

ROTATIONAL ANALYSIS OF THE 0-0 BAND OF THE A $^3\Pi_{inv}$ -X $^3\Sigma^-$ SYSTEM OF ND*

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ABSTRACT

The 0-0 band of the A $^3\Pi_{inv}$ -X $^3\Sigma^-$ system of ND was excited in an electrodeless microwave oscillator (2450 Mc./s.) discharge and photographed on a 6.6 meter concave grating spectrograph in the second order at a dispersion of 0.56 Å/mm. Twenty-five out of the predicted twenty-seven branches have been identified in the rotational structure of the 0-0 band. From a rotational analysis, the following rotational constants have been determined:

(i) X $^3\Sigma^-$ state—

B_0'' (cm. ⁻¹)	D_0'' (cm. ⁻¹)	$(2\lambda + \gamma)$ (cm. ⁻¹)
8.7757	4.68×10^{-4}	- 1.8356.

(ii) A $^3\Pi_{inv}$ state—

B_0' (cm. ⁻¹)	D_0' (cm. ⁻¹)	A (cm. ⁻¹)	C_0^4 (cm. ⁻¹)	C_2^4 (cm. ⁻¹)	ν_{00} (cm. ⁻¹)
8.7688	5.02×10^{-4}	- 31.89	- 1.40	+ 0.0118	29799.5

INTRODUCTION

ONE triplet system, A $^3\Pi_{inv}$ -X $^3\Sigma^-$, and three singlet systems (i) $d^1\Sigma^+ - c^1\Pi$, (ii) $c^1\Pi - b^1\Sigma^+$ and (iii) $c^1\Pi - a^1\Delta$ are known for NH. The positions of the singlets with respect to the ground state, X $^3\Sigma^-$, are yet unknown since no intercombination band system has been observed. The triplet system is the most intense and is readily excited. The rotational analysis of the 0-0 and 1-1 bands of the triplet system was first carried out by Funke (1935-36). Dixon, in 1959, produced NH molecules during flash photolysis of HNCO vapour and obtained their absorption spectrum in the third order of 6.6 meter concave grating spectrograph. He carried out a detailed rotational analysis of the 0-0 and 1-0 bands and determined the rotational constants of the A $^3\Pi_{inv}$ and X $^3\Sigma^-$ states of NH. Pannetier and Guenebaud

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(1959) photographed the 0-0, 1-1, 2-2, 1-0, 2-1, 1-2 and 0-1 bands of the triplet system of ND under low dispersion and carried out their vibrational analysis. In order to study the rotational structure of some of the above triplet bands of ND, the present study was undertaken. During the course of our investigations, the publications of Ingovan Kopp *et al.* (1965) and Shimauchi (1966) appeared which contained partial analyses of the 0-0 and 1-1 bands belonging to the triplet system of ND. Since, in our studies nearly all the branches of the 0-0 band of the A $^3\Pi_{inv}$ - X $^3\Sigma^-$ transition of ND are found, the results of their structural analysis are presented in this paper.

EXPERIMENTAL

The spectrum of ND was obtained in a closed quartz discharge tube which was thoroughly degassed earlier and filled with a mixture of specpure deuterium, trace quantity of nitrogen and neon at about 2.5 mm. of pressure. Under these conditions, the triplet system of ND was excited intensely in an electrodeless microwave oscillator (2450 mc./s.) discharge. The 0-0 band of ND around 3360 Å was photographed on the 6.6 meter concave grating spectrograph in the second order at a dispersion of 0.56 Å/mm.

ROTATIONAL ANALYSIS

The structure of the 0-0 band of ND is similar to that of the 0-0 band of NH which was shown to involve A $^3\Pi_{inv}$ - X $^3\Sigma^-$ transition. The Q branches are confined to very narrow spectral regions whereas P and R branches of the three sub-bands involving $^3\Pi_0$, $^3\Pi_1$, and $^3\Pi_2$ sub-states are very well separated and lie on both sides of the Q heads without any overlap. Twenty-five out of the twenty-seven predicted branches have been observed. Nine of them are intense main branches (R_1 , R_2 , R_3 , Q_1 , Q_2 , Q_3 and P_1 , P_2 , P_3) and sixteen are satellite branches. The two satellite branches NP_{13} and TR_{31} are too weak to be observed. The $^3\Pi_{inv}$ state belongs to Hund's case (a) for the first few values of N and very rapidly changes over to Hund's case (b) with increasing rotation.

The rotational structure showing the 25 branches of the 0-0 band of ND is marked in the spectrogram in Fig. 1. That the $^3\Pi$ state is an inverted state, could be established from the observation of first lines, R_1 (0), Q_1 (1), P_1 (2), R_2 (1), Q_2 (1), P_2 (2) and R_3 (1), Q_3 (2), P_3 (2) which are expected for the three sub-bands involving $^3\Pi_2$, $^3\Pi_1$ and $^3\Pi_0$ states respectively. Assignment of the satellite and main branches (in particular the closely packed Q_1 , Q_2 and Q_3 branches) have been made taking into consideration the various

combination differences shown in Fig. 2. Dixon's data (1959) on the combination differences of NH were of considerable help since corresponding

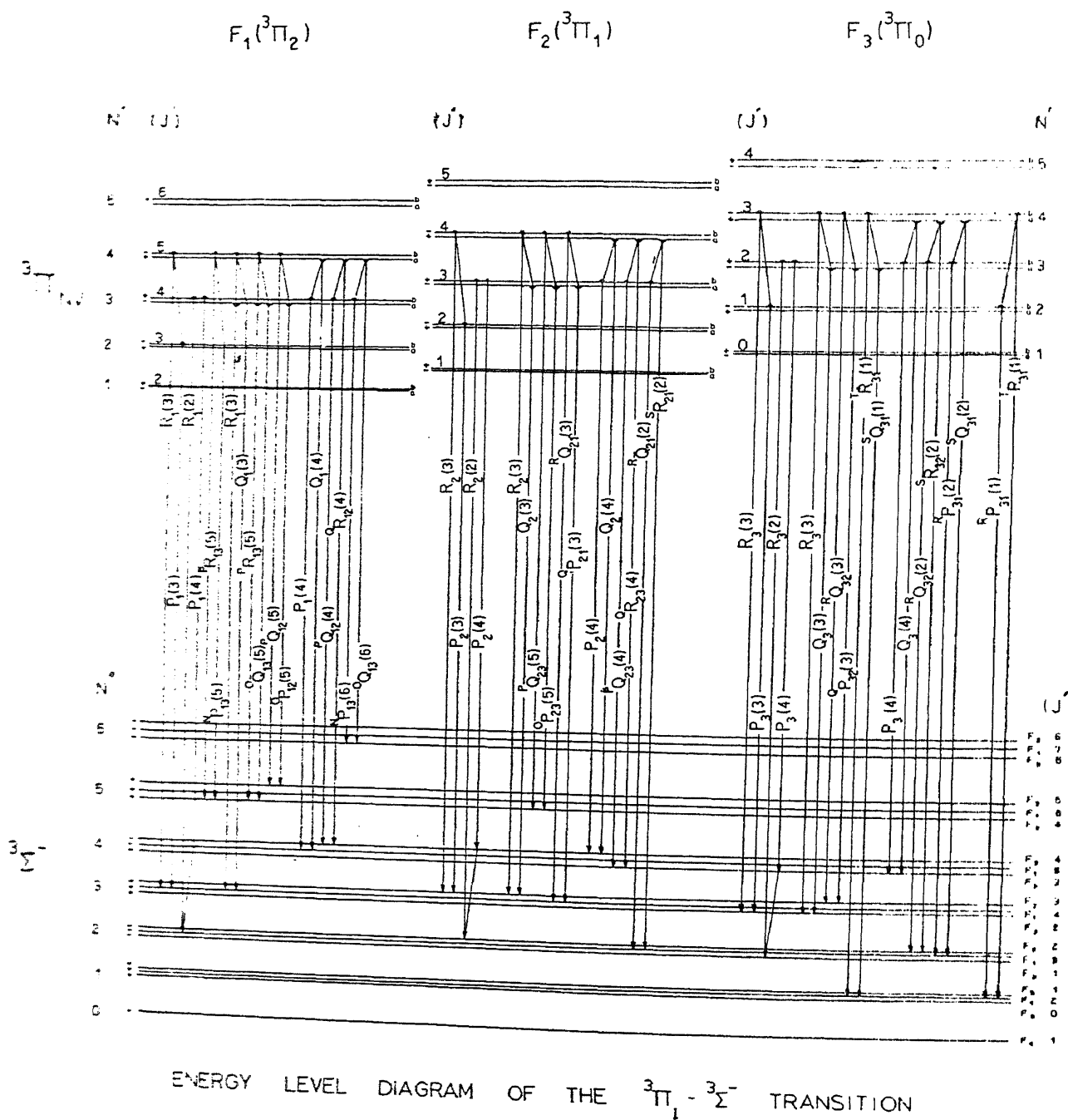


FIG. 2.

combination differences of ND could be readily computed and compared with the values derived from wave numbers of rotational lines of ND. The vacuum wave numbers of all the branches observed and assigned are given in Tables I and II.

TABLE II
Vacuum wave numbers and line assignments for the main branches of the O O band of ND

ν	P_1	R_2	Q_1	Q_2	Q_3	P_3	P_2	P_1
0	29777.27							
1	806.00	29848.01	29707.22	29790.11	29810.01	29733.70	29703.80	29777.27
2	827.12	847.32	772.84	790.77	806.00	719.79	744.85	757.54
3	846.06	863.76	774.60	794.87	803.04	704.63	724.56	737.10
4	860.69	880.07	777.27	793.55	801.25	689.75	706.06	716.05
5	880.44	896.06	778.05	792.47	801.25	674.32	687.57	696.71
6	903.76	913.24	779.10	791.28	799.01	658.61	669.39	677.40
7	921.66	929.89	780.28	789.81	797.62	642.02	651.47	658.61
8	939.26	946.41	781.14	788.64	796.24	625.58	633.09	640.08
9	956.59	962.94	781.94	787.93	793.35	608.96	616.01	621.81
10	973.63	979.26	781.94	787.17	792.47	592.34	598.57	603.75
11	990.44	995.42	781.04	786.38	790.26	575.63	581.20	585.92
12	30006.93	30015.43	781.94	785.58	789.26	558.94	563.96	568.30
13	023.18	027.20	781.14	784.70	789.81	542.31	546.72	550.64
14	039.13	042.75	781.14	783.69	788.64	529.58	529.72	533.28
15	054.73	058.00	780.28	781.94	787.17	509.06	512.68	515.98
16	070.08	073.06	779.10	780.28	785.68	492.53	495.78	498.85
17	085.07	087.73	777.27	778.05	783.69	476.06	478.95	481.79
18	099.65	102.09	776.11	778.05	781.94	459.61	462.24	464.83
19	113.96	116.18	774.60	776.71	780.28	443.21	445.62	448.00
20	127.91	129.85	773.63	774.60	778.44	426.87	429.01	431.17
21	141.36	143.16	771.87	771.87	776.11	410.60	412.52	414.58
22	154.40	156.05	769.71	770.53	773.92	393.94	396.05	397.97
23	30167.01	30168.45	29767.22	29768.26	29771.87	378.27	381.89	381.89
24	179.18	180.40	764.53	765.73	768.26	362.09	365.06	365.06
25	190.75	191.87	767.29	762.39	765.73	345.98	347.22	348.65
26	201.78	202.75	765.58	759.50	762.39	329.92	330.96	332.29
27	212.33	213.15	755.27	756.34	759.50	313.88	315.12	316.00
28	222.26	222.98	751.68	752.53	755.27	297.82	293.56	298.83
29	231.54	232.14	748.03	748.03	750.68	281.72	282.38	283.34
30	240.19	240.65	744.22	744.82	747.12	265.60	266.12	267.02
31	248.07	248.43	739.39	739.39	742.80	249.41	249.41	250.58
32	255.47	256.21	734.53	734.33	737.10	233.19	233.42	234.06
33	261.83	261.83	728.79	728.79	731.76	216.85	216.85	217.59
34	267.40	267.40	723.30	723.30	725.09	200.14	200.14	201.05
35	272.05	272.05	717.14	717.14	718.92	183.50	183.50	183.49
36	276.08	276.08	710.07	710.07	711.16	166.61	166.61	166.61
37	279.19	279.19	702.86	702.86	704.53	149.56	149.56	149.56
38	279.19	279.19	694.14	694.14	695.94	131.99	131.99	131.99
39	278.79	278.79
40	277.53	277.53

Rotational constants of the $A^1\Sigma^+$ state—The three energy levels F_1 , F_2 and F_3 of the $^3\Sigma$ state are given by the following expressions:

$$F_1(N) = B_v N(N-1) + D_v N(N-1)^2 + \delta_{12}''(N)$$

$$F_2(N) = B_v N(N-1) + D_v N(N-1)^2$$

$$F_3(N) = B_v N(N-1) + D_v N(N-1)^2 + \delta_{32}''(N)$$

where $\delta_{12}''(N)$ and $\delta_{32}''(N)$ are the spin splittings and are, according to Schlapp (1937),

$$\delta_{12}''(N) = \frac{\lambda}{2} (2N-1) B_v + \frac{1}{2} (2N-1) \gamma B_v^2 + \frac{1}{2} (2N-1) \gamma^2 B_v^3$$

$$\delta_{32}''(N) = \frac{\lambda}{2} (2N-1) B_v + \frac{1}{2} (2N-1) \gamma B_v^2 + \frac{1}{2} (2N-1) \gamma^2 B_v^3$$

where λ and γ are the spin splitting constants.

$$\delta_{12}''(N-1) + \delta_{32}''(N-1) = (2\lambda + \gamma)$$

The quantity $(2\lambda + \gamma)$ was obtained by taking different sets of $\delta_{12}''(N)$ and $\delta_{32}''(N)$ values which were obtained from the main and satellite branches in the three sub-bands. The rotational constants B_v' and D_v' were evaluated from $\frac{1}{2}(F_2 - F_3)(N)$ combination differences. The agreement between the values derived from the present data and those calculated from the data of NH was good.

The graphs in Fig. 3 show variation of the spin splittings $\delta_{12}''(N)$ and $\delta_{32}''(N)$ of NH and ND with respect to N . The graphs are similar indicating that the spin splittings and hence the constants λ and γ of the $X^3\Sigma^-$ state, remain unchanged from one isotopic molecule to another, i.e., NH to ND.

Rotational constants of the $A^1\Pi_{gr}$ state—Although the $A^1\Pi_{gr}$ state of ND tends to Hund's case (a) at low N values and rapidly changes over to Hund's case (b) at higher N values, the general expression for the F_1 , F_2 and F_3 levels of the $^3\Pi_2$, $^3\Pi_1$ and $^3\Pi_0$ states is given by Gilbert's (1936) equation,

$$\sum F_1'(J) = B_v' \{3J(J-1) + 1\} + D_v' \{9J^2(J-1)^2 + 12J(J-1) + 2\}$$

where B_v' and D_v' are the rotational constants of the $^3\Pi_{gr}$ state. These constants were calculated for the $N=0$ level using the Gilbert's (1936) relationship

$$\frac{\sum \Delta_2 F_1'(J)}{3(J + \frac{1}{2})} = (4B_v' + 22D_v') - 8D_v'(J + \frac{1}{2})^2$$

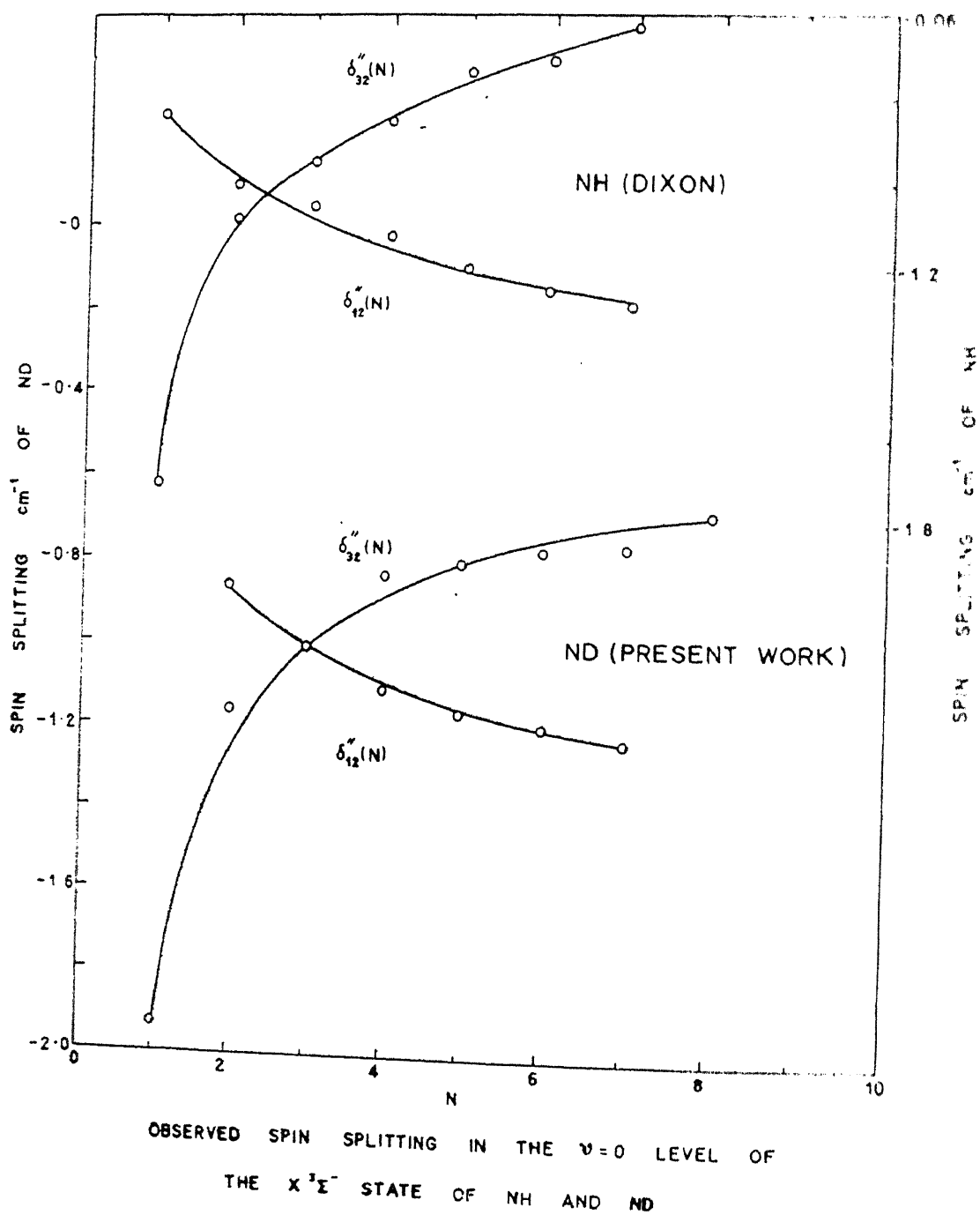


FIG. 3.

where $\Sigma \Delta_2 F_i'(J)$ are the mean of $\Delta_2 F_{ia}'(J)$ and $\Delta_2 F_{ib}'(J)$ taking into consideration the considerable Λ -doubling in the rotational levels of the $^3\Pi_{inv}$ state. The constants B_0 and D_0 show good agreement with the calculated values.

Band origin ν_{00} . Since the usual graphical method using the R and P branches will not give the correct band origin, the following expressions have been used for the determination of the band origin of the O-O band of ND:

$$\nu_{00} = \frac{1}{3} [\Sigma R_1(J) + \{\Sigma F_1'(J) - D\} + \Sigma F_4''(J)] \\ = \frac{1}{3} [\Sigma P_4(J) + \{\Sigma F_4'(J) - D\} + \Sigma F_4''(J)]$$

where $\Sigma F_1'(J)$ represents the Gilbert's expression as a summation of the rotational energies for the same J in the three substates of ${}^3\Pi_{inv}$ state and $\Sigma F_4''(J)$ represents the summation of the energy for X ${}^3\Sigma^-$ state for the same J value. The ν_{00} was calculated for each line of R and P branches and extended for several J values. At higher J values the energy values show deviation which is due to the neglect of the H term in the above formulae. The calculations were limited upto $J = 18$ only.

Spin coupling constant A. The coupling constant A representing the interaction between the spin and the electronic angular momentum of the ${}^3\Pi_{inv}$ state was obtained from Gilbert's (1936) expression:

$$\frac{1}{3} B^{-2} [3(F_3 - F_1)^2 + (F_3 - F_2)^2 + (F_2 - F_1)^2] \\ = 3(Y - 2)^2 - 8 - 12J(J + 1) - 24\mu J(J + 1)\{2J(J + 1) + 1\} \\ + 12Y\mu\{2J(J + 1) + 1\} - 48\mu^2 J^2(J + 1)^2\{J(J + 1) + 1\}$$

where $Y = A/B$ and $\mu = D/B$.

The quantities $(F_3 - F_1)$, $(F_3 - F_2)$ and $(F_2 - F_1)$ have been experimentally obtained from the differences in the main as well as the satellite branches belonging to transition involving the three substates ${}^3\Pi_0$, ${}^3\Pi_1$ and ${}^3\Pi_2$ states and for each J value. The mean value of A for ND differs from that of NH which is expected to be invariant, this is perhaps due to an inaccuracy in the assignment of Q branch lines and their satellites. The value of A is given in Table III.

Λ -doubling in the ${}^3\Pi_{inv}$ state. The Λ -doubling in the three substates ${}^3\Pi_0$, ${}^3\Pi_1$ and ${}^3\Pi_2$ of ${}^3\Pi_{inv}$ state was treated in detail by Hebb (1936) who deduced an expression

$$\delta_4(J) = C_0 S_{44}^2 + C_1 [2J(J + 1)]^4 S_{44} S_{24} + [C_2 + C_3 J(J + 1)] \\ [(J(J + 1) S_{24}^2 - 2\{J(J + 1)J(J + 1)(J + 2)\}^4 S_{44} S_{34})]$$

where $\delta_4(J)$ is half the value of the combination defect which is approximately equal to the Λ -doubling of each rotational level of the Π state. C_0 , C_1 , C_2 and C_3 are the Λ -doubling constants and S_{44} , S_{24} and S_{34} are the matrix

TABLE III

Rotational constants (in cm^{-1}) of $X^3\Sigma^-$ and $A^3\Pi_{\text{inv}}$ states of ND(a) $X^3\Sigma^-$ state—

Constants	Present work	Calculated	Dixon's values of NH
B_0''	8.7757	8.7733	16.3454
D_0''	4.68×10^{-4}	4.80×10^{-4}	16.85×10^{-4}
$(2\lambda + \gamma)$	-1.8356	...	-1.803

(b) $A^3\Pi_{\text{inv}}$ state—

Constants	Present work	Calculated	Dixon's values of NH
B_0'	8.7688	8.7679	16.3221
D_0'	5.02×10^{-4}	5.01×10^{-4}	17.58×10^{-4}
A	-31.89	...	-34.72
C_0'	-1.40	-1.40	-2.63
C_2'	+0.0118	+0.010	+0.0318
ν_{00}	29799.5	...	29776.76

elements. If we consider the Λ -doubling in the three substates $^3\Pi_0$, $^3\Pi_1$ and $^3\Pi_2$ together, then the above equation will be reduced to the form

$$\delta_i(J) = C_0 + C_2 J(J+1) + C_3 J^2(J+1)^2$$

where

$$\delta_i(J) = [(F_{1a} - F_{1b}) - (F_{2a} - F_{2b}) + (F_{3a} - F_{3b})].$$

In the case of NH, Dixon found it necessary to add an extra term $C_3 J^2(J+1)^2$ to Hebb's expression at values $J > 10$. Since the Λ -doubling in the case of ND is comparatively smaller than that of NH, the constant C_3 was neglected. The constants C_0 and C_2 were calculated from a graph plotted between $\delta_i(J)$ and $J(J+1)$. The constants C_0^i and C_2^i of ND were also

found to be equal to $\rho^2 C_0$ and $\rho^4 C_2$ respectively of NH where $\rho = \sqrt{\mu/\mu_1}$. Also the constant C_2^4 was calculated from Van Vleck's "pure precision" formula $\epsilon = [2B^2L(L+1)]^{1/2}$, where $C_2 = \epsilon$ and B is the rotational constant, $L = 1$ and $\nu \approx \nu_{00}$. The calculated values compared well with the observed values given in Table III.

The Λ -doubling $\delta_{a\beta}(N)$ was plotted against N for all the three substates ${}^3\Pi_0$, ${}^3\Pi_1$ and ${}^3\Pi_2$. For purposes of comparison, the values of Dixon for NH were also shown in the same Fig. 4. It is interesting to note that in both

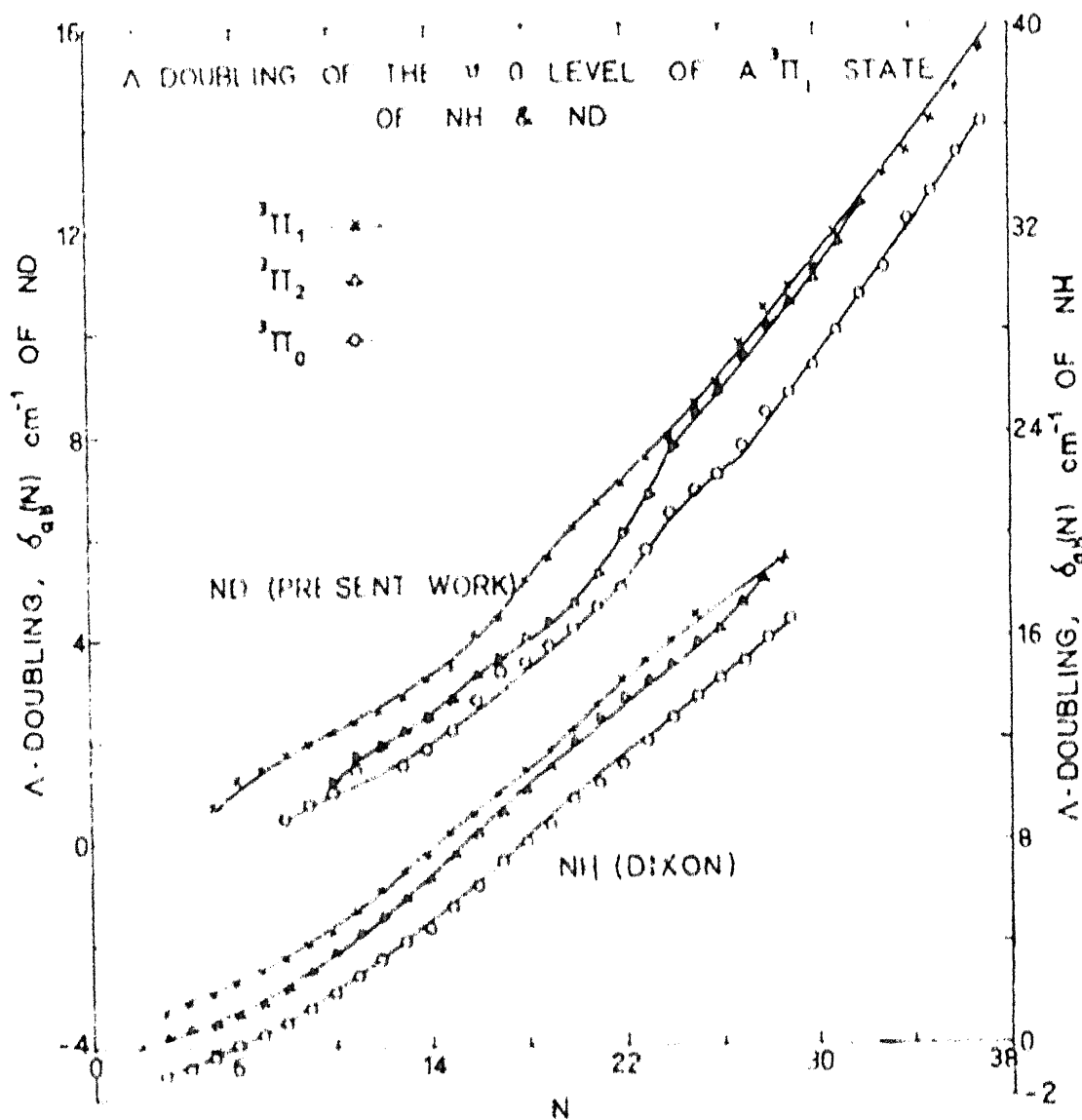


FIG. 4.

the curves of NH and ND the Λ -doubling is maximum for ${}^3\Pi_1$ state and minimum for the ${}^3\Pi_0$ state although usually the Λ -doubling is expected to be minimum in the ${}^3\Pi_2$ state and maximum in the ${}^3\Pi_0$ state, since the ${}^3\Pi_{1,2}$ and ${}^3\Pi_{0,1}$ states of ${}^3\Pi_0$ are non-degenerate even for zero rotation. All the constants derived for X ${}^3\Sigma$ and A ${}^3\Pi$ states are given in Table III.

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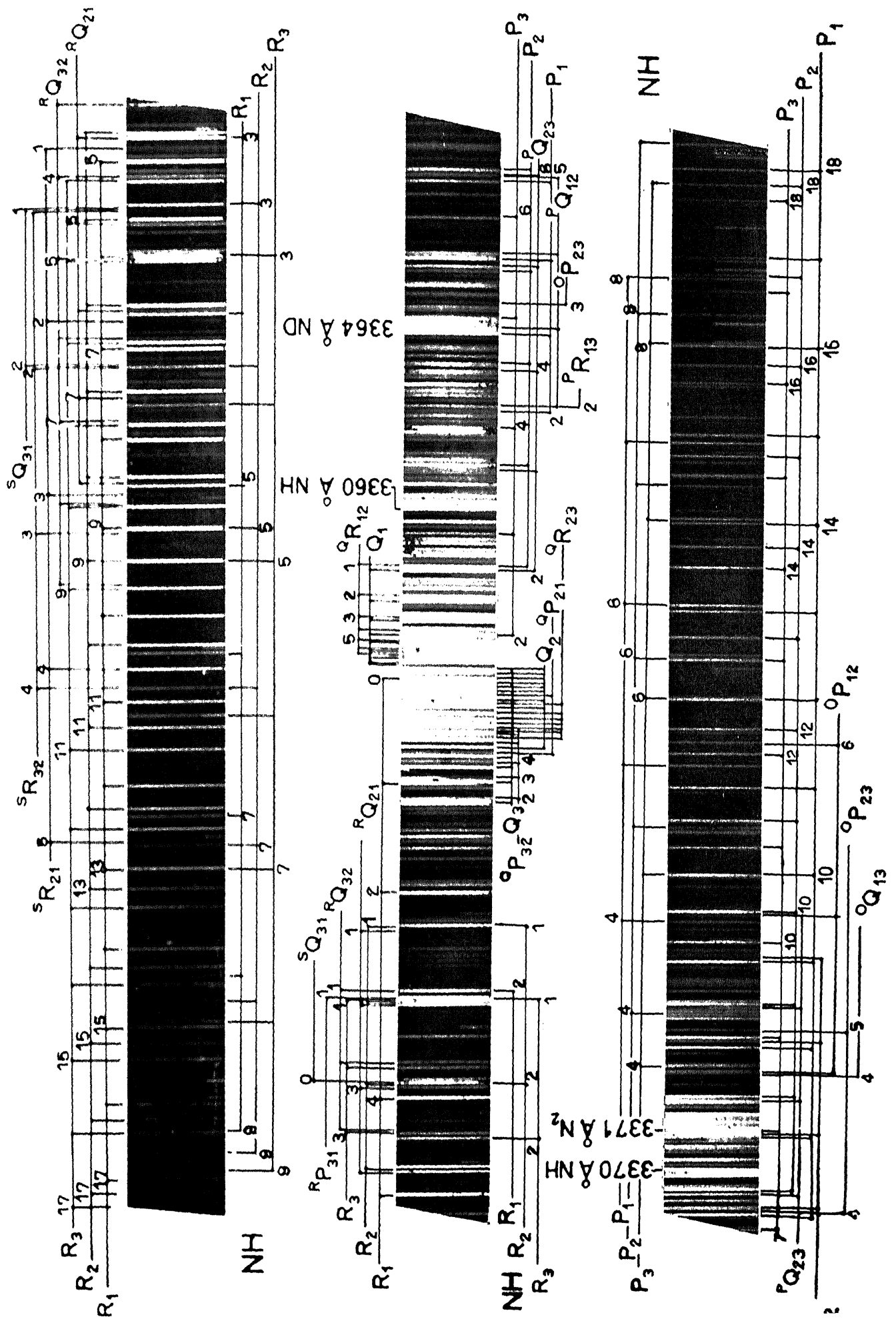


FIG. 1 Rotational structure of the $\Omega=0$ band of a $3\sigma_g^2$ system of N_2