$ are shown in Table III. Also listed in the table are Moore's results for comparison. The constant x_{12} was not obtainable from the present data alone. The excellent agreement of $\bar{\nu}_1$

TABLE III
 VIBRATIONAL CONSTANTS (cm⁻¹)

Constant	N ¹⁴ O ₂ ^a	N ¹⁴ O ₂ ^b	N ¹⁵ O ₂ ^b
ω_1	1361.4 \pm 1.7	1357.8	1342.5
ω_2	770.2 \pm 6.6	756.8	747.1
ω_3	1668.6 \pm 1.7	1665.5	1628.0
x_{11}	-7.1 \pm 0.3	-9.0	-8.8
x_{12}	-16.0 \pm 3.3	-9.7	-9.5
x_{13}	-33.4 \pm 0.1	-28.7	-27.7
x_{22}	-8.1 \pm 3.3	-0.5	-0.4
x_{23}	-8.2 \pm 3.3	-2.7	-2.6
x_{33}	-15.9 \pm 0.2	-16.4	-15.6

^a Moore's results.^b Present work.

and $\bar{\nu}_2$ with the results of Harris, Benedict, Pearse, and King (4) makes it reasonable to accept their results of $\bar{\nu}_1 + \bar{\nu}_2 = 2060$ cm⁻¹ and $2\bar{\nu}_1 = 2624$ cm⁻¹ to calculate x_{12} .

VI. EVALUATION OF THE FORCE CONSTANTS

The four force constants in the general potential function were determined by the method of Polo and Wilson (12). The most general form (in the harmonic oscillator approximation) for the potential energy function may be written as

$$2V = f_d(\Delta d_1^2 + \Delta d_2^2) + 2f_{dd}\Delta d_1\Delta d_2 + f_\alpha(d\Delta\alpha)^2 + 2fd_\alpha(\Delta d_1 + \Delta d_2)(d\Delta\alpha), \quad (7)$$

where Δd_1 and Δd_2 are changes in the N—O bond distances and $\Delta\alpha$ is a change in the O—N—O angle. Using the structural parameters as given by Bird,

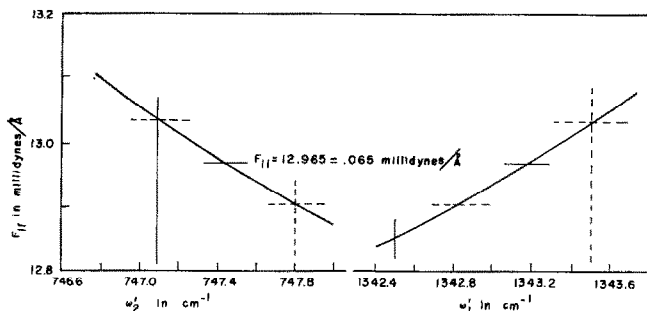
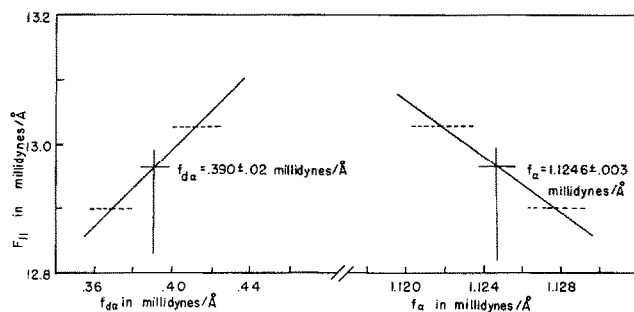
$$\alpha = 134^\circ 15', \quad r_{\text{N-O}} = 1.197 \text{ \AA},$$

we obtain the frequencies for N¹⁴O₂ given in (8)

$$\begin{aligned} \lambda_3 &= 5.88889 \times 10^{-7} \omega_3^2 = 0.183706(f_d - f_{dd}), \\ \lambda_1 + \lambda_2 &= 0.084075F_{11} + 0.367412f_\alpha - 0.204497f_{d\alpha}, \\ \lambda_1\lambda_2 &= 0.012831(F_{11}f_\alpha - 2f_{d\alpha}^2), \end{aligned} \quad (8)$$

where the ω 's are in cm⁻¹, all the force constants are in millidynes per angstrom, and, similarly, the frequencies for N¹⁵O₂ are given by (9)

$$\begin{aligned} \lambda_3 &= 0.175648(f_d - f_{dd}), \\ \lambda_1 + \lambda_2 &= 0.082641F_{11} + 0.351296f_\alpha - 0.19092f_{d\alpha}, \\ \lambda_1\lambda_2 &= 0.012237(F_{11}f_\alpha - 2f_{d\alpha}^2). \end{aligned} \quad (9)$$

FIG. 7. Force constant F_{11} plotted versus ω_2 and ω_1 of N^{15}O_2 .FIG. 8. Force constant F_{11} plotted versus f_{da} and f_a .

The following procedure was used to determine the four force constants: The values of $(f_d - f_{da})$ can be determined directly from ω_3 of both N^{15}O_2 and N^{14}O_2 and are 8.8855 and 8.8913 millidynes/Å, respectively. By substituting ω_1 and ω_2 of N^{14}O_2 into Eqs. (8) and (9), values of f_a and f_{da} were calculated as functions of $F_{11} = f_d + f_{da}$. From the force constants determined in this way, the frequencies of N^{15}O_2 were calculated as functions of F_{11} . These frequencies can be plotted as a function of F_{11} as shown in Fig. 7. The influence of errors in

TABLE IV
FORCE CONSTANTS FOR NO_2 IN MILLIDYNES/Å

	I ^a	II ^b
f_d	$10.927 \pm .065$	$10.406 \pm .025$
f_a	$1.125 \pm .003$	$1.0968 \pm .0009$
f_{da}	$2.038 \pm .065$	$2.024 \pm .025$
f_{da}	$.390 \pm .020$	$.535 \pm .005$

^a From harmonic frequencies.

^b From observed fundamental frequencies.

the frequency measurements on F_{11} , and consequently on f_α and $f_{d\alpha}$ (Fig. 8), can be seen on the graphs where the solid vertical lines represent the harmonic frequencies and the dotted lines show the estimated errors. The results of this analysis are given in Table IV. Also shown in Table IV are the results obtained by substituting the observed fundamental frequencies instead of the harmonic frequencies.

VII. DISCUSSION

The energy levels of a near prolate symmetric top have been given by Wang (13) as

$$W = \frac{1}{2}(B + C)J(J + 1) + \frac{1}{2}(2A - B - C)w, \quad (10)$$

where w is written as a power series in $b = (C - B)/(2A - B - C)$:

$$w = K_{-1}^2 + C_1b + C_2b^2 + C_3b^3 + C_4b^4 + C_5b^5. \quad (11)$$

The values of K_{-1}^2 and the C_i 's have been tabulated for $J = 1$ to $J = 40$ by Schwendeman (14). The spectra obtained by substituting the experimentally determined rotational constants into the above equations, using appropriate selection rules, and intensities computed according to the symmetric top relations given by Dennison (15), show excellent agreement with the experimentally obtained spectra as shown in Figs. 9 and 10. It may be seen in Fig. 9 that the abnormal appearance and spacing of the central four lines of $\bar{\nu}_2$ is a direct result of the slight asymmetry of the molecule.

With the present investigation, the fundamental bands of N¹⁴O₂ and N¹⁵O₂ have all been observed under high dispersion. Their resolution has permitted band analyses which, together with overtone and combination bands also resolved here, and by Moore, have established the vibrational, rotational, and force constants of the molecule.

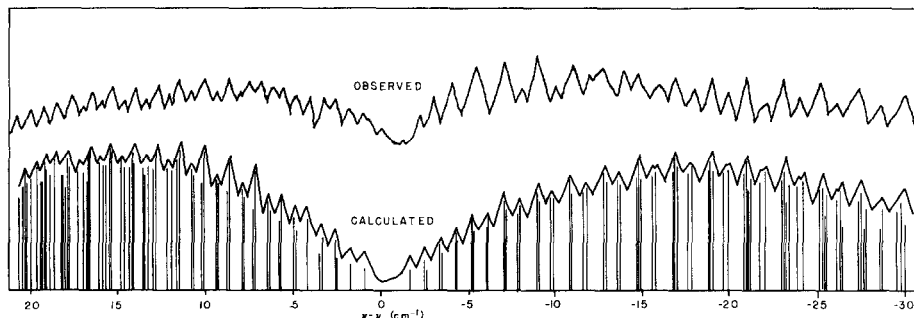


FIG. 9. The $\bar{\nu}_1 + \bar{\nu}_3$ vibration-rotation band of N¹⁴O₂ showing the actual record and the theoretical envelope computed from the rotational constants.

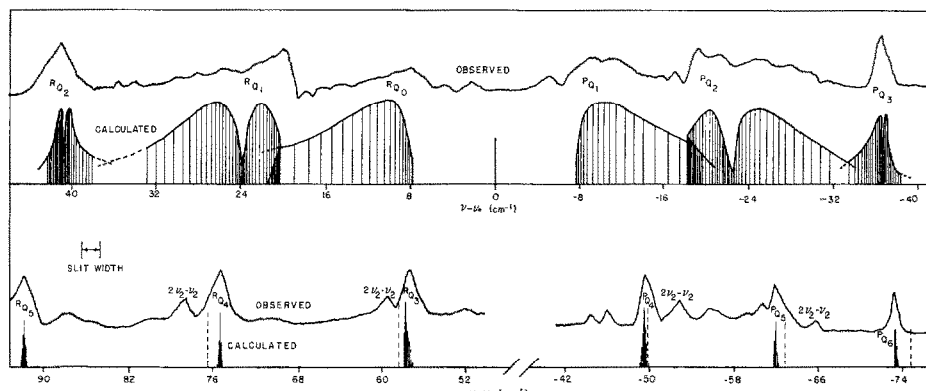


FIG. 10. The $\bar{\nu}_2$ vibration-rotation band of N^{14}O_2 showing the actual record and the theoretical envelope computed from the rotational constants.

Because all the harmonic frequencies are now accurately known, it also seemed worthwhile to reevaluate the partition function ratio for the two isotopic species. This was accomplished following the method outlined by Begun and Fletcher (16). The value obtained for the ratio $f(\text{N}^{15}\text{O}_2/\text{N}^{14}\text{O}_2) = 1.1080$ at 25°C . This accidentally agrees exactly with Weston's value despite the fact that the frequencies used were not the same.

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NOTE ADDED IN PROOF

Through private communication the authors have been informed by Dr. G. E. Moore (Ref. 2) that the D -values found in his Table V are too large by a factor of 2. This correction makes the agreement with the present values satisfactory.

Also through private communication, Dr. G. R. Bird has informed the authors that the pure rotational spectra of NO_2 have been observed with a grating spectrometer by Danti, Lord, and Bird. These results are scheduled to be published in the August *Spectrochimica Acta* and were reported by Lord at the Molecular Spectroscopy Symposium in Columbus, Ohio, June 1958. From their data they derive the centrifugal distortion constant D_K to be $2.24 \times 10^{-3} \text{ cm}^{-1}$, which is also in excellent agreement with present results.

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