THE NEAR INFRARED SPECTRA

OF

DEUTERIUM CHLORIDE AND NITRIC OXIDE

by

Beverley Hall Van Horne

AN ABSTRACT

Submitted to the School for Advanced Graduate Studies of
Michigan State University of Agriculture and
Applied Science in partial fulfillment of
the requirements for the degree of

DOCTOR OF PHILOSOPHY

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1957

Approved C. D. Hause

Beverley H. Van Horne

ABSTRACT

The first (2-0) and second (3-0) overtone bands of DCl have been obtained with high dispersion in the 2.4 and 1.6 micron regions. The (3-0) band of Nitric Oxide at 1.8 microns was obtained with increased resolution and the molecular constants re-evaluated.

The molecular constants obtained for DCl are:

	DCl^{35}	DCl^{37}
B_e	$5.449_o cm^{-1}$	$5.432\ cm^{-1}$
I_e	$5.135_4 \times 10^{-40}$ $g\text{-}cm^2$	$5.151_6 \times 10^{-40}$ $g\text{-}cm^2$
r_e	$1.274_4 \times 10^{-8}$ cm	$1.274_5 \times 10^{-8}$ cm
w_e	$2144.77\ cm^{-10}$	$2141.82\ cm^{-1}$
$w_e x_e$	$26.92\ cm^{-1}$	$26.99\ cm^{-1}$
$w_e y_e$	$0.036\ cm^{-1}$	$0.063\ cm^{-1}$

The values for the rotational constants, B_e, I_e, and r_e are essentially in agreement with those obtained by Pickworth and Thompson for the fundamental band. These data also agree with values calculated from the data for HCl.

The (3-0) band of NO was resolved sufficiently to obtain good frequencies on all lines of R&R branches for both sub-bands through J = 45/2 and 37/2 respectively. The Q branches were resolved but due to their overlapping only one line in the

Q_1 and two lines in the Q_2 branches were measurable. The data was more reliable than previous work, largely because of a Fabry-Perot fringe calibration system. The molecular constants obtained are listed as follows:

$(B_o)_{eff}\ ({}^2\Pi\ 1/2)$	$1.6720\ cm^{-1}$
$(B_o)_{eff}\ ({}^2\Pi\ 3/2)$	$1.7197\ cm^{-1}$
B_o	$1.6958\ cm^{-1}$
B_3	$1.6433\ cm^{-1}$
B_e	$1.7044\ cm^{-1}$
α_e	$.0174\ cm^{-1}$
I_e	$16.422 \times 10^{-40}\ gm\text{-}cm^2$
r_e	$1.1509^{6} \times 10^{-8}\ cm$

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INTRODUCTION

General

The spectra of two diatomic molecules, deuterium chloride and nitric oxide were studied in the near infrared by means of a high resolution vacuum recording spectrometer. Two rotation-vibration bands of deuterium chloride were examined; the 2-0 and the 3-0 bands, at 2.4 and 1.6 microns respectively. One band of nitric oxide, the 3-0 band at 1.8 microns was obtained at higher resolution than previously and the constants re-evaluated.

In 1953 Pickworth and Thompson[1] re-examined the fundamental band of deuterium chloride at 5 microns. This had previously been obtained under low resolution by Hardy, Barker, and Dennison[2] in 1932. The work of Pickworth and Thompson gave more reliable rotational constants since they were able to obtain with good resolution lines out to $J = 16$. The present work includes results of an investigation of the first and second overtone bands of DCl at 2.4 and 1.6 microns respectively.

In 1939, Nielsen and Gordy[3], and Gillette and Eyster[4] published the results of investigations of the fundamental of nitric oxide. Gillete and Eyster[4] gave a complete analysis of the observed structure and obtained the vibrational and rotational constants of the molecule. In 1955 Nichols, Hause and Noble[5] analyzed the first (2-0), and the second (3-0) overtone bands and obtained the molecular constants. The envelope of the third overtone (4-0) was also obtained and its origin determined. A comprehensive survey of all previous work on the ground state of NO, including the results from the electronic bands, is given by Nichols.[6] More recently, Shaw[7] has re-examined the fundamental at 5.3 microns with increased resolution and re-evaluated the molecular constants.

The present work includes a re-examination of the 3-0 band at 1.8 microns. The purpose of the investigation was to search for evidence of lambda-type doubling in the infrared spectrum. The magnitude of the expected splitting could be predicted from the micro-wave studies of Burrus and Gordy[8], and of Gallagher, Bedard, and Johnson.[9] The doublet separation of the $^2\pi(1/2)$, $J = 1/2 \rightarrow J = 3/2$ line as observed by them was 355 Mc/sec. (0.012 cm^{-1}). Although the direct splitting would not be observable even with the increased resolving power available, its presence presumably might be detected by combination defects employing the Q branches. Unfortunately the intensity falls off so rapidly in the component showing observable doubling, $(^2\pi_{1/2})$, that this could not be verified.

The 3-0 band of NO was, however, obtained with better resolution than previous studies and so was analyzed and the vibrational and rotational constants re-evaluated.

The work on each molecule will be discussed separately.

THEORY

Deuterium Chloride

Deuterium chloride, a diatomic molecule with an even number of electrons (18), has a ground state of the $^1\Sigma$ type. This is a state of zero resultant spin angular momentum and zero orbital angular momentum.

For such a simple molecule the non-rigid rotating vibrator becomes an acceptable model. The total energy of the molecule (expressed in wave numbers) may be written as the sum of three terms; the electronic energy, vibrational energy, and rotational energy.

$$T = T_{el} + T_{vib} + T_{rot} \qquad \text{eq 1}$$

The rotational energy or term value for the rotational motion is given by:

$$F(J) = B_v J(J+1) - D_v J^2 (J+1)^2 \qquad \text{eq 2}$$

where J is the rotational quantum number, and :

$$B_v = B_e - \alpha_e (v + 1/2),$$

$$B_e = \frac{h}{8\pi^2 I_e c}, \qquad I_e = \mu r_e^2 \qquad \text{eqs 3}$$

$$D_v = \text{centrifugal stretching constant}$$

The subscripts indicate the dependence of the rotational constants upon the state of vibration.

The anharmonic approximation is necessary for the vibrational energy. The term value is given by:

$$G(v) = \omega_e (v + 1/2) - \omega_e x_e \ (V + 1/2)^2 + \omega_e y_e \ (v + 1/2)^3 \quad ..\text{eq } 4$$

For a vibration-rotation band in the infrared no change occurs in the electronic state. The frequency (in cm^{-1}) emitted or absorbed is given by

$$\nu = G'(v) - G''(v) + F'(J) - F''(J) \qquad \text{eq } 5$$

where the single prime refers to the upper state and the double prime to the lower state.

Performing the indicated subtraction of the G terms one obtains:

$$\Delta G(v' - v'') = \omega_e - 2\omega_e x_e \ (v + 1) + 3\omega_e y_e \ (v^2 + 2v + 13/12) \quad ..\text{eq } 6$$

The rotational transitions for $^1\Sigma$ states are governed by the selection rule, $\Delta J = \mp 1$, resulting in two branches called the P and R branches.

If the vibrational change, ΔG, is indicated by ν_o, the band origin, the observed frequencies are given by:

$$\nu = \nu_o + (B_{v'} + B_{v''})m - (B_{v'} - B_{v''} + D' - D'')m^2 - (D' + D'')m^3 \quad ..$$

$$m = \mp 1, \ \mp 2, \ \mp 3, \ .... \qquad \text{eqs } 7$$

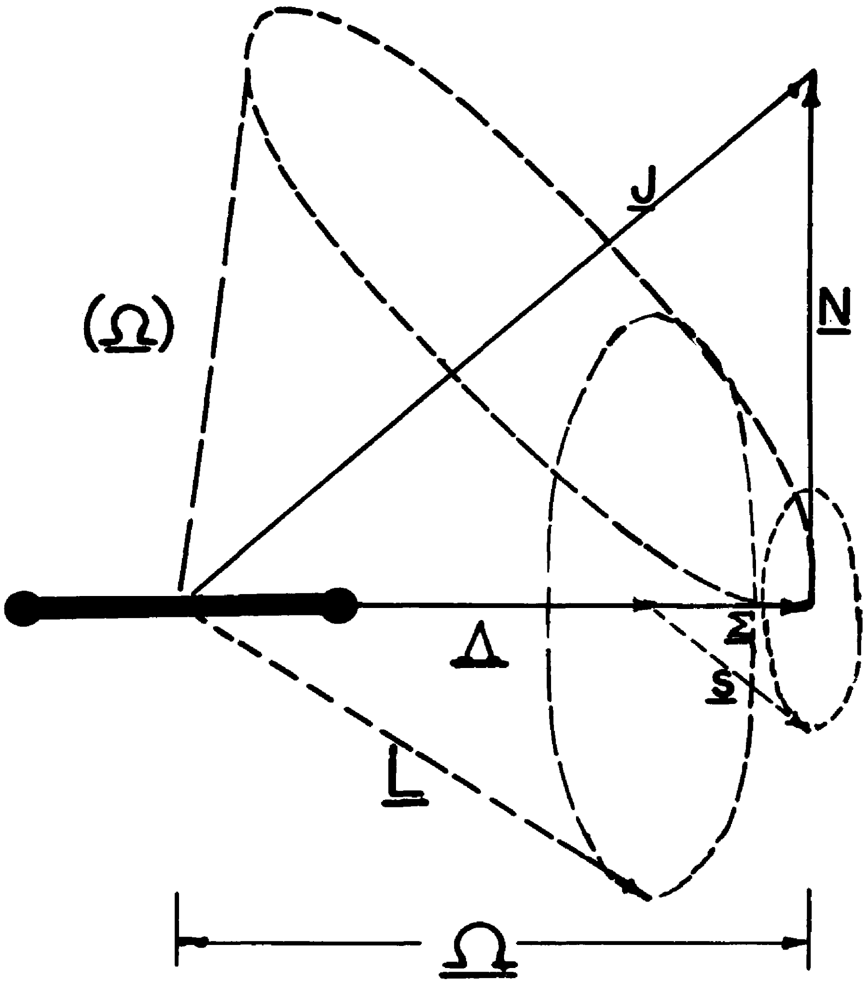
When m = -J or -1, -2, etc., one obtains the P branch; P(1), P(2), etc.. When m = J+1 or +1, +2, etc., one obtains the R branch; R(0), R(1), etc.. The P and R branches form a single series with a missing line at the band origin corresponding to m = 0. Since the vibrational intervals are much larger than the rotational intervals energywise, a vibration-rotation band is observed as rotational fine structure in the region corresponding to the vibrational energy change.

THEORY

Nitric Oxide

Nitric oxide is the only stable diatomic molecule having an odd number of electrons. Thus the resultant spin, S, and its projection on the internuclear axis, Σ, must be half-integral. This spin vector combines with Λ, the projection of L, the orbital angular momentum vector, on the internuclear axis, in either of two directions resulting in a ground state of two components. These substates are $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, indicating a Λ value of 1.

Modes of coupling of the electronic orbital angular momentum, L, and spin, S, with rotation, N, of the molecule about an axis perpendicular to the inter-nuclear axis were first considered by Hund[10]. In Hund's case "a" the interaction of electronic motion, both spin and orbital, with nuclear rotation is weak, while the coupling of electronic motion with the internuclear axis is strong. This is shown in the vector schematic of Figure 1. Expressions for the energy of the molecule in intermediate coupling cases were first derived by Hill and VanVleck[11]. Since NO approaches case "a" coupling it is possible to expand these expressions and



NITRIC OXIDE (HUND'S COUPLING CASE "a")

FIGURE 1.

obtain adequate relations for the energies of the substates. These are as follows:

$$({}^2\pi_{1/2}) \qquad T_1 = T_e - A/2 + G_1(v) + B_v(1)/4 + B_v(1)J(J+1) - D_v(1)J^2(J+1)^2 + \ldots \text{eqs } 8$$

$$({}^2\pi_{3/2}) \qquad T_2 = T_e + A/2 + G_2(v) + 7B_v(2)/4 + B_v(2)J(J+1) - D_v(2)J^2(J+1)^2 \ldots\ldots\ldots$$

The $B_v(i)$ and the $D_v(i)$ appearing in these equations are effective values and are related to the actual rotational constants of the molecule by the following relations:

$$B_v = (B_{v1} + B_{v2})/2 \qquad D_v = (D_{v1} + D_{v2})/2 \qquad \text{eqs } 9$$

Allowed frequencies emitted or absorbed by the molecule are given in general by the difference between two expressions for T_1 or T_2 ($\Delta S = 0$). If the T_e terms differ, an electronic transition has occurred. Different v's refer to the vibrational energy change, different J's to the rotational energy change. For the 3-0 band of the vibration-rotation spectrum of NO the electronic state, the ground state, does not change, v assumes the values of 0 and 3, and J assumes half-integral values beginning with either 1/2 or 3/2. Observed frequencies are governed by the selection rule $\Delta J = 0, \pm 1$.

APPARATUS

Spectrograph

The vacuum infrared spectrograph used in this work was built and previously described by Noble[12]. This instrument operates at f/5. (See Figure 2) For the work with deuterium chloride it was equipped with a Bausch and Lomb 15000 line per inch grating blazed at 1.5 microns. A Baird Associates phase sensitive amplifier and chopper system was installed. The chopper generator which operates at a frequency of 450 cycles per second was placed inside the vacuum tank just in front of the entrance slit. The detector was a lead sulfide Ektron (Kodak) cell and for the work with DCl was placed directly in back of the exit slit. Various other refinements were made in the mounting of the optical elements. A 100 watt zirconium concentrated arc was used as a source.

During the course of the work further improvements were made on the spectrograph. Most important of these was the installation of a Fabry-Perot etalon to allow simultaneous recording of fringes for calibration. This is described separately below. For the work with the 3-0 band of NO the multiple traverse cell

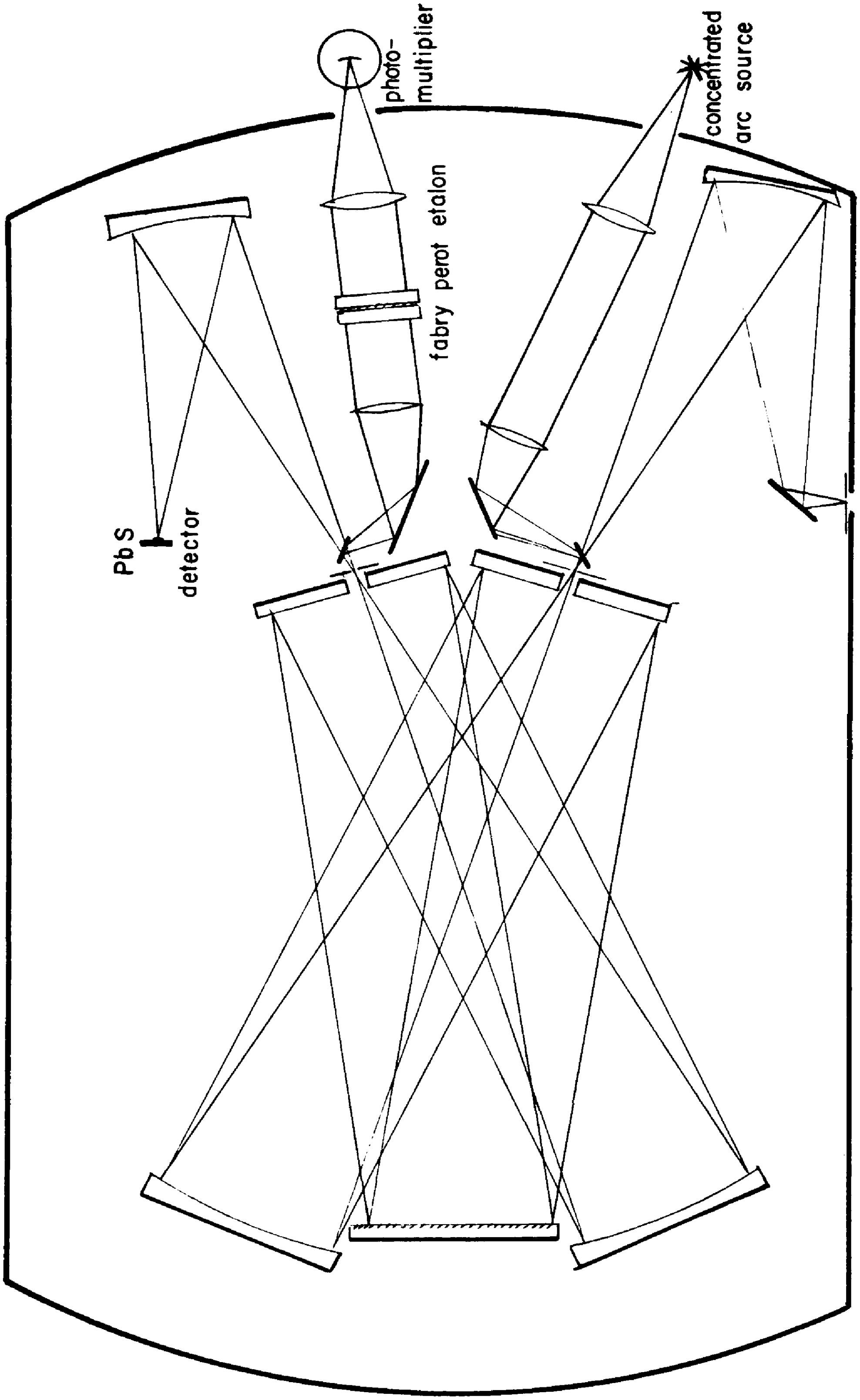


Figure 2

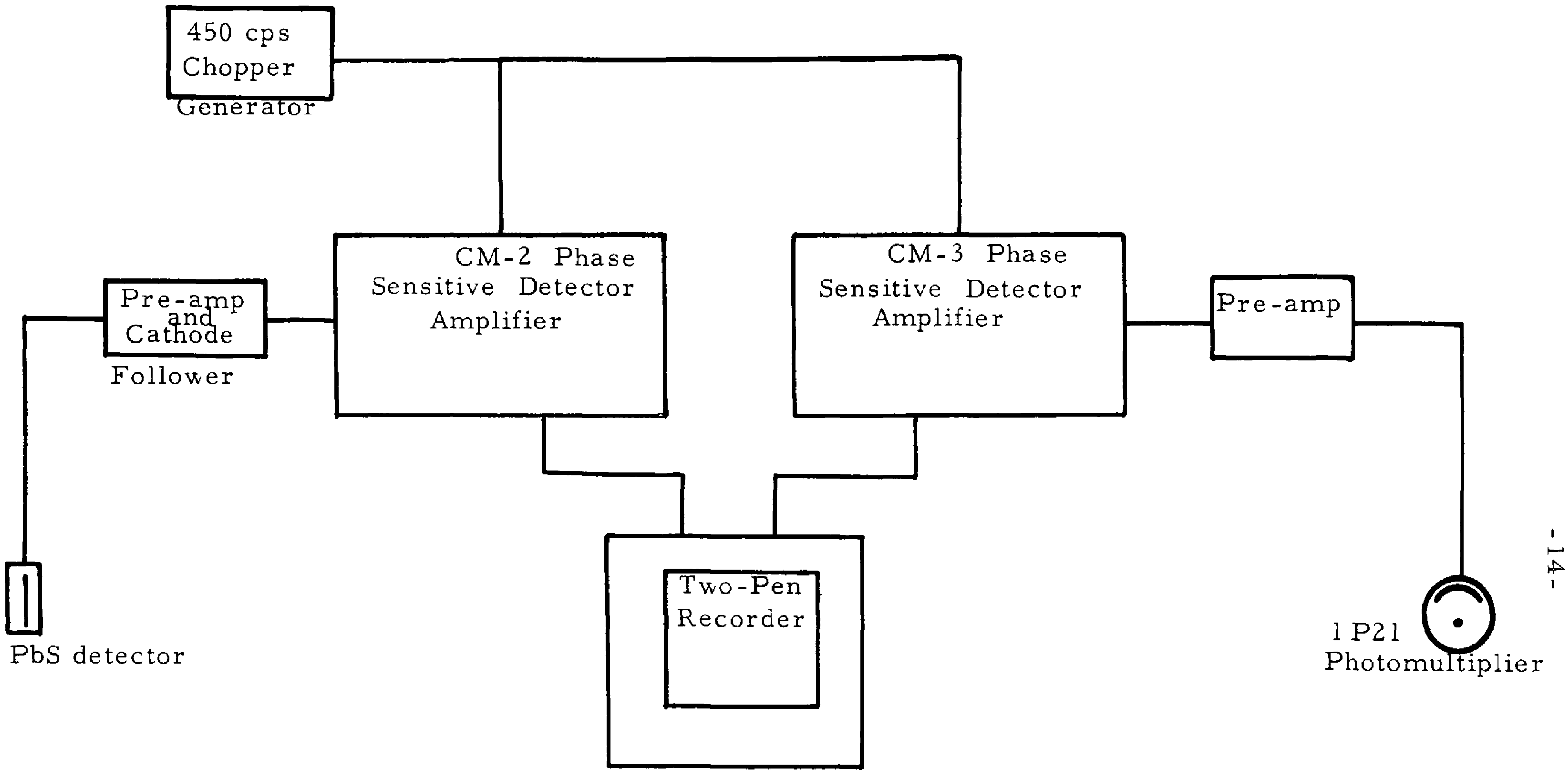
OPTICAL SYSTEM OF SPECTROGRAPH

was used and in order to obtain sufficient radiation through the system a 300 watt concentrated zirconium arc source was used. A new narrower lead sulfide detector was installed for increased resolution. A Bausch and Lomb grating, 6" by 8", with 10000 lines per inch was also installed. This has a theoretical resolving power in the first order of 60,000. It is blazed at 39° or about 3 microns and was used in the second order for the investigation of nitric oxide.

FRINGE CALIBRATION SYSTEM

In the work with deuterium chloride a Fabry-Perot etalon with a 3 mm. spacer was placed in parallel light in front of the entrance slit. This gave equally spaced fringes about 1.6 cm^{-1} apart. The actual value of this constant fringe separation was secured from the super position of known second-order argon emission lines on all runs. These same lines were used as reference points when superimposed on the DCl records. Later, the present system was built which incorporates the Fabry-Perot etalon into the optical system of the spectrograph and places it inside the vacuum tank. By means of a two-pen L and N strip chart recorder the calibration Fabry-Perot fringes were recorded simultaneously with the spectra. Figure 2 shows a rough sketch of the optical system with the fringe system incorporated. The block diagram shown in Figure 3 gives the relationship of the associated pre-amps, amplifiers, and power supplies.

In order not to interfere with the infrared signal the incoming light from a 100-watt concentrated arc lamp was brought into the entrance slit low and the mirror at the exit slit was placed above the position of the infrared signal. The Fabry-Perot etalon



BLOCK DIAGRAM OF DETECTION AND RECORDING SYSTEM
for
VACUUM INFRARED SPECTROGRAPH

Figure 3

was placed on an adjustable mount in parallel light from the exit beam. Suitable collimating lenses were employed and the beam emerged from the last lens, through the wall of the tank to a 1P21 photomultiplier just outside the tank window. It was found necessary to completely shield this photomultiplier from all stray light, and to build a low noise level preamp. A special regulated power supply for the photomultiplier high voltage supply was also found desirable. To reduce the number of orders received, optical filters were placed in front of the photomultiplier. In the 1.8 micron region a light yellow filter was very satisfactory.

Alignment of the Fabry-Perot fringe system for maximum modulation is done visually. The photomultiplier is replaced by a magnifying eye-piece and a mercury arc placed at a point back of the exit slit such that it was plainly visible through the system. The position of the line with respect to the fringe pattern was adjusted by moving the adjustable base of the etalon. When the image is seen in the central zone of the Fabry-Perot fringes and centered the modulation will be a maximum. The mercury arc is then removed and the eyepiece replaced by the photomultiplier. With the zirconium arc in operation final adjustments were made on the photomultiplier by observing the recorder signal and peaking the system from this signal. With proper adjustment a modulation of 80% or better was available.

The regular arc source supplied known argon emission lines in most regions. These were superimposed on the infrared record and together with the adjacent fringes provided an excellent calibration. Thus the measurements were independent of paper stretch or gear irregularities. The measured number of fringes and fractions thereof between any two known argon lines yield a constant for the fringe separation in wave numbers per fringe. Being adjacent to the spectrum to be measured the accuracy of line frequency determination was greatly enhanced.

This completed system of calibration was utilized for the run of the 3-0 band of nitric oxide.

ABSORPTION CELLS

For the 2-0 band of DCl it was only necessary to use a sample glass cell 40 cm. long. This consisted of a glass tube about 6 centimeters in diameter with provisions for clamping the end windows securely and a side tube with a stopcock for filling.

The 3-0 bands of DCl and NO both were obtained by use of a multiple traverse absorption cell of the White type.[13] This cell was built by Nichols[6] who describes its construction details. Its mirrors are about 6" in diameter and have a 35 cm. separation. The f-number of this cell is f/5 and it was designed to match the relative aper~~a~~ture of the spectrograph. This cell has been tested with over 100 traversals. However the signal after so many reflections is so weak that for practical work only 40 traversals were used. If 30 traversals are chosen the absorption path length of 30 x 35 centimeters gives about 11 meters of absorption path.

EXPERIMENTAL DETAILS

Deuterium Chloride

The gas was prepared by the use of acetyl chloride. The reaction was: $CH_3COCL + D_2O \longrightarrow CH_3COOD + DCL$. This reaction was carried out in a vacuum to help eliminate H_2O. The 2-0 band was obtained by using a 40 cm absorption cell. This was filled to a pressure of 35 cm Mercury and gave a maximum absorption of approximately 20%. For the 3-0 band it was necessary to use a multiple traverse cell of the White[13] type. An adjustment of the cell for 30 traversals and a gas pressure of 15 cm. Mercury gave a total absorption path of 2 meter atmospheres. The maximum absorption for this band was about 15%. In each case a 100-watt concentrated arc was used as a source.

Calibration was obtained by the use of Fabry-Perot fringes. An etalon with a 3-mm spacer was placed in parallel light in front of the entrance slit, giving equally spaced fringes about 1.6 cm^{-1} apart. The actual value of this constant fringe separation was secured from the superposition of known second-order argon emission lines on all runs. These same lines were used as reference points when superimposed on the DCL records. Figure 4 shows a portion of the 3-0 band and a tracing of the fringe pattern used in calibration.

3-0 Absorption Band of D Cl at 1.64 μ

R- Branch

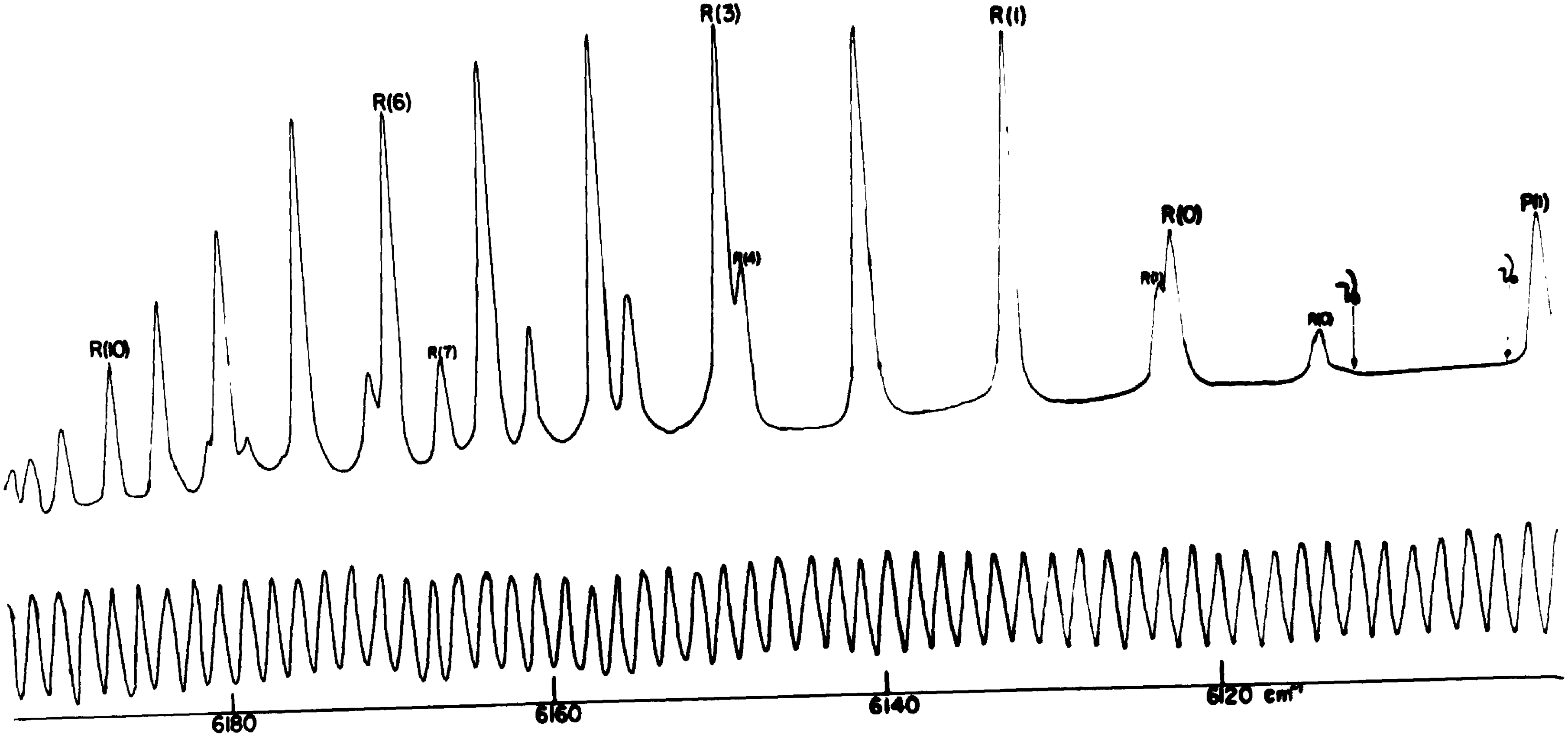


Figure 4

EXPERIMENTAL DETAIL

Nitric Oxide

The nitric oxide gas used was from a tank obtained from the Matheson Gas Company. A purity of 99 percent was claimed and thus it was used direct from the supplied tanks. The multiple traverse cell described above was set for 24 traversals and filled with NO to an approximate pressure of 25 cm. of Mercury. This gave about 2. 8 meter-atmospheres of absorbing path. A 300 watt zirconium concentrated arc source was used. This gave adequate signal and a maximum absorption of approximately 30 percent was realized in the P and R branches of the 3-0 band.

Several records of the 3-0 band were obtained and of these three were chosen and complete measurements of the line frequencies were obtained. These records were run at the grating rotation speed of 1. 25 minutes of arc every 60 sec. The two sets of data from the runs with the narrowest slit widths--less than 50 microns--were chosen. These are listed as the records of March 11th and March 12th. Figure 5 shows a similar faster run through the 3-0 band taken for illustration purposes and of lower resolution than those measured.

3-0 Absorption Band of Nitric Oxide at 1.8 μ

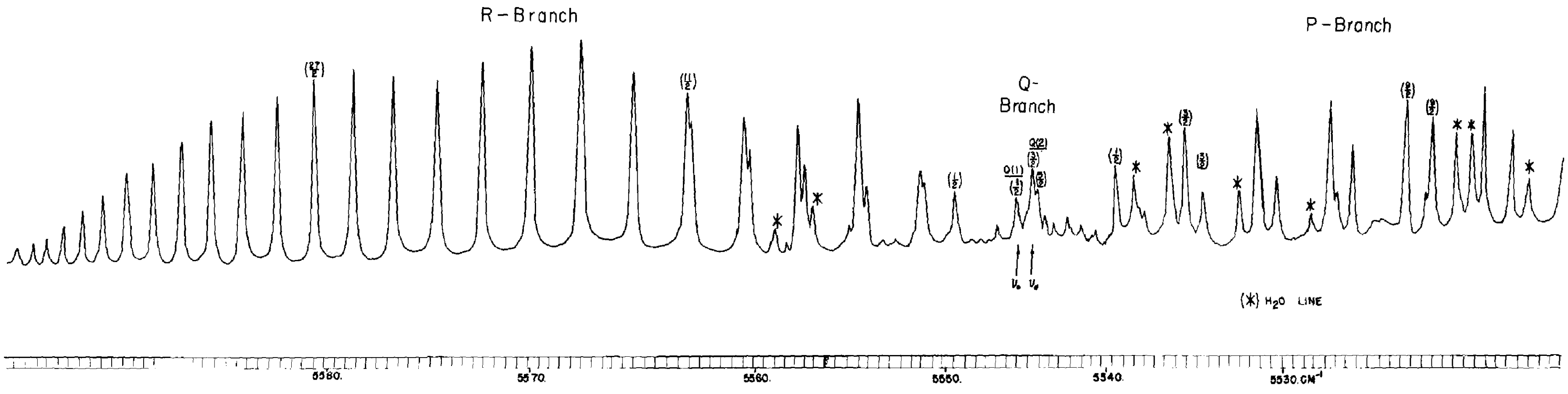


Figure 5

Each of the records was a simultaneous record of the 3-0 band of NO and of Fabry-Perot fringes spaced an equal number of wave numbers apart. Two argon emission lines appeared superimposed on the NO record. These lines were 12112.20 A° (5502.54 cm^{-1}) and 9122.966A° (5479.171 cm^{-1}) and were 23.37 cm^{-1} apart. The number of calibration fringes between these two argon lines was carefully measured to the nearest 0.02 of a fringe. The measurements on the spectral lines were made using this measured constant of the wave numbers between fringes. The constant used for the measurement of frequencies was 0.5361 cm^{-1} per fringe.

RESULTS AND DISCUSSION

Molecular Constants of Deuterium Chloride

The observed frequencies of DCl are shown for the 2-0 band in Table 1 and for the 3-0 band in Table 2. All lines showing evidence of any disturbance from close neighbors or overlapping were rejected. In all cases the frequencies listed are averages from two records. It should be noted that overlapping of the DCl^{35} isotopic species lines with the DCl^{37} lines prevented accurate determination of the position of several of the lines. The frequencies of all such lines have been indicated in parentheses as approximate values.

The molecular constants were obtained by standard graphical and least squares methods. Typical graphical determinations of the band origins are given for the 2-0 band in Figures 6 & 7. As mentioned in the foregoing all the origins were verified by a least squares fit to the data. The ordinates of Figures 6 & 7 are plotted as suggested by Herzberg[10] on a much expanded scale. This is obtained by subtracting $2(B'-B'')_{av}J^2$ from the combination sums. The combination sums used in the origin plots are given in Table III. The relationship shown in the plots is expressed by the equation

$$R(J-1)+P(J) - 2(B'-B'')_{av}J^2 = 2\nu_o - 2\Delta(B'-B'')J^2. \qquad \text{eq. 10}$$

TABLE I

2-0 BAND LINE POSITIONS (cm^{-1})

DCl^{35}

J	R-branch Observed	R-branch Calculated	P-branch Observed	P-branch Calculated
0	4138.88	4138.91		
1	4148.80	4148.80	4117.74	4117.78
2	4158.24	4158.23	4106.57	4106.55
3	4167.22	4167.20	4094.92	4094.88
4	4175.70	4175.72	4082.81	4082.77
5	4183.80	4183.77	4070.24	4070.23
6	4191.33	4191.35	4057.26	4057.25
7	4198.46	4198.46	4043.84	4043.85
8	4205.13	4205.10	4030.00	4030.02
9	4211.27	4211.26	4015.79	4015.77
10	4216.97	4216.94	4001.10	4001.10
11	4222.20	4222.14	3986.04	3986.02
12	4226.87	4226.84		

DCl^{37}

0	4133.03	4132.99		
1	4142.90	4142.85	4111.88	4111.93
2	4152.34	4152.26	4100.72	4100.73
3	4161.28	4161.22	4089.09	4089.10
4	4169.80	4169.72	4077.05	4077.04
5	4177.75	4177.76	4064.50	4064.54
6	4185.35	4185.33	4051.61	4051.61
7	4192.44	4192.44	4038.27	4038.26
8	4199.03	4199.08	4024.49	4024.49
9	(4205.13)[a]	4205.24	4010.29	4010.30
10	(4211.29)[a]	4210.93	3995.72	3995.70
11			3980.59	3980.68

[a] These lines overlapped by R(8) and R(9) of DCl^{35}

TABLE II

3-0 BAND LINE POSITIONS (cm^{-1})

DCl^{35}

	R-branch		P-branch	
J	Observed	Calculated	Observed	Calculated
0	(6123.05)	6122.91		
1	6132.38	6132.36	(6102.15)	6102.01
2	6141.13	6141.13	(6090.70)	6090.56
3	6149.27	6149.23	6078.49	6078.45
4	(6156.55)	6156.65	6065.69	6065.68
5	6163.46	6163.39	6052.23	6052.27
6	6169.45	6169.44	(6038.09)	6038.19
7	6174.74	6174.80	6023.43	6023.48
8	6179.39	6179.47	6008.07	6008.12
9	(6183.23)	6183.44	5992.20	5992.12
10	6186.67	6186.71	(5975.69)	5975.48
11	6189.25	6189.28	5958.23	5958.21

DCl^{37}

0	6114.24	6114.37		
1	(6123.99)	6123.78	6093.65	6093.53
2	(6132.35)	6132.52	6082.15	6082.11
3	(6141.13)	6140.59	6070.07	6070.04
4	6147.98	6147.98	(6057.08)	6057.31
5	6154.64	6154.68	(6044.10	6043.92
6	6160.80	6160.70	6029.84	6029.89
7	(6166.14)	6166.03	(6015.41)	6015.20
8	(6170.76)	6170.67	(5999.98)	5999.88

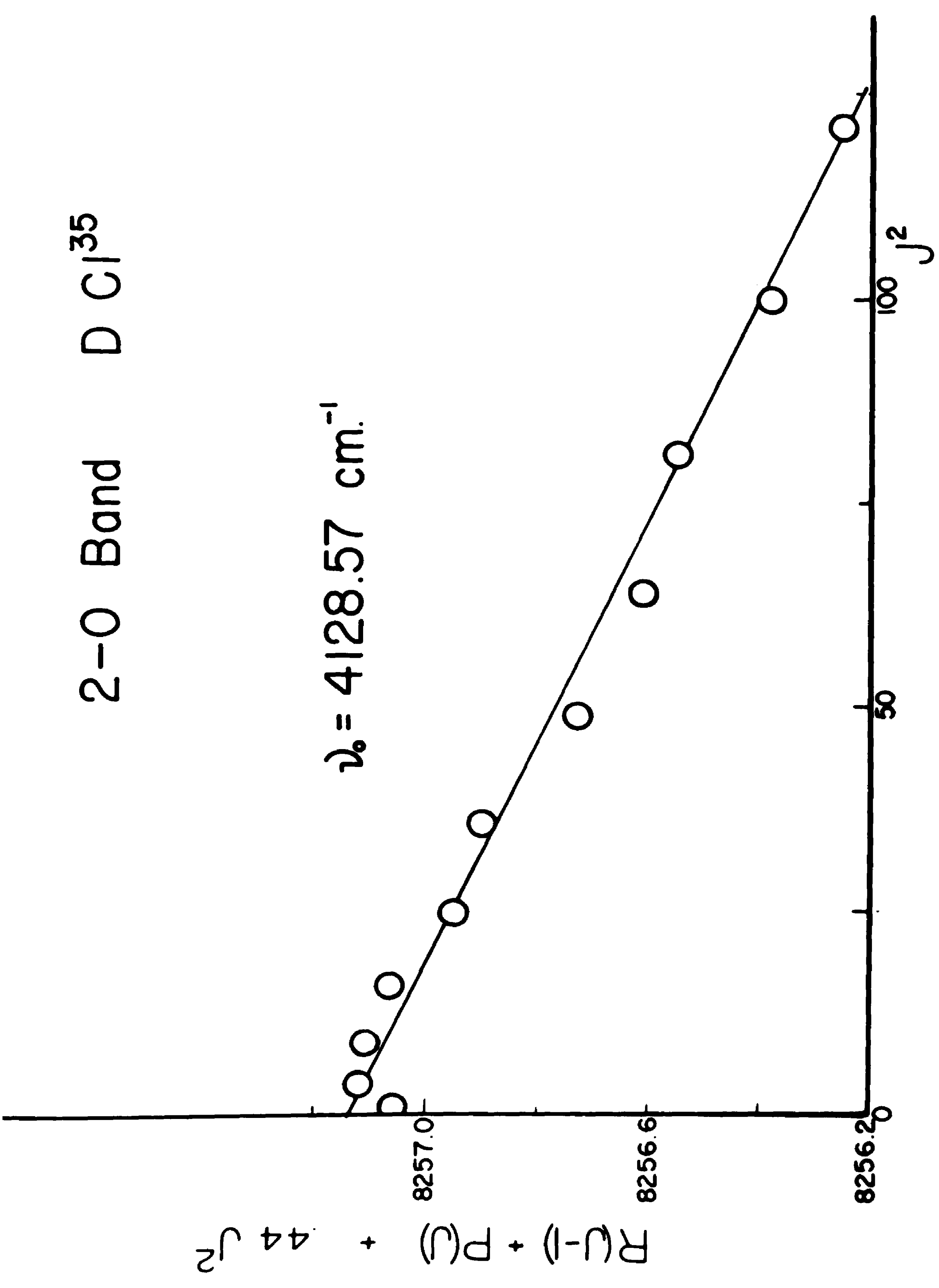

2-0 Band
D Cl^{35}
ν_0 = 4128.57 cm.$^{-1}$
R(J-1) + P(J) + .44 J^2
8257.0
8256.6
8256.2
0
50
100
J^2

Figure 6

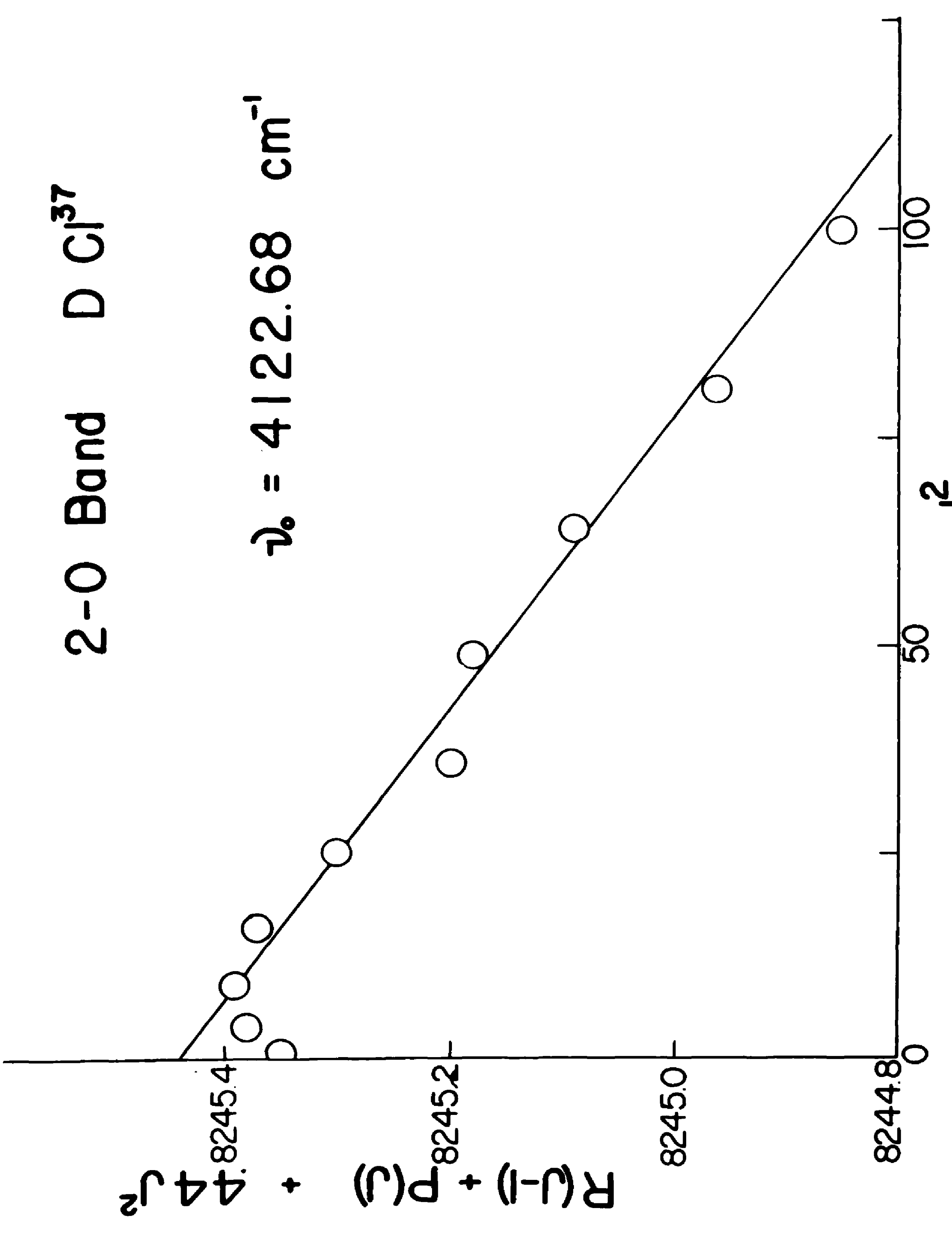

2-0 Band
D Cl^{37}
ν_0 = 4122.68 cm^{-1}
R(J-1) + P(J) + .44 J^2
8245.4
8245.2
8245.0
8244.8
0
50
100
J^2

Figure 7

TABLE III

COMBINATION SUMS FOR DCl

$R(J-1)+P_1(J)$

J^2	$(2-0)DCl^{35}$	$(2-0)DCl^{37}$
1	8256.62 cm^{-1}	8244.91
4	8255.37	8243.62
9	8253.16	8241.43
16	8249.99	8238.33
25	8245.94	8234.30
36	8241.06	8229.36
49	8235.17	8223.62
64	8228.46	8216.93
81	8220.92	8209.32
100	8212.37	8200.85
121	8202.99	8191.88

J^2	$(3-0)DCl^{35}$	$(3-0)DCl^{37}$
1	12225.20	12207.89
4	12223.08	12206.14
9	12219.62	12202.36
16	12214.96	12198.21
25	12208.78	12192.08
36	12201.55	12184.48
49	12192.88	12176.21
64	12182.81	12166.12
81	12171.59	
100	12158.92	
121	12144.90	

The Y-intercepts give the origins, and the slopes are proportional to the needed added correction, $\Delta(B' - B'')$, the average difference of the B-values chosen. This furnishes an additional check on the value of the rotational constants obtained from the combination differences.

Final values of the rotational constants were obtained from combination differences. While a least squares fit to these data was obtained for each of the constants as a final value, a graphical determination was also made in each case. Figure 8 shows such a graphical determination of the B_o values of the two species plotted from the data shown in Table IV of the combination differences for the lower state.

The B_v values thus obtained are plotted against v, the vibrational quantum number, to give B_e, the equilibrium rotational constant. Such a plot is shown in Figure 9 for the DCl^{35} molecule and in Figure 10 for DCl^{37}. The relation is expressed by the equation

$$B_v \doteq B_e - \alpha_e(v + 1/2). \qquad \text{eq. 3a}$$

The values for B_1 are taken from the results of Pickworth and Thompson. The slope of the line determines α_e, a measure of the dependence of B_v on the vibrational state .

TABLE IV

B_o COMBINATION DIFFERENCES

DCl^{35}

J	(2-0) $_2F''$	(3-0) $_2F''$	$_2F''$(Average)
1	32.31	32.35	32.33_5
2	53.88	53.89	53.88_5
3	75.43	75.44	75.43_5
4	96.98	97.04	97.01
5	118.44	118.46	118.45_5
6	139.96	140.03	139.99_5
7	161.33	161.38	161.35_5
8	182.67	182.54	182.60_5
9	204.03	203.70	203.87
10	225.23	225.00	225.12

DCl^{37}

1	32.31	32.09	32.20
2	53.81	53.92	53.86_5
3	75.29	75.27	75.28
4	96.78	97.03	96.90_5
5	118.19	118.14	118.16_5
6	139.48	139.23	139.35_5
7	160.86	160.82	160.84
8	182.15	—	(182.15)
9	203.31	—	(203.31)
10	224.54	—	(224.54)

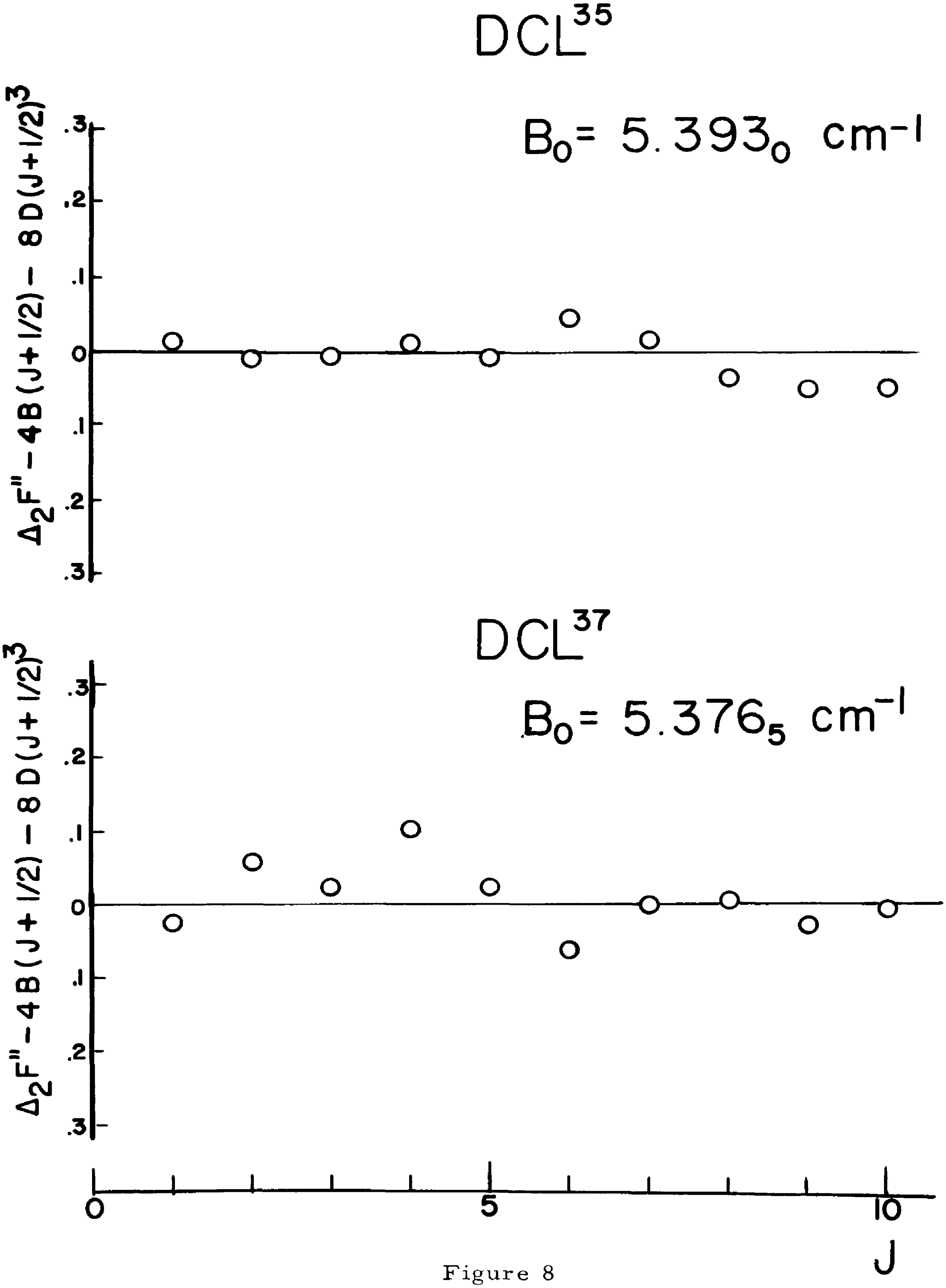

DCL^{35}
$B_0 = 5.393_0$ cm^{-1}
$\Delta_2 F'' - 4B(J+1/2) - 8D(J+1/2)^3$
.3
.2
.1
0
.1
.2
.3
DCL^{37}
$B_0 = 5.376_5$ cm^{-1}
$\Delta_2 F'' - 4B(J+1/2) - 8D(J+1/2)^3$
.3
.2
.1
0
.1
.2
.3
0
5
10
J

Figure 8

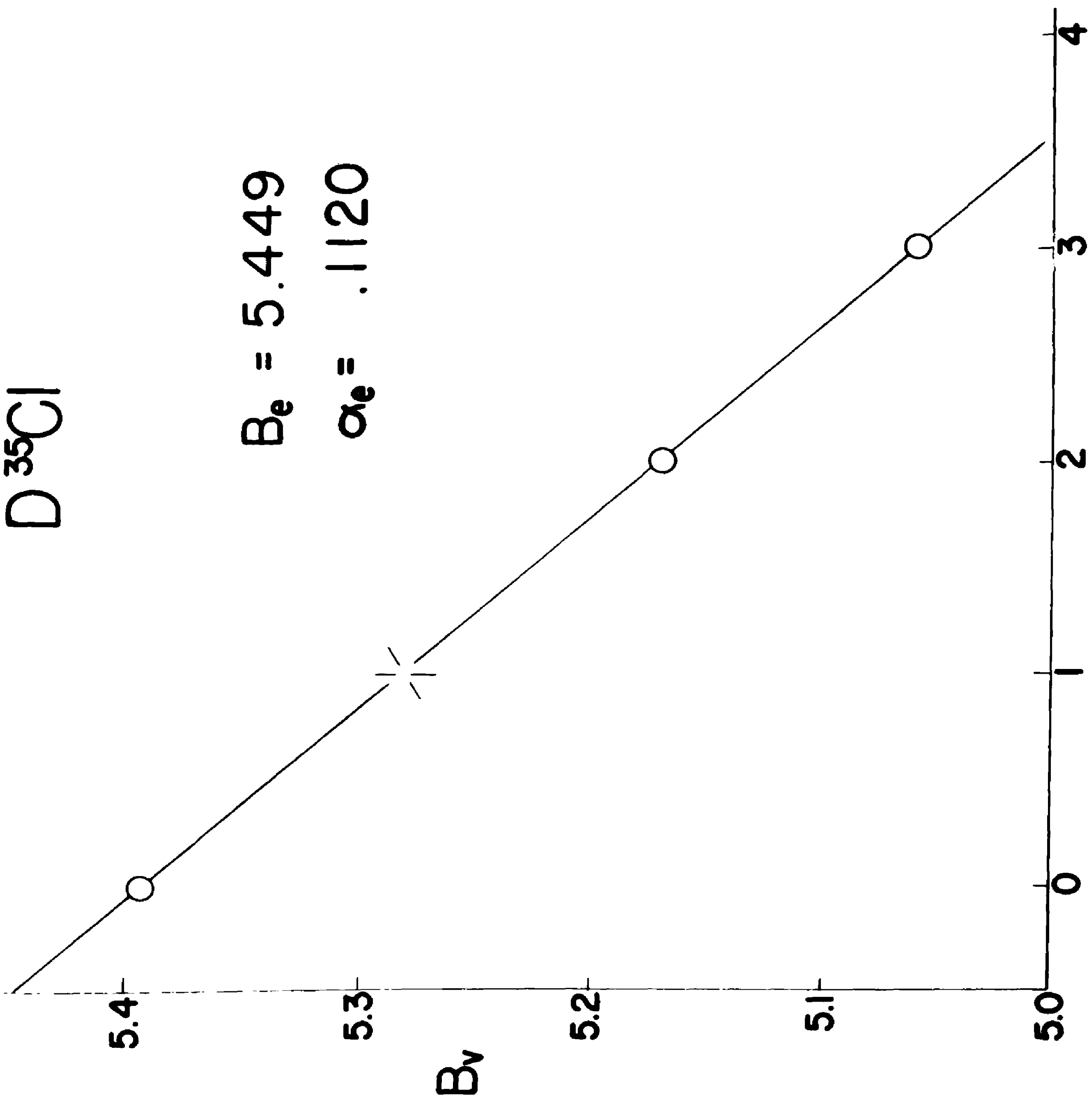


Figure 9

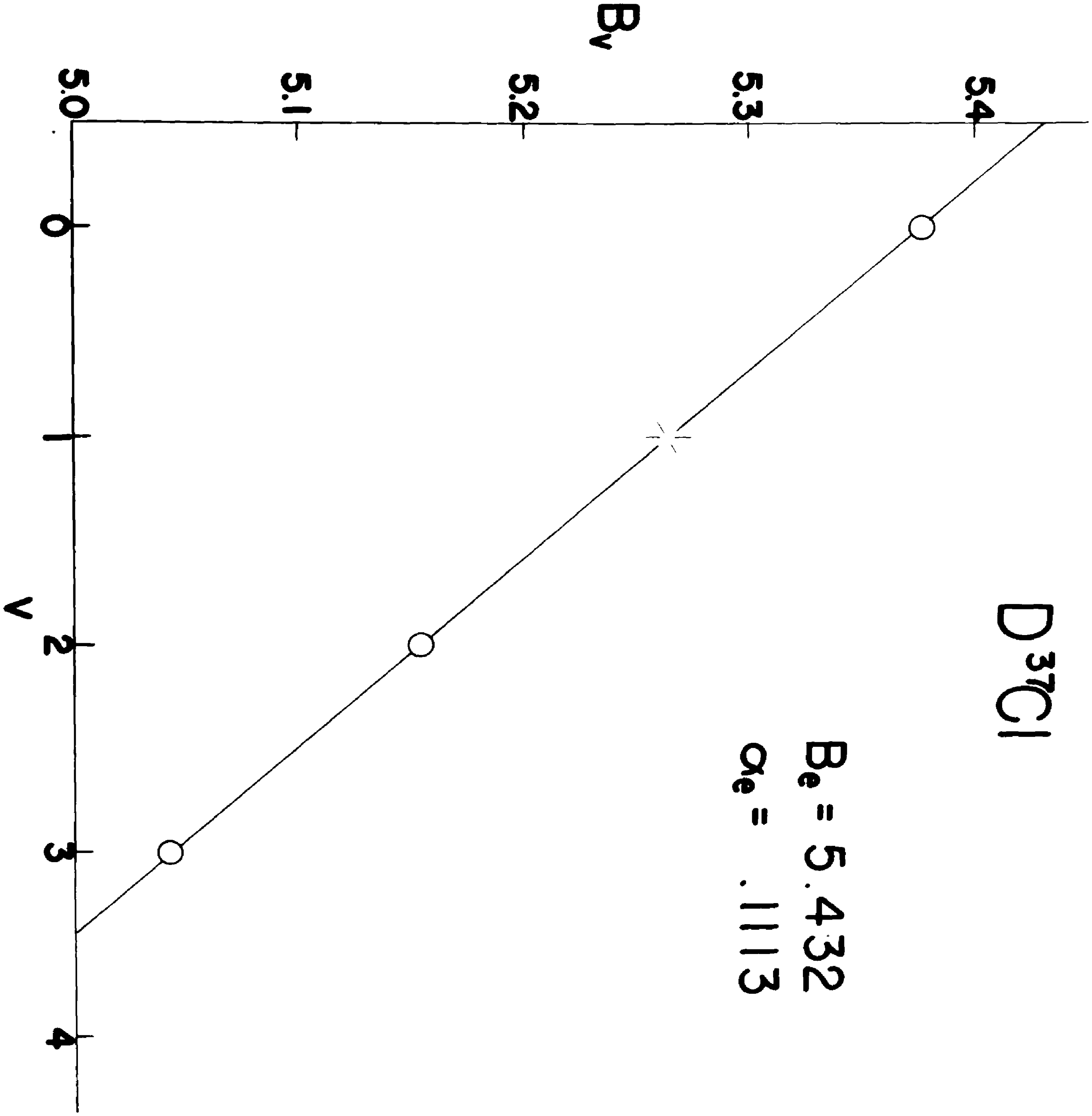


Figure 10

Convergence and low intensity in the R-branch of the 2-0 band, and to a still greater extent in the 3-0 band, prevented the measurement of any lines in this branch beyond J = 12 and J=11, respectively. Since the combination differences which are used in determining the rotational constants could not go beyond these J-values it was not possible to secure accurate values of D_e, the centrufugal stretching constant. The data, however, at least as far as J=10, indicated no significant change in this constant from the value given by Pickworth and Thompson.[1] The value of D_e and β given in Table V are those from Pickworth and Thompson.[1] The remainder of this table summarizes the results for the rotational constants and the band origins. It includes the equilibrium moments of inertia, I_e, and the equilibrium separation, r_e. The value of $r_e = 1.274_4 \times 10^{-8}$ cm and 1.274_5 are in excellent agreement with the value obtained by Mills, Thompson, and Williams[14] for HCl; $r_e = 1.274_4 \times 10^{-8}$cm. The atomic masses used to obtain r_e were $m_H = 1.008142$ and $m_D = 2.014735$ and are taken from DuMond and Cohen[15]. The isotopic masses of chlorine due to Segrè[16] are $m_{Cl^{35}} = 34.980175$ and $m_{Cl^{37}} = 36.977624$. Using the rotational constants listed in Table V, the frequencies of the lines were calculated by

TABLE V

ROTATIONAL CONSTANTS FOR DCl

	$D^{35}CL$		$D^{37}CL$
(2-0)	$\nu_o = 4128.57 \text{ cm}^{-1}$	(2-0)	$\nu_o = 4122.68 \text{ cm}^{-1}$
(3-0)	$\nu_o = 6112.79$	(3-0)	$\nu_o = 6104.28$
	$B_e = 5.449_0$		$B_e = 5.432_1$
	$\alpha_e = .112_0$		$\alpha_e = .111_3$
	$(D_e = 1.37_4 \times 10^{-4})$		$(D_e = 1.36_6 \times 10^{-4})$
	$(\beta = 6 \times 10^{-7})$		$(\beta = 6 \times 10^{-7})$
	$I_e = 5.135_4 \times 10^{-40} \text{ gm-cm}^2$		$I_e = 5.151_6 \times 10^{-40} \text{ gm-cm}^2$
	$r_e = 1.274_4 \times 10^{-8} \text{ cm}$		$r_e = 1.274_5 \times 10^{-8} \text{ cm}$

TABLE VI

VIBRATIONAL CONSTANTS

$D^{35}CL$	$D^{37}CL$
$\omega_e = 2144.77 \text{ cm}^{-1}$	$\omega_e = 2141.82 \text{ cm}^{-1}$
$\omega_e x_e = 26.92$	$\omega_e x_e = 26.99$
$\omega_e y_e = .036$	$\omega_e y_e = .063$

substitution in the following equation:

$$\nu = \nu_o + (B' + B'')\, m - (B' - B'' + D' - D'')m^2 - (D' + D'')m^3 + (D' - D'')m^4 + \ldots\ldots \text{eq. } 7$$

These are given in Tables I and II along with the observed values.

Since the publication of the above, the work on DCl in the submillimeter microwave region by Cowan & Gordy[17] yields for DCl^{35}, B_e = 5.4484 and r_e = 1.27462 and for DCl^{37}, B_e = 5.4324 and $r_e = 1.27463 \times 10^{-8}$ cm. The values found compare very well with these recent microwave values.

The position of band origins here obtained together with that of the fundamental provided sufficient information to enable solution for the three vibrational constants: ω_e, $\omega_e x_e$ and $\omega_e y_e$. Substituting into the expression for the vibrational energy,

$$G(v) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \omega_e y_e(v + 1/2)^3 + \ \ldots\ldots \text{eq. } 4.$$

for the various vibrational states and subtracting successive equations yields three difference equations of the form,

$$G_{(v'-v'')} = \omega_e - 2\,\omega_e x_e(v + 1) + 3\omega_e y_e(v''^2 + 2v'' + 13/12) + \ \ldots \text{eq. } 6$$

The results of solving these three equations are given in Table VI.

The assumption of identical electron configurations for the HCl and DCl isotopic forms makes the isotope shift a function of mass alone. The justification for this is shown in Tables VII and VIII where the expected values of the constants and band positions calculated from the isotope shift are compared with the observed values. If ρ is defined as the ratio of the square roots of the reduced isotopic masses, ω_e varies as ρ, $\omega_e x_e$ as ρ^2, and B_e as ρ^2. The frequency shift can be expressed with sufficient accuracy using only the first two vibrational constants by the equation from Herzberg[10] as follows:

$$\Delta \nu = (1-\rho)\left\{\left[\omega_e - \omega_e x_e (1+\rho)\right] v - \omega_e x_e (1+\rho) v^2\right\} \quad \text{eq. 11}$$

The results are shown in Table VIII. The agreement is within experimental error.

For the constants which are accurately determined the variation occurs in the 5th place which is probably all that can be expected from the data. The individual frequencies throughout the two regions are felt to be good to ± 0.05 cm^{-1}. The undertainty in the values for B_e is ± 0.0005 cm^{-1}.

Table VII Isotope Shift

	$D^{35}CL$-$H^{35}CL$		$D^{35}CL$ - $D^{37}CL$	
	Observed	Calculated	Observed	Calculated
ω_e	2144.77	2144.47 cm^{-1}	2141.82	2141.61 cm^{-1}
$\omega_e x_e$	26.92	26.77	26.99	26.84
B_e	5.449_o	5.449_5	5.432_1	5.433_o

Table VIII Isotope Shift ($\Delta\nu$)

$D^{35}CL$ - $D^{37}CL$

Band	Observed	Calculated	
2-0	5.89 cm^{-1}	5.84 cm^{-1}	+.05
3-0	8.51	8.52	-.01

$D^{35}CL$ - $H^{35}CL$

Band	Observed	Calculated	
2-0	1539.98 cm^{-1}	1539.49 cm^{-1}	+.49
3-0	2234.19	2233.41	+.78

RESULTS AND DISCUSSION

Molecular Constants of Nitric Oxide

The ground state of the NO molecule is a $^2\pi$ state and thus the 3-0 rotation-vibration band at 1.8 microns consists of two sub-bands corresponding to energy transitions in the $^2\pi$ (1/2) and $^2\pi$ (3/2) substates. Each sub-band has a separate P, Q, and R branch. The separation of the two substates is only about 123.8 cm^{-1}. The Q branches are therefore crowded and their detail not resolved, except that it was possible to measure the first line of the Q(1/2) branch and the first two of the Q(3/2) branch.

The lines of the two substates in the R branch were well resolved as far as J = 11/12, but beyond this J value the two species merged to the extent that only a single frequency was obtainable for R branch lines from J = 13/2 to J = 45/2. (see Figure 5.) The lines of the P branch diverge and were farther apart so that the frequencies of the lines of each substate were easily obtained. These are given in Table IX and those of the R and Q branch are shown in Table X.

TABLE IX

WAVE NUMBERS FOR 3-0 BAND OF NO

J + 1/2		Wave Numbers From Record of Mar. 11		Wave Numbers From Record of Mar. 12	
P_1	P_2				
2		**		5539.04	cm^{-1}
	2		**		**
3		5535.58		5535.49	
	3		**		5534.65
4		5531.97		5531.94	
	4		5530.89		5530.88
5		5528.30		5528.21	
	5		5527.14		5527.11
6		5524.45		5524.42	
	6		5523.24		5523.19
7		5520.54		5520.54	
	7		5519.14		5519.11
8		5516.57		5516.51	
	8		5515.05		5515.04
9		5512.42		5512.34	
	9		5510.76		5510.77
10		5508.17		5508.20	
	10		5506.46		5506.34
11		5503.82		5503.84	
	11		5501.96		5501.93
12		5499.41		5499.38	
	12		5497.41		5497.35
13		5494.90		5494.85	
	13		**		**
14		5490.30		5490.26	
	14		**		5487.94*
15		5485.55		5485.50	
	15		5483.09		5483.06
16		5480.68		5480.65	
	16		5478.12		5478.08
17		**		**	
	17		**		5473.00
18		5470.66		5470.73	
	18		**		**
19		5465.54		5465.54	

**Lines obscured by H_2O lines

*H_2O line at 5488.20 cm^{-1}

TABLE X

WAVE NUMBERS FOR 3-0 BAND OF NO

J + 1/2		Wave Numbers From Record of Mar. 11		Wave Numbers From Record of Mar. 12	
R_1	R_2				
1		5548.92		5548.95 cm^{-1}	
	2		5551.54		5551.55 cm^{-1}
2		5551.98		5551.99	
	3		5554.63		5554.64
3		5555.01		5554.99	
	4		5557.64		5557.60
4		5557.89		5557.86	
	5		5560.42		5560.43
5		5560.66		5560.66	
	6		5563.28*		5563.14
6		5563.28		5563.27	
7*		5565.86		5565.81	
8		5568.33		5568.34	
9		5570.73		5570.70	
10		5572.99		5572.93	
11		5575.15		5575.13	
12		5577.19		5577.20	
13		5579.14		5579.14	
14		5581.00		5580.95	
15		5582.77		5582.74	
16		5584.38		5584.32	
17		5585.88		5585.89	
18		5587.34		5587.34	
19		5588.63		5588.60	
20		5589.85		5589.83	
21		5590.94		5590.95	
22		5591.90		5591.89	
23		5592.81		5592.82	

*The two R components were unresolved from this line on through higher J value.

J 1/2		Wave Numbers From Record of Mar. 12.	
Q_1	Q_2		
1		5544.09 cm^{-1}	
	2		5543.24 cm^{-1}
2		--	
	3		5542.94

In general the intensities of lines in the P and R branches showed that the $^2\Pi(1/2)$ state lines were from 20 to 50 percent stronger than $^2\Pi(3/2)$ lines of corresponding J value. In contrast to this the stronger lines of the Q branch are those of the $^2\Pi(3/2)$ substate. This result agrees with the intensities calculated from the Honl and London formulae quoted by Herzberg[10] on page 422.

The molecular constants were found by graphical methods as described above and these results checked by the method of least squares. The graphical determination of the band origins are shown in Figure 11. The combination sums used in plotting the origins are shown in Table XI. The 3-0 band origins thus found are listed in Table XII and compared with those previously found by Nichols, Hause, and Noble[5] and Gillette and Eyster[4].

Figure 12 shows a graphical determination of $B_3(1)$, the rotational constant for the upper state of the $^2\Pi(1/2)$ state. Figure 13 shows the plot of $B_3(2)$, for the $^2\Pi(3/2)$ state. And Figure 14 gives the plots for the values of B_o for each component. It is to be noted that the vertical scale here is

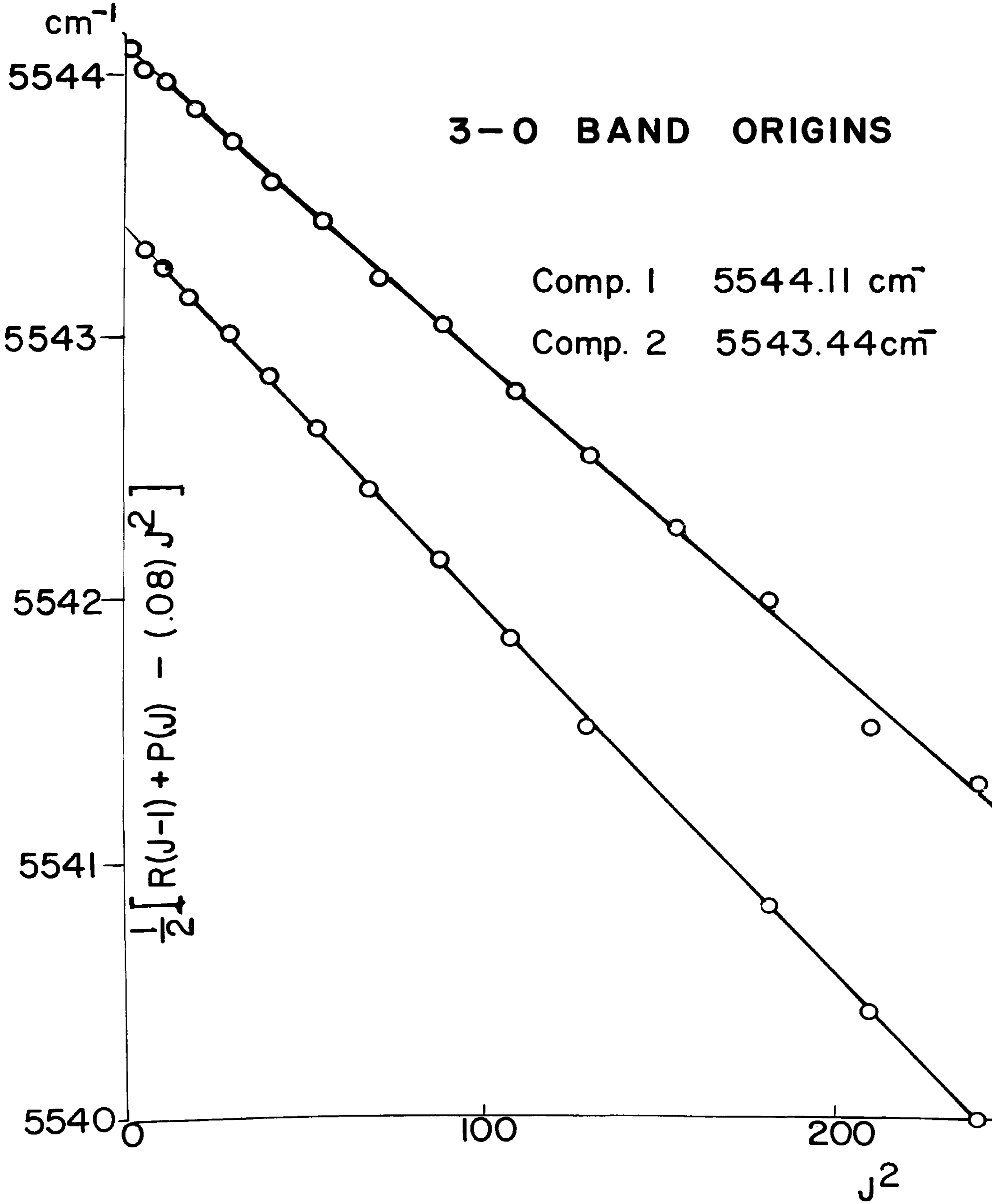

cm⁻¹
5544
5543
5542
5541
5540
3-0 BAND ORIGINS
Comp. 1 5544.11 cm⁻
Comp. 2 5543.44cm⁻
$\frac{1}{2}[R(J-1)+P(J) - (.08)J^2]$
0
100
200
J^2

Figure 11

TABLE XI

COMBINATION SUMS

$J^2 - .25$	$R_1(J-1) + P_1(J)$		$R_2(J-1) + P_2(J)$	
	March 11	March12	March 11	March 12
2	—	11087.992	--	--
6	11087.564	11087.477	11086.186	11086.197cm^{-1}
12	11086.979	11086.979	11085.521	11085.521
20	11086.191	11086.068	11084.781	11084.701
30	*11085.109	11085.082	*11083.655	11083.623
42	*11083.816	11083.806	*11082.423	11082.245
56	*11082.433	11082.315	*11080.911	11080.851
72	*11080.750	11080.681	*11079.093	11079.110
90	*11078.895	11078.894	*11077.190	11077.040
110	*11076.810	11076.772	*11074.949	11074.864
132	*11074.568	11074.516	*11072.563	11072.478
156	*11072.087	11072.054	--	--
182	*11069.443	11069.401	--	*11067.080**
210	*11066.549	11065.907	--	11064.007
240	*11063.444	11063.386	--	11060.812
272	--	--	--	11057.317
306	--	11056.620	--	--
342	--	11052.878	--	--

*Lines of this branch were not resolved from this point on through lines of higher J value.

*Near H_2O line

TABLE XII

3-0 BAND ORIGINS

	VH & H	NHN	G & E
3-0 (1)	5544.11cm^{-1}	5544.28cm^{-1}	5544.21cm^{-1}
3-0 (2)	5543.44	5543.69	5543.35

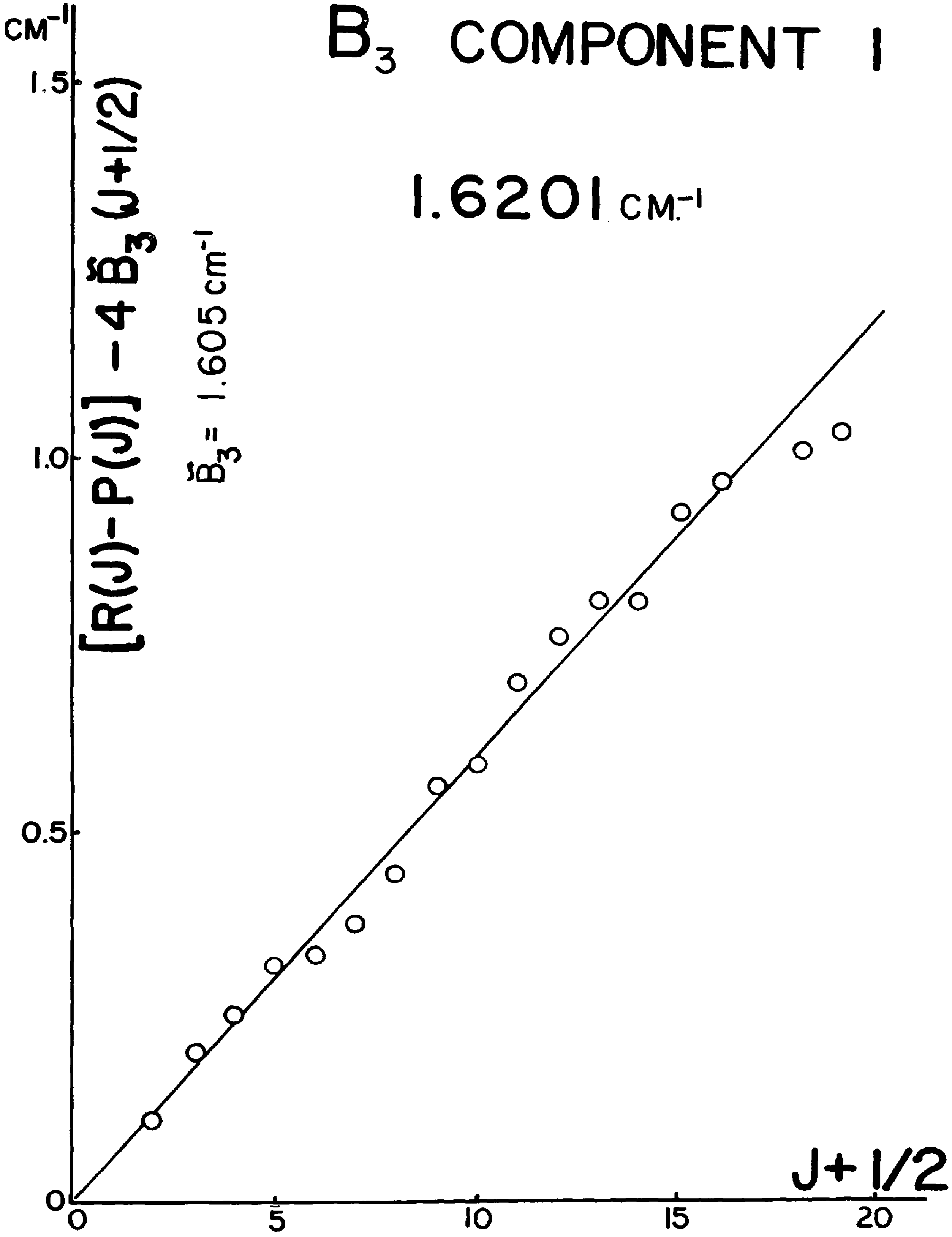

B$_3$ COMPONENT 1
1.6201 CM^{-1}
CM^{-1}
[R(J)-P(J)] - 4 $\tilde{B}_3$ (J+1/2)
$\tilde{B}_3$ = 1.605 cm^{-1}
1.5
1.0
0.5
0
0
5
10
15
20
J+1/2

Figure 12

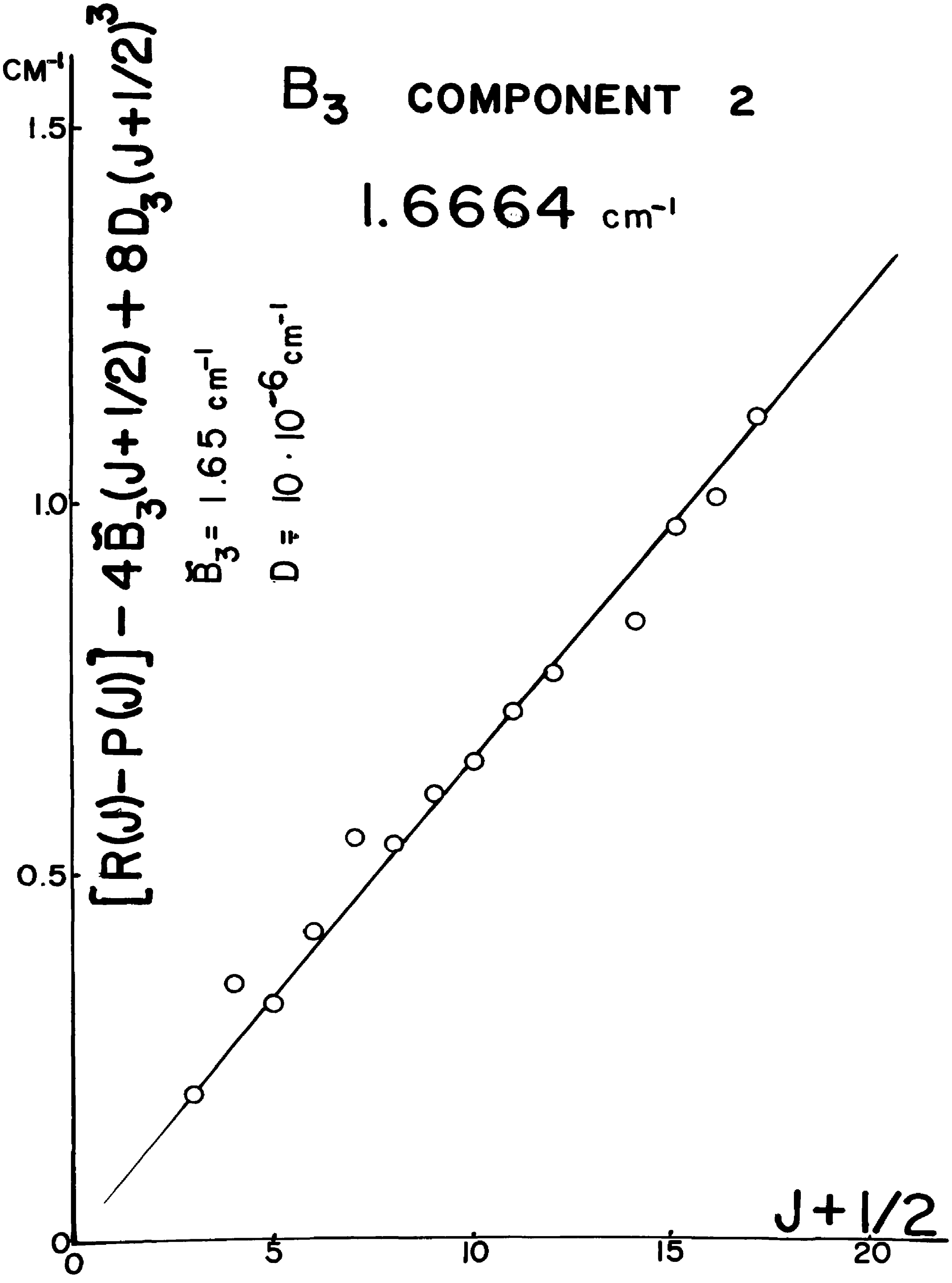

B$_3$ COMPONENT 2
1.6664 cm^{-1}
$\tilde{B}_3$ = 1.65 cm^{-1}
D = 10 · 10^{-6} cm^{-1}
[R(J)-P(J)] - 4$\tilde{B}_3$(J+1/2) + 8D$_3$(J+1/2)^3
CM^{-1}
1.5
1.0
0.5
0
J+1/2
0
5
10
15
20

Figure 13

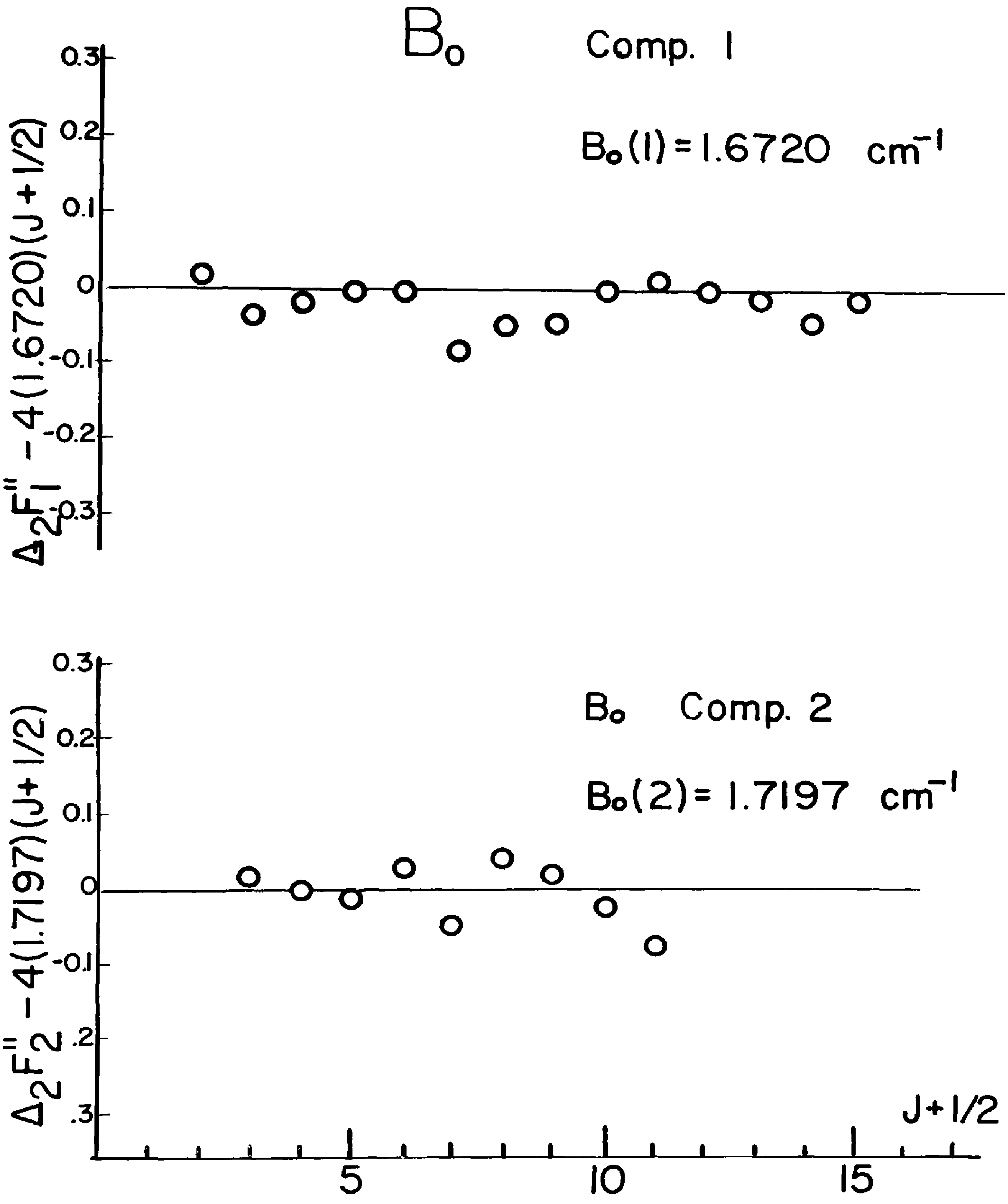

B₀ Comp. 1
B₀(1) = 1.6720 cm⁻¹
Δ₂F₁'' − 4(1.6720)(J + 1/2)
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
B₀ Comp. 2
B₀(2) = 1.7197 cm⁻¹
Δ₂F₂'' − 4(1.7197)(J + 1/2)
0.3
0.2
0.1
0
-0.1
.2
.3
J + 1/2
5
10
15

Figure 14

greatly exaggerated by subtracting from the second differences a value equal to $4B_o$ $(J + 1/2)$. The average combination differences used for this plot are given in Table XIII. The rotational constants for nitric oxide are listed in Tables XIV and XV. Table XIV lists the values of B_3 obtained and for comparison the results quoted from Nichols, Hause and Noble[3] are included. Table XV lists the results for B_o and includes three recent results. The values of Palik and Rao[18] from the pure rotational spectra, the microwave results of Burrus and Gordy[8] and the still more recent work of Gallagher, Bedard, and Johnson[9] (B_o (1) = 1.67196), are especially to be noted. The values obtained for this constant agree very well with this recent work.

Figure 15 is a plot of the values of B_v obtained against $v + 1/2$ in order to determine B_e, the equilibrium rotational constant. The value of B_2 was taken from Nichols, Hause, and Noble[5] and B_1 value is that of Shaw[7]. The value of B_e thus obtained (1.7044 cm^{-1}) is in very good agreement with the recent work of Gallagher and Johnson[19] who give a value of B_o = 1.69578. Using the value of α_e just obtained this yields a B_e = 1.7045 cm^{-1}.

TABLE XIII

B_0 - COMBINATION DIFFERENCES

J	$\Delta_2 F_1''$ (Mar. 11)	$\Delta_2 F_1''$ (Mar. 12)	$\Delta_2 F_2''$ (Mar. 11)	$\Delta_2 F_2''$ (Mar. 12)
3/2	13.34cm^{-1}	13.46cm^{-1}		
5/2	20.00	20.06	20.65cm^{-1}	20.66cm^{-1}
7/2	26.71	26.78	27.49	27.54
9/2	33.45	33.44	34.40	34.36
11/2	40.13	40.12	41.27	41.33
13/2	46.71	46.76	48.23	48.10
15/2	53.44	53.47	55.10	55.04
17/2	60.16	60.15	61.87	62.00
19/2	66.91	66.86	68.77	68.77
21/2	73.58	73.55	75.59	75.59
23/2	80.26	80.28	**	**
25/2	86.89	86.94	**	89.26
27/2	93.59	93.64	96.05	96.08
29/2	100.32	100.29	102.88	102.88
31/2	**	**	**	109.74
33/2	**	113.59	**	**
35/2	**	120.35	**	**

J	$\Delta_2 F_1''$ (Average)	$\Delta_2 F_2''$ (Average)
3/2	13.40cm^{-1}	
5/2	20.03	20.66cm^{-1}
7/2	26.74	27.52
9/2	33.44	34.38
11/2	40.13	41.30
13/2	46.74	48.10
15/2	53.46	55.07
17/2	60.15	61.93
19/2	66.88	68.77
21/2	73.56	75.59
23/2	80.27	**
25/2	86.92	89.26
27/2	93.62	96.06
29/2	100.31	102.88
31/2	**	109.74

** Lines missing due to H_2O

TABLE XIV

ROTATIONAL CONSTANTS FOR N O

B_3 Infrared and Electronic Values

$B_3(1)$	$B_3(2)$	B_3	Source
1.6201	1.6664	1.6438	*(3-0)Infrared VH & H
1.6156	1.6665	1.6408	(3-0)Infrared NHN
1.6193	1.6651	1.6422	Electronic(aver.7 bands)
1.6199	1.6629	1.6414	Electronic (0-3)

* Results of this investigation

TABLE XV

B_o Infrared and Electronic Values

$B_o(1)$	$B_o(2)$	B_o	Source
1.6720	1.7197	1.6959	*Infrared (3-0) VH & H
1.6680	1.7222	1.6951	" (3-0)NHN
1.6762	1.7207	1.6985	" (2-0) NHN
1.6706	1.7224	1.6965	Infrared(3-0 2-0)NHN
1.6696	1.7200	1.6948	Infrared (1-0) G & E
1.6703	1.7182	1.6943	Electronic 1-0, 2-0
1.6706	1.7239	1.6973	Electronic 0-0,1-0
1.6733	1.7200	1.6966	Infrared(1-0)Shaw
1.6720	1.7198	1.6959	Palikand Rao-Pure Rotat.
1.67198		(1.6951)**	Burrus and Gordy (microwave)

**using the $B_o(2)$ value from G & E

*Results of this investigation

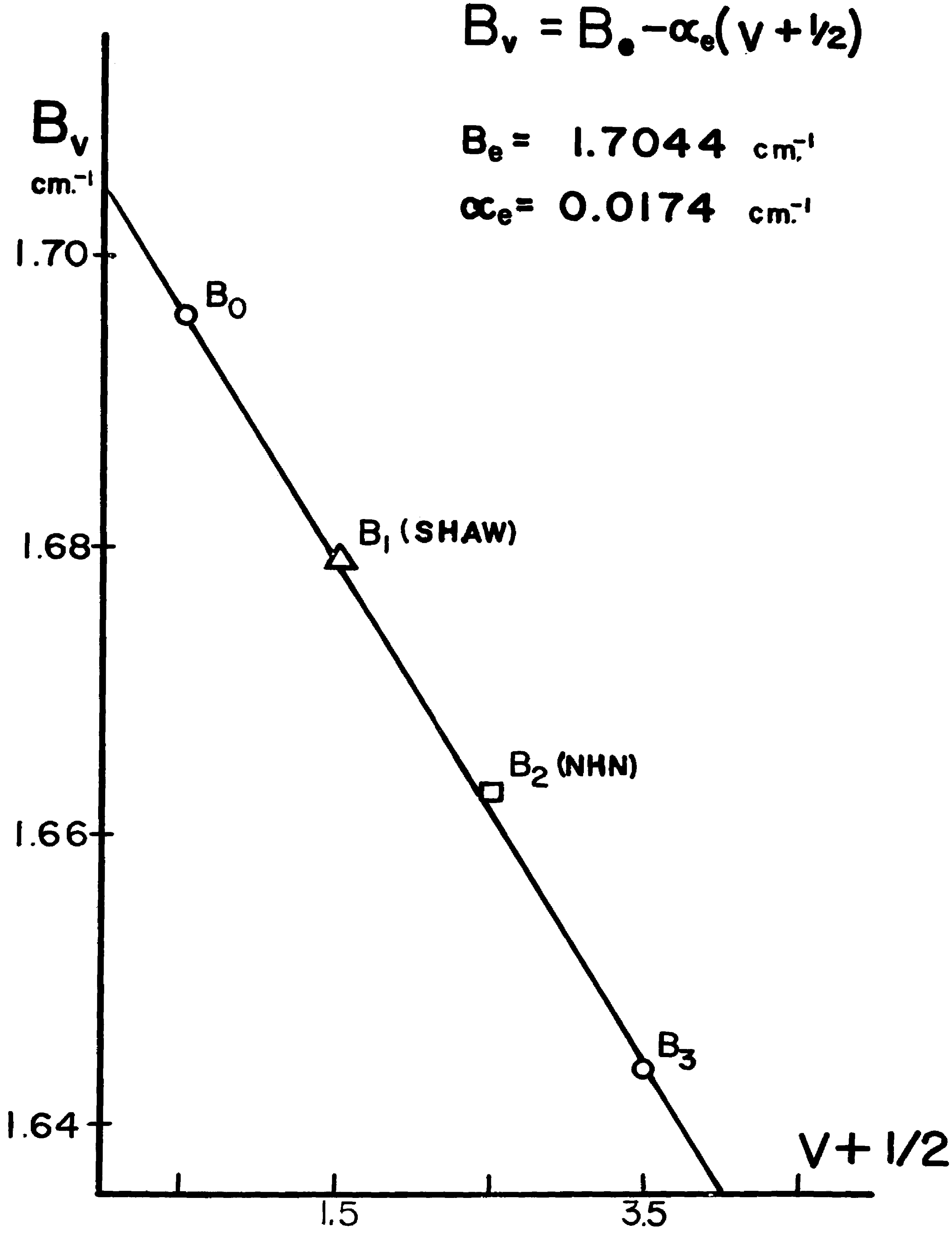

$B_v = B_e - \alpha_e(v + 1/2)$
B_e = 1.7044 cm.⁻¹
α_e = 0.0174 cm.⁻¹
B_v
cm.⁻¹
1.70
1.68
1.66
1.64
B_0
B_1 (SHAW)
B_2 (NHN)
B_3
V+1/2
1.5
3.5

Figure 15

It is to be noted that greater weight was given to the values of B_0 and B_3 obtained in this present work. The value of α_e used here is lower than the value of Gillette and Eyster (0.0180 cm^{-1}). It is in agreement with the value of α_e calculated from the results of Fletcher and Begun[22] on $N^{15}O$ for the fundamental. This gives a value of B_e slightly lower than the value recently published by Gallagher and Johnson[19].

Values I_e and r_e together with the above constants are listed in Table XVI.

The molecular coupling constant, A, was first determined by Jenkins, Barton, and Mullikan[20] from electronic band spectra yielding a value of 124.4 cm^{-1}. This value was used by microwave investigators, Gallagher, Bedard, and Johnson[9]. More recently Beringer, Rawson, and Henry[21] have used 123.8 cm^{-1} and state that this may be in error by as much as 0.5 cm^{-1}. Although A cannot be obtained directly from the infrared data, it is of interest to check the consistency of the value 123.8 with the infrared data. This was done as follows: Using the expression

$$(B_v)_{eff} = B_v \pm B_v^2 / \left[A(A-4B_v)\right]^{1/2} + D_v \qquad \ldots\text{eq. } 12$$

and substituting present experimental values for $(B_v)_{eff}$

from each species and the value for B_v we obtain some measure of the reliability of A by checking the equality.

A	$B_v^2 / [A(A-4B_v)]^{1/2}$	$(B_v)_{eff} - B_v$
123.4 cm^{-1}	.0240 cm^{-1}	.0239 cm^{-1}
123.8	.0239	.0239
124.2	.0238	.0239

From the results it is obvious that the value of A is at least as good as 123.8 ± 0.4 cm^{-1}.

TABLE XVI

MOLECULAR CONSTANTS OF NO

$(B_o)_{eff}$ $(^2\Pi\ 1/2)$	1.6720 cm^{-1}
$(B_o)_{eff}$ $(^2\Pi\ 3/2)$	1.7197 cm^{-1}
B_o	1.6958 cm^{-1}
B_3	1.6433 cm^{-1}
B_e	1.7044 cm^{-1}
α_e	.0174 cm^{-1}
I_e	16.422 x 10^{-40} $gm\text{-}cm^2$
r_e	1.1509^6 x 10^{-8} cm

CONCLUSION

The use of a Fabry-Perot etalon incorporated into the spectrograph to give calibration fringes simultaneously with the record has greatly increased the accuracy with which the frequency of any absorption line may be determined. For the work on the 3-0 band of nitric oxide the accuracy of frequency determination is better than $\pm .04$ cm^{-1}.

This increased accuracy has resulted in more dependable rotational constants and changes slightly the previously published values of the equilibrium constants for the molecule. The major change occurred in α_e. This work gives $\alpha_e = .0174$ cm^{-1}; the former value was $.0180$ cm^{-1}. This new value is thought to be more valid for two reasons; first, the rotational constants from which it was derived are consistent with recent microwave values; and secondly, this value is consistent with the value obtained from recent measurements of Fletcher and Begun on the fundamental of the isotopic molecule, $N^{15}0^{16}$. Measurements of the overtone bands of the isotope, $N^{15}0^{16}$, in this region would be of interest.

In addition to the above we are able to show that the molecular constant, $A = 123.8$ cm^{-1} can not be varied by more than ± 0.4 cm^{-1} and remain consistent with the infrared frequencies.

BIBLIOGRAPHY

1. Pickworth, J., and H. W. Thompson. The fundamental vibration-rotation band of deliterium chloride. Proc. Roy. Soc. (London) 218, 37 (1953).

2. Hardy, J. D., E. F. Barker, and D. M. Dennison. The infrared spectrum of H^2Cl. Phys. Rev. 42, 279 (1932).

3. Neilsen, A. H., and W. Gordy. The infrared spectrum and molecular constants of nitric oxide. Phys. Rev. 56, 781 (1939).

4. Gillette, R. H., and E. H. Eyster. The fundamental rotation-vibration band of nitric oxide. Phys. Rev. 56, 1113 (1939).

5. Nichols, N. L., C. D. Hause, and R. H. Noble. Near infrared spectrum of nitric oxide. Jour. Chem. Phys. 23, 57 (1955).

6. Nichols, N. L. The near infrared spectrum of nitric oxide. Ph. D. Thesis, Michigan State University (1953).

7. Shaw, J. H. Nitric oxide fundamental. Jour. Chem. Phys. 24, 399 (1956).

8. Burrus, C. A., and W. Gordy. One-to-two millimeter wave wave spectroscopy III. NO and DI. Phys. Rev. 92, 1437 (1953).

9. Gallagher, J. J., F. D. Bedard, and C. M. Johnson. Microwave spectrum of $N^{14}O^{16}$. Phys. Rev. 93, 729 (1953).

10. Herzberg, G. Spectra of Diatomic Molecules, ed. 2, D. VanNostrand Co., Inc., New York, 1950 p. 219.

11. Hill, E. and J. H. VanVleck "On the Quantum Mechanics of the Rotational Distortion of Multiplets in Molecular Spectra" Phys. Rev. 32, 250 (1928).

12. Noble, R. H. A vacuum spectrograph for the infrared J. Opt. Soc. Am., 43, 330 (1953).

13. White, J. U. Long optical paths of large aperature. J. Opt. Soc. Am. 32, 285 (1942).

14. Mills, I. M., H. W. Thompson and R. L. Williams. The fundamental vibration-rotation band of hydrogen chloride. Proc. Roy. Soc. (London) 218, 29 (1953).

15. DuMond, J. W. M., and E. R. Cohen. Rev. Mod. Phys. 25, 691 (1953).

16. Segre, E., editor, Experimental Nuclear Physics. John Wiley and Sons, Inc., New York, 1954 p. 746.

17. Cowan, M. J. and W. Gordy. Submillimeter wave spectroscopy. Bul. Am. Phys. Soc. Apr. 25, 1957 Paper QA1O p. 212.

18. Palik, E. D. and K. N. Rao. Pure rotational spectra of CO, NO, and N_2O between 100 and 600 microns. Jour. Chem. Phys. 25, 1174 (1956).

19. Gallagher, J. J. and C. M. Johnson. Uncoupling effects in the microwave spectrum of nitric oxide. Phys. Rev. 103, 1727 (1956).

20. Jenkins, F. A., H. A. Barton and R. S. Molliken. The beta bands of nitric oxide. Phys. Rev. 30, 152, (1927)

21. Beringer, R., E. B. Rawson and A. F. Henry. Microwave resonance in nitric oxide: lambda doubling and hyperfine structure. Phys. Rev. 94, 343 (1954).

22. Fletcher, W. H., and G. M. Begun. Fundamental of $N^{15}O$. Journ. Chem. Phys. 27, 579 (1957).