

THE $d\ ^1\Sigma^+-c\ ^1\Pi$ SYSTEM OF NH

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INTRODUCTION

THREE singlet systems and one triplet system are known for NH. The singlet systems involve transitions, (i) $d\ ^1\Sigma^+-c\ ^1\Pi$, (ii) $c\ ^1\Pi-b\ ^1\Sigma^+$ and (iii) $c\ ^1\Pi-a\ ^1\Delta$ and lie in the regions 2530, 4502 and 3240 Å respectively. The triplet band system, which lies at 3360 Å, arises out of $^3\Pi-^3\Sigma^-$ transition, $^3\Sigma^-$ being the ground state of the molecule. The relative positions of the singlets with respect to the ground state of NH are yet unknown since no intercombination band system is observed. In the $d\ ^1\Sigma^+-c\ ^1\Pi$ system, the 0-0 band at 2530 Å was analysed by Lunt, Pearse and Smith (1936) who had also assigned a few weaker lines which overlapped the rotational structure of the 0-0 band to the P, Q and R branches of 1-1 band. Feast (1951) while studying the NH⁺ spectrum observed among the NH bands, a weak structure at 2684 Å which he suggested as the 0-1 band of the $d\ ^1\Sigma^+-c\ ^1\Pi$ system. During the course of our studies of the $d\ ^1\Sigma^+-c\ ^1\Pi$ system, we have been able to photograph all the three bands and carry out a complete rotational analysis of the bands, the results of which are reported in this paper.

EXPERIMENTAL

A mildly condensed transformer discharge (0.25 kVA and 0.005 μF) through flowing ammonia gas was used to excite the NH spectrum. The flow of ammonia was maintained at a constant rate, as read off from a flow meter. The 0-0, 0-1 and 1-1 bands of the $d\ ^1\Sigma^+-c\ ^1\Pi$ system were developed with moderate intensity and photographed on a Jarrell-Ash 3.4 m. grating spectrograph in the second order at a dispersion of 2.6 Å/mm. Figure 1 shows a representative spectrogram of the three bands. The 2730 Å band of NH⁺ can also be seen in the spectrogram and has an intensity stronger than the 0-1 band at 2683 Å of NH. The 0-0 band of the $c\ ^1\Pi-a\ ^1\Delta$ system at 3240 Å was also excited under the same conditions of discharge. This band was photographed on the 6.6 m. concave grating spectrograph in the second order at a dispersion of 0.56 Å/mm. and its data on the Λ -doubling

TABLE I
Vacuum wavenumbers and line assignments for the bands of $d^1\Sigma^+-c^1\Pi$ system of NH

J	0-0 band			0-1 band			1-1 band		
	R	Q	P	R	Q	P	R	Q	P
1	..	39510.41	39482.71	..	37393.70	..	39975.78
2	39595.11	510.41	454.42	..	396.42	..	998.74
3	622.60	510.41	425.82	37515.63	403.13	..	40032.70	399924.44	39844.98
4	649.82	510.41	397.48	..	413.78	37301.97	064.29	931.03	823.28
5	677.54	510.41	369.32	..	426.57	286.08	096.25	937.55	803.13
6	703.91	509.18	341.41	..	442.18	273.61	131.29	945.45	784.58
7	730.94	509.18	313.89	..	460.52	264.58	166.77	955.14	768.12
8	757.59	509.18	286.65	730.27	483.56	260.38	204.23	968.01	754.46
9	784.58	509.18	260.53	782.43	508.09	260.38	243.38	982.27	743.11
10	811.51	511.78	235.14	836.75	538.21	260.38	284.66	998.74	734.62
11	838.77	514.33	210.70	..	571.70	268.10	328.46	40019.67	728.30
12	866.70	517.38	187.82	..	610.05	280.35	375.61	042.42	728.30
13	894.92	521.53	166.39	..	653.73	298.73	426.05	070.04	730.94
14	924.44	527.02	146.85	..	704.02	323.53	480.96	102.63	739.78
15	955.14	534.40	129.50	..	761.24	356.38	541.64	141.47	754.78
16	986.60	543.70	114.61	..	827.53	398.69
17	40019.67	555.62	103.27
18	056.20	570.43	095.26
19	096.25	590.55	091.82
20	137.68	611.74	091.82
21	166.77	639.87	095.26
22	..	674.26

of the $c\ ^1\Pi$ state were compared with corresponding values obtained from the $d\ ^1\Sigma^+ - c\ ^1\Pi$ system.

RESULTS AND DISCUSSION

(a) Rotational Structure of 2683 Å and 2516 Å Bands and Their Identification as the 0-1 and 1-1 Bands of the $d\ ^1\Sigma^+ - c\ ^1\Pi$ System.

The rotational structure of the bands at 2683 Å and 2516 Å consists of single series of P, Q, and R branches (Fig. 1) and is identical with that of the 2530 Å band. Vacuum wave numbers and J assignments of the rotational lines for the three bands are given in Table I. The combination differences $\Delta_2 F(J)$, viz.,

$$\Delta_2 F'(J) = R(J) - P(J) \text{ of the initial } ^1\Sigma^+ \text{ state and}$$

$$\Delta_2 F''(J) = R(J-1) - P(J+1) \text{ of the final } ^1\Pi \text{ state}$$

are shown in an energy level diagram (Fig. 2) for 0-0, 0-1 and 1-1 transitions. The combination differences obtained from the rotational lines of the bands at 2530, 2516 and 2683 Å are given in Table II. A comparison of columns 3 and 4 of Table II shows that the upper state combination differences of the 0-0 band at 2530 Å agree with those of the 2683 Å band, indicating that the two bands have a common initial level, $v' = 0$. The lower state combination differences of the 2683 Å band are in good agreement with those of 2516 Å band (columns 5 and 6) indicating that the two bands have a common final level. Thus, the rotational structure studies fully support the vibrational assignments of the 2683 Å and 2516 Å bands as the 0-1 and 1-1 bands respectively of the $d\ ^1\Sigma^+ - c\ ^1\Pi$ system.

(b) Λ -Doubling in the $C\ ^1\Pi$ State

On account of Λ -doubling in the $^1\Pi$ state, the Q branch lines of the $^1\Sigma^+ - ^1\Pi$ transitions go to one of the Λ -components, say the a level while P and R branches go to the other component, the b level (Fig. 2). Consequently, the upper state combination differences, $\Delta_1 F'(J)$'s are not equal (Table III). They differ by a small quantity, ϵ , called the combination effect, as shown below:

$$R(J) - Q(J) = Q(J+1) - P(J+1) + \epsilon \simeq \Delta_1 F'(J).$$

A similar situation obtains for the following lower state combination differences (Table IV),

$$R(J) - Q(J+1) = Q(J) - P(J+1) + \epsilon \simeq \Delta_1 F''(J).$$

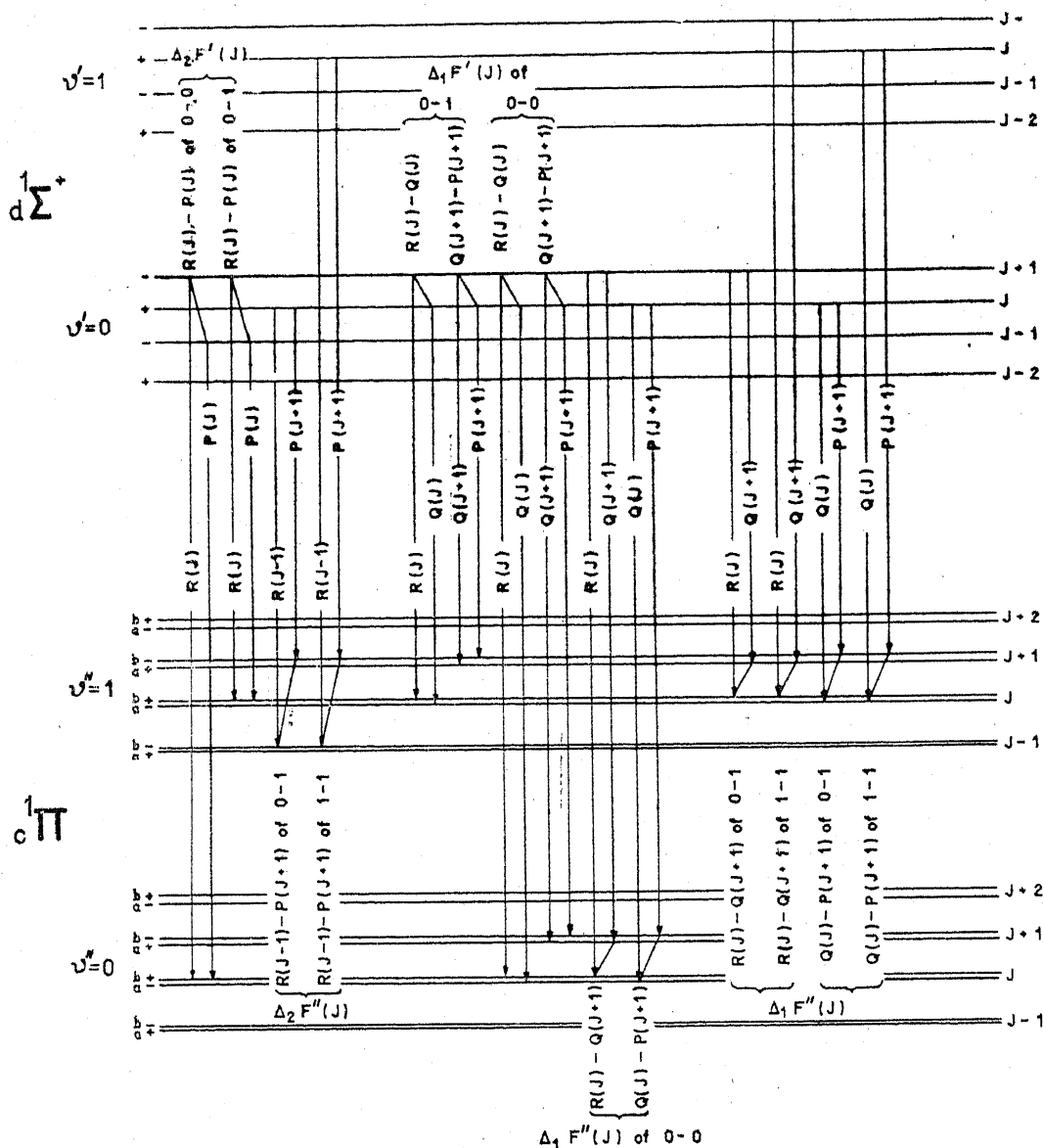


FIG. 2. Combination differences.

However, $\Delta_1 F''(J)$ values of the 0-1 band should be equal to the corresponding $\Delta_1 F''(J)$'s of the 1-1 band since in both bands, the transitions are to the same rotational levels of $v'' = 1$ (see Fig. 2). It is indeed found that the $\Delta_1 F''(J)$ values in columns 4 and 5 are in agreement, within permissible errors, with those in columns 6 and 7 respectively of Table IV. But this is not true of $\Delta_1 F'(J)$'s of 0-0 and 0-1 bands as the Λ -doublings of $v' = 0$ and 1 levels are slightly different, as borne out in Table III.

TABLE II
 $\Delta_2 F(J)$ values of the $v = 0$ and 1 levels of d $^1\Sigma^+$ and c $^1\Pi$ states of NH

J	0-0 band		0-1 band		1-1 band	
	R(J-1) -P(J+1)	R(J)-P(J)	R(J)-P(J)	R(J-1) -P(J+1)	R(J-1) -P(J+1)	R(J)-P(J)
1
2	..	140.69	130.80	..
3	197.63	196.78	..	—	175.46	187.72
4	253.28	252.34	..	229.55	229.57	241.01
5	308.41	308.22	279.71	293.12
6	363.65	362.50	328.13	346.71
7	417.26	417.05	376.83	398.65
8	470.41	470.94	469.89	—	423.66	449.77
9	522.45	524.05	522.05	469.89	469.61	500.27
10	573.88	576.37	576.37	514.33	515.08	550.04
11	623.69	628.07	..	556.40	556.36	600.16
12	672.38	678.88	597.52	647.31
13	719.85	728.53	635.83	695.11
14	765.42	777.59	671.27	741.18
15	809.83	825.64	786.86
16	851.87	871.99
17	891.34	916.40
18	927.85	960.94
19	964.38	1004.43
20	1000.99	1045.86
21	..	1071.51

TABLE III

 $\Delta_1 F'(J)$ values of the $v' = 0$ and 1 levels of the $d^1\Sigma^+ - c^1\Pi$ system of NH

J	0-0 band		0-1 band		1-1 band	
	R(J)-Q(J)	$\frac{Q(J+1)}{-P(J+1)}$	R(J)-Q(J)	$\frac{Q(J+1)}{-P(J+1)}$	R(J)-Q(J)	$\frac{Q(J+1)}{-P(J+1)}$
1	..	55.99
2	84.70	84.59	79.46
3	112.21	112.93	112.50	111.81	108.26	107.75
4	139.41	141.09	..	140.49	133.26	134.42
5	167.13	167.77	..	168.57	158.70	160.87
6	194.73	195.29	..	195.94	185.84	187.02
7	221.76	222.53	..	223.18	211.63	213.55
8	248.41	248.65	246.71	247.71	236.22	239.16
9	275.40	276.64	274.34	277.83	261.11	264.12
10	299.73	303.63	298.54	303.60	285.92	291.37
11	324.44	329.56	..	329.70	308.79	314.12
12	349.32	355.14	..	355.00	333.19	339.10
13	373.39	380.17	..	380.49	356.01	362.85
14	397.42	404.90	..	404.86	378.33	386.69
15	420.74	429.09	..	428.84	400.17	..
16	442.90	452.35
17	464.05	475.17
18	485.77	498.73
19	505.70	519.92
20	525.94	540.53

(c) Comparison of Λ -Doubling Data of the $^1\Pi$ State in the Three Singlet Systems

The Λ -doubling data obtained in the present investigation are compared, in Tables V and VI, with corresponding data of $c^1\Pi - b^1\Sigma^+$ (4502 Å) and

TABLE IV

 $\Delta_1 F''(J)$ values of the $v'' = 0$ and 1 levels of the $d^1 \Sigma^+ - c^1 \Pi$ system of NH

J	0-0 band		0-1 band		1-1 band	
	R(J) -Q(J+1)	Q(J) -P(J+1)	R(J) -Q(J+1)	Q(J) -P(J+1)	R(J) -Q(J+1)	Q(J) -P(J+1)
1	..	55.99
2	84.70	84.59
3	112.21	112.93	101.85	101.16	101.67	101.16
4	139.41	141.09	..	127.70	126.74	127.90
5	168.36	169.00	..	152.96	150.80	152.97
6	194.73	195.29	..	177.60	176.15	177.33
7	221.76	222.53	..	200.14	198.76	200.68
8	248.41	248.65	222.18	223.18	221.96	224.90
9	272.80	274.04	244.22	247.71	244.64	247.65
10	297.18	301.08	265.05	270.11	264.99	270.44
11	321.39	326.51	..	291.35	286.04	291.37
12	345.17	350.99	..	311.32	305.57	311.48
13	367.90	374.68	..	330.20	323.42	330.26
14	390.04	397.52	..	347.64	339.49	347.85
15	411.44	419.79	..	362.55
16	430.98	440.43
17	449.24	460.36
18	465.65	478.61
19	484.51	498.73
20	497.81	516.48

$c^1 \Pi - a^1 \Delta$ (3240 Å) systems which have the $c^1 \Pi$ state in common. The data on the 4502 Å band are from low dispersion studies of Lunt *et al.* (1935) and so the combination differences are accurate to 0.1 cm^{-1} . The 3240 Å

band was however studied at a higher dispersion and resolution by Pearse (1933), by Shimauchi (1964) and by the authors in the present investigation. In comparing the data, it is important to distinguish which of the two sets of combination differences in the $c^1\Pi-a^1\Delta$ transition corresponds to that in $c^1\Pi-b^1\Sigma^+$ or $d^1\Sigma^+-c^1\Pi$ transition. The energy level diagram given in Fig. 3 shows the different transitions that give rise to the common combination differences of $v = 0$ level of the $c^1\Pi$ state. The lower energy components of the Λ -doublets of the degenerate Π and Δ states are designated as the a states and the higher energy components the b states. The combination differences given under different columns in Tables V and VI correspond to the following transitions (Fig. 3):

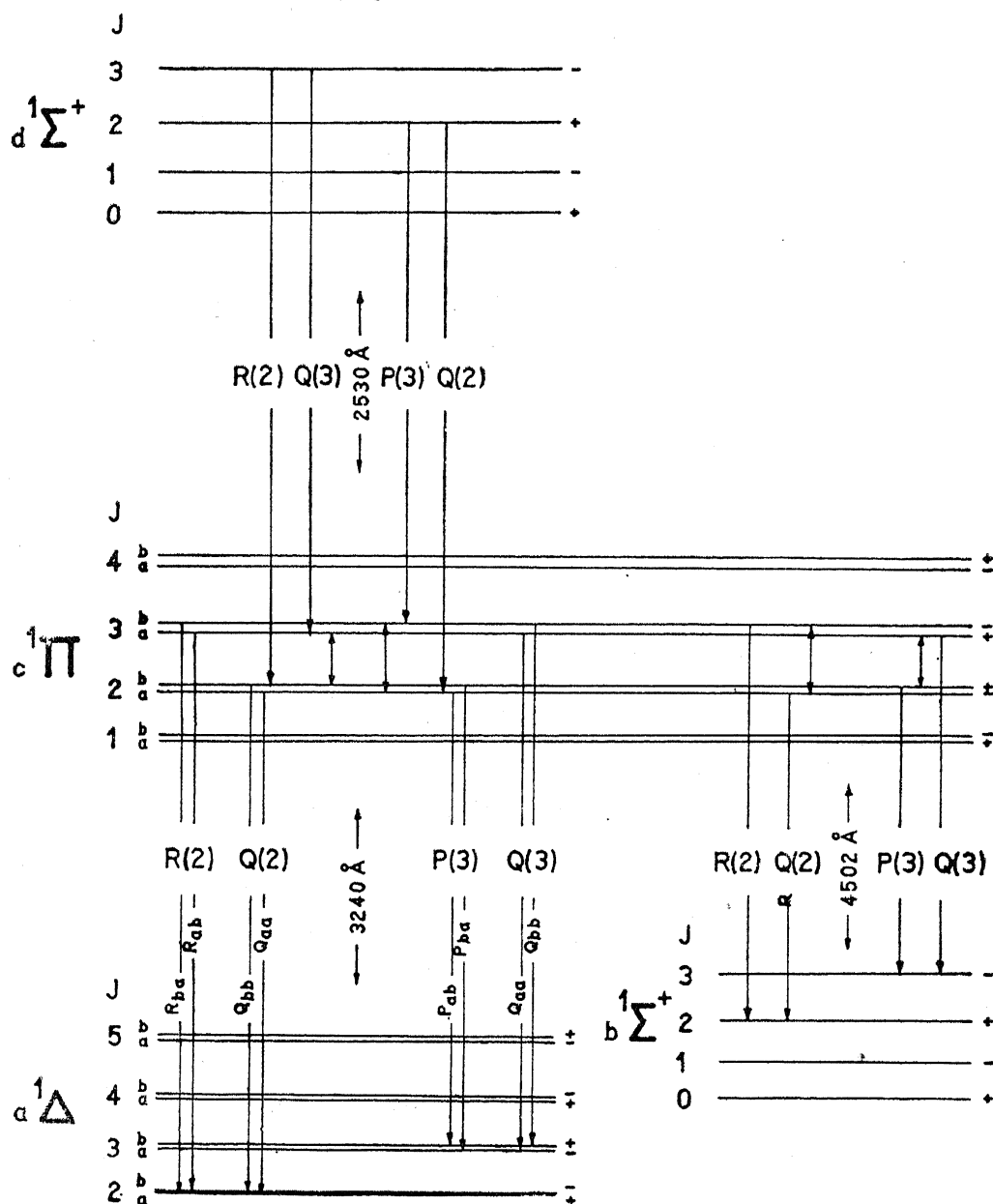


FIG. 3. Singlet systems of NH.

TABLE VI
Common combination differences of $v = 0$ level of the $c^1\Pi$ state of NH

J	$c^1\Pi-a^1\Delta$ (3240 Å) Pearse		$c^1\Pi-x^1\Delta$ (3240 Å) Shimauchi		$c^1\Pi-b^1\Sigma^+$ (4502 Å) Pearse		$d^1\Sigma^+-c^1\Pi$ (2530 Å) Present work		$c^1\Pi-a^1\Delta$ (3240 Å) Present work	
	$R_{ba}(J)$ $-Q_{aa}(J)$	$Q_{bb}(J+1)$ $-P_{ab}(J+1)$	$R_{ba}(J)$ $-Q_{aa}(J)$	$Q_{bb}(J+1)$ $-P_{ab}(J+1)$	$R(J)$ $-Q(J)$	$Q(J)$ $-P(J+1)$	$R_{ba}(J)$ $-Q_{aa}(J)$	$Q_{bb}(J)$ $-P_{ab}(J+1)$	$R_{ba}(J)$ $-Q_{aa}(J)$	$Q_{bb}(J+1)$ $-P_{ab}(J+1)$
1	..	56.52	56.6	55.99
2	84.62	84.61	84.6	84.59	84.91	84.58	84.91	84.58
3	112.74	112.76	112.8	112.8	112.84	112.64	112.84	112.64
4	140.50	141.00	140.9	140.9	140.71	140.84	140.71	140.84
5	168.54	168.56	168.3	168.3	168.44	168.55	168.44	168.55
6	195.83	195.87	196.2	196.2	195.94	195.84	195.94	195.84
7	222.90	222.96	222.7	222.7	223.02	222.97	223.02	222.97
8	249.46	248.37	249.5	248.65	249.53	250.02	249.53	250.02
9	275.70	275.70	275.7	274.04	275.61	275.94	275.61	275.94
10	301.31	..	301.35	301.34	301.4	301.08	301.32	301.63	301.32	301.63
11	326.31	..	326.25	326.20	326.3	326.51	326.34	326.75	326.34	326.75
12	350.81	..	351.07	350.76	..	350.99	350.82	351.55	350.82	351.55
13	374.12	374.58	..	374.68	374.40	..	374.40	..
14	397.06	397.36	..	397.52	397.61	..	397.61	..
15	419.46	419.79	419.76	..	419.76	..
16	439.90	440.43	440.50	..	440.50	..
17	460.36
18	478.61
19	498.73
20	516.48

(a) First set

$$\begin{aligned}
 & R(J) - Q(J+1) \text{ of } d^1\Sigma^+ - c^1\Pi \\
 &= Q(J+1) - P(J+1) \text{ of } c^1\Pi - b^1\Sigma^+ \\
 &= R_{ab}(J) - Q_{bb}(J) \\
 &= Q_{aa}(J+1) - P_{ba}(J+1) \left. \vphantom{\begin{aligned} & R(J) - Q(J+1) \text{ of } d^1\Sigma^+ - c^1\Pi \\ &= Q(J+1) - P(J+1) \text{ of } c^1\Pi - b^1\Sigma^+ \\ &= R_{ab}(J) - Q_{bb}(J) \\ &= Q_{aa}(J+1) - P_{ba}(J+1) \end{aligned}} \right\} \text{ of } c^1\Pi - a^1\Delta
 \end{aligned}$$

(b) Second set

$$\begin{aligned}
 & Q(J) - P(J+1) \text{ of } d^1\Sigma^+ - c^1\Pi \\
 &= R(J) - Q(J) \text{ of } c^1\Pi - b^1\Sigma^+ \\
 &= R_{ba}(J) - Q_{aa}(J) \\
 &= Q_{bb}(J+1) - P_{ab}(J+1) \left. \vphantom{\begin{aligned} & Q(J) - P(J+1) \text{ of } d^1\Sigma^+ - c^1\Pi \\ &= R(J) - Q(J) \text{ of } c^1\Pi - b^1\Sigma^+ \\ &= R_{ba}(J) - Q_{aa}(J) \\ &= Q_{bb}(J+1) - P_{ab}(J+1) \end{aligned}} \right\} \text{ of } c^1\Pi - a^1\Delta.
 \end{aligned}$$

There is good agreement between the above differences.

In these tables, $\Delta_1 F$ values of 3240 Å band given under column marked Shimauchi, are computed from the listed P, Q and R lines in the manner described above. Shimauchi on the other hand obtained $\Delta_1 F$ values by subtracting higher frequency component of Q branch line from the higher frequency component of R branch line and the lower frequency Q from lower frequency R lines (similarly for differences between Q and P lines). As is clear from Fig. 3, the values thus obtained, should not and therefore do not correspond to the differences given in Tables V and VI. However, once, the proper $\Delta_1 F$ values are deduced from Shimauchi's data there is complete agreement with the rest of the combination differences.

(d) Determination of the Coefficient of Λ -Type Doubling

The coefficient of Λ -type doubling, q , in the $c^1\Pi$ state can be calculated from a plot of the combination defect, ϵ , against $(J+1)^2$. This value, according to Van Vleck is,

$$q = \frac{2B_v^2 l(l+1)}{\nu(\Pi, \Sigma)}$$

Assuming that $\nu(\Pi, \Sigma) \simeq 39511.70 \text{ cm.}^{-1}$ the ν_{00} of the $d^1\Sigma^+ - c^1\Pi$ band system and taking B_v as an average of $B_0(d^1\Sigma)$ and $B_0(c^1\Pi)$, one obtains $q = 0.020 \text{ cm.}^{-1}$ which is in good agreement with the $q = 0.017 \text{ cm.}^{-1}$ obtained graphically from plots of combination defects. For $v' = 1$, the coefficient, q , is smaller as expected.

(e) *Rotational and Vibrational Constants of the $d^1\Sigma^+$ State*

Because of the combination defect in the Δ_1F (J) values, exact values of rotational constants cannot be obtained. The best possible data were used to compute B, α and other constants which are given in Table VII. The constants derived by Dieke and Blue (1934), Lunt *et al.* (1936), Nakamura and Shidei (1934) and Shimauchi (1964) are also included in Table VII for comparison.

TABLE VII

Rotational and vibrational constants of $d^1\Sigma^+$ and $c^1\Pi$ states of NH in cm.^{-1}

(a) $d^1\Sigma^+$ state

	Present work	Lunt, Pearse and Smith
B_0	14.074 ₉	14.09
$D_0 (10^{-3})$	1.613	1.60
B_1	13.463	..
$D_1 (10^{-3})$	1.625	..
B_e	14.380 ₉	..
α_e	0.6119	..
$D_e (10^{-3})$	1.638	..
$\beta_e (10^{-3})$	0.012	..
$\Delta G_{\frac{1}{2}}$	2530.30	..
r_e	1.1165 Å	..

(b) $c^1\Pi$ state

	Present work	Dieke and Blue	Lunt, Pearse and Smith	Nakamura and Shidei	Shimauchi
B_a	14.175	14.171	14.168
B_b	14.155	14.154	14.151
B_{ave}	14.165	14.163	14.16	14.19	14.159 ₅
$D_e (10^{-3})$	2.310	2.44	2.18	2.39	2.295
B_{ave} for $v=1$	12.898	12.80	..
$D_1 (10^{-3})$	3.091	2.40	..
B_e	14.798 ₅	14.88	..
α_e	1.267	1.39	..
$D_e (10^{-3})$	1.957
$\beta_e (10^{-3})$	0.756
$\Delta G_{\frac{1}{2}}$	2122.50
r_e	1.1005 Å	1.10 Å	..

TABLE VII—(Contd.)

(c) Band Origins in a Deslandres Scheme

v' \ v''	0		1
0	39511.70	(2122.50)	37389.20 (2530.30)
1			39919.50

SUMMARY

The singlet systems of NH have been excited in a mildly condensed transformer discharge through flowing ammonia gas. The 0-0 bands, 2530 Å of $d\ ^1\Sigma^+-c\ ^1\Pi$ and 3240 Å of $c\ ^1\Pi-a\ ^1\Delta$ systems, appear with considerable intensity compared to the 4502 Å band of the $c\ ^1\Pi - b\ ^1\Sigma^+$ system. Besides the 2530 Å bands, two weaker bands at 2683 Å and 2516 Å are also excited. They are photographed in the second order of a Jarrell Ash 3.4 m. grating spectrograph at a dispersion of 2.6 Å/mm. Rotational analysis of the two weaker bands show that they belong to the $d\ ^1\Sigma^+-c\ ^1\Pi$ system and further supports their assignment as the 0-1 and 1-1 bands. The vibrational and rotational constants derived for the $d\ ^1\Sigma^+$ and $c\ ^1\Pi$ states are,

	B_e	α_e	r_e	$\Delta G_{\frac{1}{2}}$
$d\ ^1\Sigma^+$ state (in cm.^{-1})	14.380 ₉	0.611 ₉	1.1165 Å	2530.30
$c\ ^1\Pi$ state (in cm.^{-1})	14.798 ₅	1.267	1.1005 Å	2122.50
$v' - v''$	<i>Band Origins in cm.^{-1}</i>			
0 - 0	39511.70			
0 - 1	37389.20			
1 - 1	39919.50			

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