CHAPTER VI

ROTATIONAL ANALYSIS OF THE (0,0) BAND OF THE B-SYSTEM OF CaCl MOLECULE

From the vibrational analysis of the B-system of CaCl molecule carried out during the present investigation, the lower state with frequency 366.2 cm^{-1} and the upper state with frequency 363.0 cm^{-1} were identified. Since the system was also observed in absorption the lower state involved must be the ground state.

In order to understand the exact nature of the electronic states involved in the transition, the B-system was photographed at higher dispersion and study the rotational structure. It was possible to resolve only the (0,0) band. The rotational analysis of the (0,0) band of the B-system is discussed in this chapter.

The (0,0) band of the B-system of CaCl molecule was photographed in the fourth order of a two meter plane grating spectrograph at a dispersion of about 1.2 A°/mm. with the slit width of about ten microns. The overlapping orders were sorted out using a filter GG14. The time of exposure was about two hours to get a satisfactory spectrogram. Ilford R-40 plates were used to photograph the spectrum. Measurements were taken against iron arc standard lines on the Abbe Comparator. The error in measurements of well resolved lines does not exceed 0.05 cm^{-1}. The reproduction of the (0,0) band is given in Plate 12 as seen on the negative.

ROTATIONAL ANALYSIS OF THE (0,0) BAND

In the spectrogram taken with a slit width of ten microns at a dispersion of about 1.2 A°/mm, the band showed two extensive branches. The separation between the branch lines increases with increasing K values. The system may be attributed to a $^2\Sigma — {}^2\Sigma$ transition and belonging to Hund's case b. In this type of transition although a sattelite Q branch can be present, due to its low intensity, it can not be observed. The two heads may be due to the effect of spin of the rotational levels. Each level splits into $J = K+\frac{1}{2}$ and $J = K-\frac{1}{2}$ components and separation increases with increasing K values. K values corresponding to P head may split into such an extent that it may resolve into two P heads namely P_1 and P_2. Thus the band can be separated into four branches P_1, R_1 and P_2, R_2.

In this spectrogram the origin is well resolved as seen in the plate. The first line of the higher wave number side of the origin corresponds to first line of the R_1 branch corresponding to $R_1(0)$. The first line of the lower wave number side of the origin corresponds to $P_1(1)$ line. Then the numbering of P_1 and R_1 branches was straight forward. Near the heads, lines were not well resolved. In the P branch lines corresponding upto $K=30$ could only be picked out because of the crowding of lines near the head.

At the origin spin splitting is so small that the origin of both the components may be taken at the same position. The splitting increases with increasing K values and numbering of P_2 and R_2 branches was done as in the case of P_1 and R_1 branches. The vacuum wave numbers and the K numbering of the rotational lines of (0,0) band are given in Table 28. The combination differences between R_1 and P_1 are calculated by the equation

$$\Delta_2 F_1'(K) = R_1(K) - P_1(K)$$

$$\Delta_2 F_1''(K) = R_1(K-1) - P_1(K+1)$$

and are given in Table 29.

Spin splitting and the nature of the electronic transition. The splitting of the branch lines into two equally intense components was found to be same for both P and R branches for same K' values. This suggests that this splitting is due to spin splitting in the upper state. When the separation between the components $\Delta\nu_{12}(R) = R_1 - R_2$ was divided by K' it was found to be a constant within the experimental error.

$$R_1(K) = \nu_0 + F_1'(K+1) - F_1''(K)$$

$$R_2(K) = \nu_0 + F_2'(K+1) - F_2''(K)$$

TABLE 28

THE VACUUM WAVE NUMBER* AND K ASSIGNMENTS FOR THE (0,0) BAND OF $B^2\Sigma$— $X^2\Sigma$ SYSTEM OF CaCl MOLECULE

K	$P_1(K)$ cm^{-1}	$P_2(K)$ cm^{-1}	$R_1(K)$ cm^{-1}	$R_2(K)$ cm^{-1}
0			16856.55	16856.50
1	16855.90	16855.90	16856.89	16856.80
2	16855.63	16855.58	16857.25	16857.08
3	16855.38	16855.25	16857.61	16857.35
4	16855.12	16854.92	16857.95	16857.66
5	16854.84	16854.60	16858.30	16857.95
6	16854.62	16854.30	16858.69	16858.24
7	16854.36	16853.89	16859.05	16858.57
8	16854.10	16853.67	16859.42	16858.89
9	16853.86	16853.40	16859.81	16859.21
10	16853.60	16853.09	16860.20	16859.53
11	16853.42	16852.82	16860.60	16859.87
12	16853.18	16852.52	16860.98	16860.22
13	16852.96	16852.25	16861.38	16860.55
14	16852.72	16851.95	16861.80	16860.88
15	16852.53	16851.68	16862.19	16861.22
16	16852.33	16851.40	16862.61	16861.58
17	16852.14	16851.16	16863.02	16861.93
18	16851.93	16850.88	16863.45	16862.30
19	16851.72	16850.65	16863.88	16862.65
20	16851.52	16850.42	16864.30	16863.04
21	16851.33	16850.15	16864.72	16863.44
22	16851.18	16849.90	16865.17	16863.80
23	16851.00	16849.68	16865.62	16864.20
24	16850.82	16849.44	16866.08	16864.58

contd...

TABLE 28 (contd.)

K	$P_1(K)$ cm^{-1}	$P_2(K)$ cm^{-1}	$R_1(K)$ cm^{-1}	$R_2(K)$ cm^{-1}
25	16850.66	16849.23	16866.50	16864.95
26	16850.53	16849.00	16866.98	16865.36
27	16850.34	16848.79	16867.45	16865.76
28	16850.18	16848.58	16867.91	16866.18
29	16850.04	16848.36	16868.34	16866.57
30	16849.89	16848.15	16868.86	16866.99
31			16869.33	16867.42
32			16869.80	16867.85
33			16870.32	16868.25
34			16870.79	16868.69
35			16871.28	16869.13
36			16871.79	16869.58
37			16872.32	16870.02
38			16872.80	16870.45
39			16873.33	16870.94
40			16873.84	16871.39
41			16874.37	16871.84
42			16874.92	16872.32
43			16875.44	16872.78
44			16875.97	16872.29
45			16876.52	16873.74
46			16877.07	16874.26
47			16877.60	16874.72
48			16878.18	16875.23
49			16878.75	16875.71
50			16879.30	16876.24

contd...

TABLE 28 (contd.)

K	$P_1(K)$ cm^{-1}	$P_2(K)$ cm^{-1}	$R_1(K)$ cm^{-1}	$R_2(K)$ cm^{-1}
51			16879.85	16876.76
52			16880.45	16877.27
53			16881.02	16877.79
54			16881.62	16878.33
55			16882.22	16878.85
56			16882.80	16879.39
57			16883.41	16879.94
58			16884.03	16880.48
59			16884.64	16881.04
60			16884.24	16881.58

TABLE 29

Δ_2F VALUES FOR THE (0,0) BAND OF $B^2\Sigma — X^2\Sigma$ SYSTEM OF CaCl MOLECULE

K	$R_1(K)-P_1(K) = \Delta_2F'_1$ cm^{-1}	$R_1(K-1)-P_1(K+1) = \Delta_2F''_1$ cm^{-1}	$R_2(K)-P_2(K) = \Delta_2F'_2$ cm^{-1}	$R_2(K-1) -P_2(K+1) = \Delta_2F''_2$ cm^{-1}
1.5	0.99	0.92	0.90	0.92
2.5	1.62	1.51	1.50	1.55
3.5	2.23	2.13	2.10	2.16
4.5	2.83	2.77	2.74	2.75
5.5	3.46	3.33	3.35	3.36
6.5	4.07	3.94	3.94	4.06
7.5	4.69	4.59	4.68	4.57
8.5	5.32	5.19	5.22	5.17
9.5	5.95	5.82	5.81	5.80
10.5	6.60	6.39	6.44	6.39
11.5	7.18	7.02	7.05	7.01
12.5	7.80	7.64	7.70	7.62
13.5	8.42	8.26	8.30	8.27
14.5	9.08	8.85	8.93	8.87
15.5	9.66	9.47	9.54	9.48
16.5	10.28	10.05	10.18	10.06
17.5	10.88	10.68	10.77	10.70
18.5	11.52	11.30	11.42	11.28
19.5	12.16	11.93	12.00	11.88
20.5	12.78	12.55	12.62	12.50
21.5	13.39	13.12	13.29	13.14
22.5	13.99	13.72	13.90	13.76

contd...

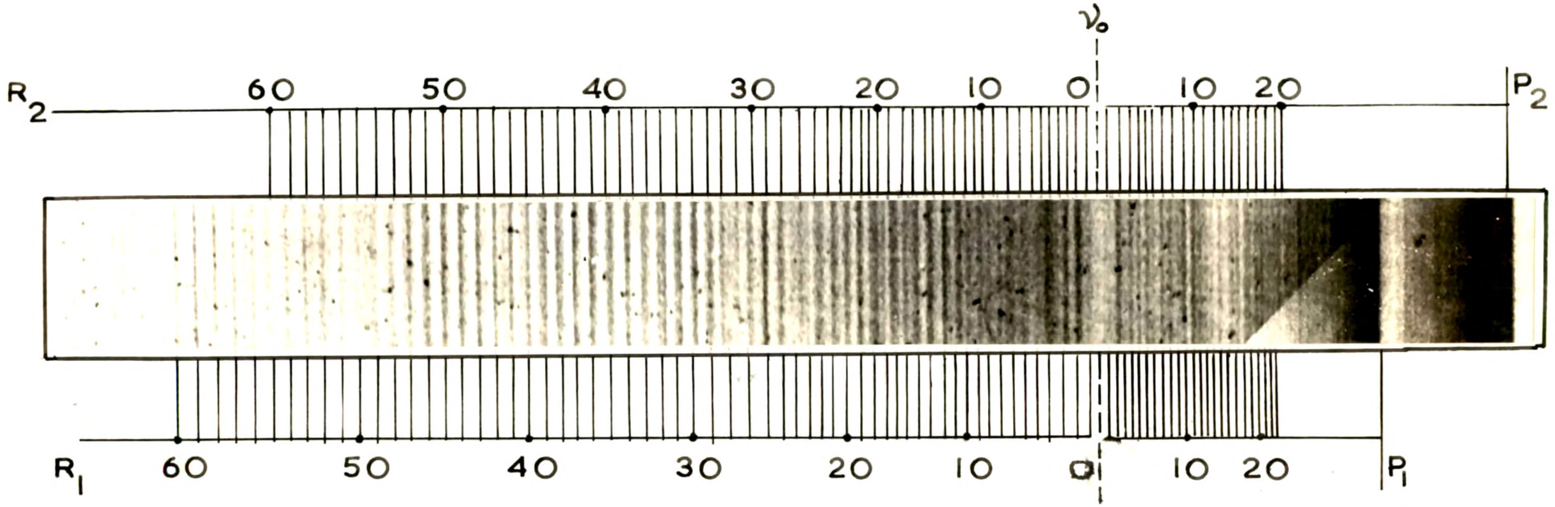

PLATE. 12.

ROTATIONAL STRUCTURE OF 0,0 BAND OF $B\,^2\Sigma — X\,^2\Sigma$ SYSTEM OF CaCl

TABLE 29 (contd.)

K	$R_1(K)-P_1(K)$ $= \Delta_2F'_1$ cm^{-1}	$R_1(K-1)-P_1(K+1)$ $= \Delta_2F''_1$ cm^{-1}	$R_2(K)-P_2(K)$ $= \Delta_2F'_2$ cm^{-1}	$R_2(K-1)$ $-P_2(K+1)$ $= \Delta_2F''_2$ cm^{-1}
23.5	14.62	14.35	14.52	14.36
24.5	15.26	14.96	15.14	14.97
25.5	15.84	15.55	15.72	15.58
26.5	16.45	16.16	16.36	16.16
27.5	17.11	16.80	16.97	16.78
28.5	17.73	17.87	17.60	17.40
29.5	18.30	18.02	18.21	18.03
30.5	18.97	-	18.84	

$$P_1(K) = \nu_0 + F''_1(K-1) - F''_1(K)$$

$$P_2(K) = \nu_0 + F''_2(K-1) - F''_2(K)$$

where $F_1(K) = B_v K(K+1) + \frac{1}{2}\gamma K$

and $F_2(K) = B_v K(K+1) - \frac{1}{2}\gamma(K+1)$

$F_1(K)$ and $F_2(K)$ refer to the components of rotational levels with $J = K+\frac{1}{2}$ and $J = K-\frac{1}{2}$ respectively and γ is the spin splitting constant.

$$\Delta\nu_{12}(R) = R_1 - R_2 = [\gamma' - \gamma''] K + \frac{1}{2}(3\gamma' - \gamma'')$$

Thus the splitting of the lines in the branches increases linearly with K.

A graph of $\Delta\nu_{12}(R)$ against K gives a straight line whose slope gives $(\gamma' - \gamma'')$ and intersept gives $\frac{1}{2}(3\gamma' - \gamma'')$

$$\Delta_2 F'_1(K) = 4B'_v\ (K+\tfrac{1}{2}) + \gamma'$$

$$\Delta_2 F''_1(K) = 4B''_v\ (K+\tfrac{1}{2}) + \gamma''$$

The slope of the graph of $\Delta_2 F_1(K)$ against $(K+\frac{1}{2})$ will give $4B_v$ and intercept gives $(2B_v+\gamma)$. These graphs are given in fig. 7 and fig. 8. Thus from the graphs one can find out the splitting constants γ and rotational constants

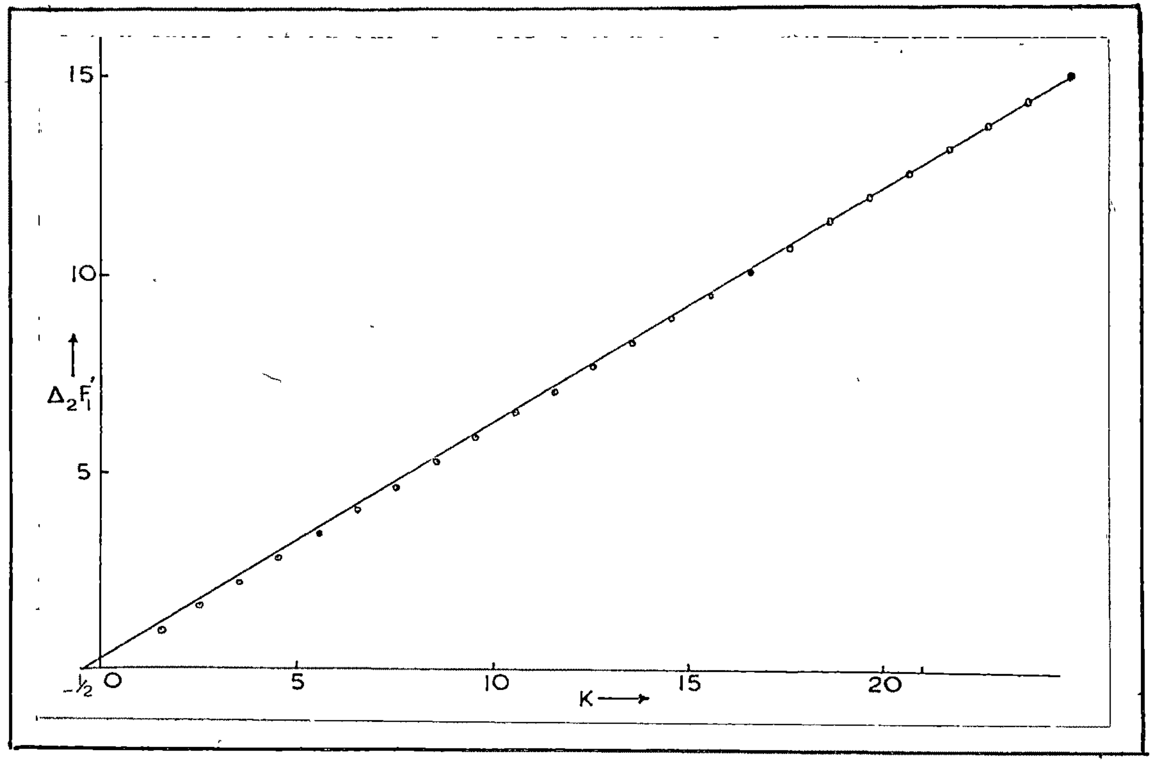

Fig. 7

Graph of rotational quantum no.K versus combination relations for $\Delta_2 F_1'(K)$

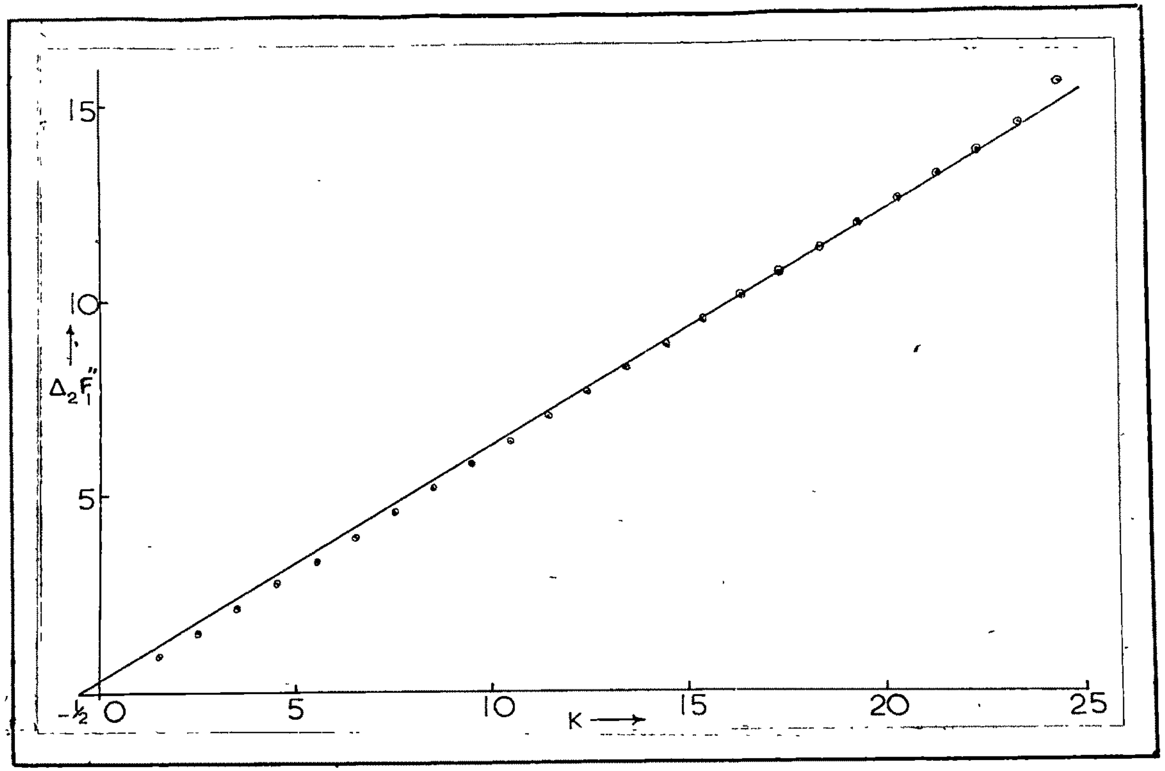

Fig. 8

Graph of rotational quantum no.K versus combination relations for $\Delta_2 F_1''(K)$

B_v for both the upper and lower states. Since the interacting $A^2\Pi$ level is lying well above the ground state we can believe that the spin splitting in the $X^2\Sigma$ state to be negligibly small.

The observed splitting can be represented by the equation

$$\Delta\nu_{12}(R) = \gamma'(K) + 3/2\, \gamma'.$$

The graph of $\Delta\nu_{12}(R)$ against K is given in fig. 9.

The rigidity constant D was calculated by the formula

$$D = 4B^3/\omega^2$$

The nature of the band is a typical one of a $^2\Sigma - {}^2\Sigma$ transition. The absence of rotational line at the origin confirms this. This result is in good agreement with the $B^2\Sigma$ level observed and established in analogous molecules of the same group. The spin splitting in the $B^2\Sigma$ level may be explained due to an interaction with the $A^2\Pi$ level which is lying very close to it. A calculation of the spin splitting constants in the B level assuming that the spin splitting is only due to the interaction of A level on B level was made using the

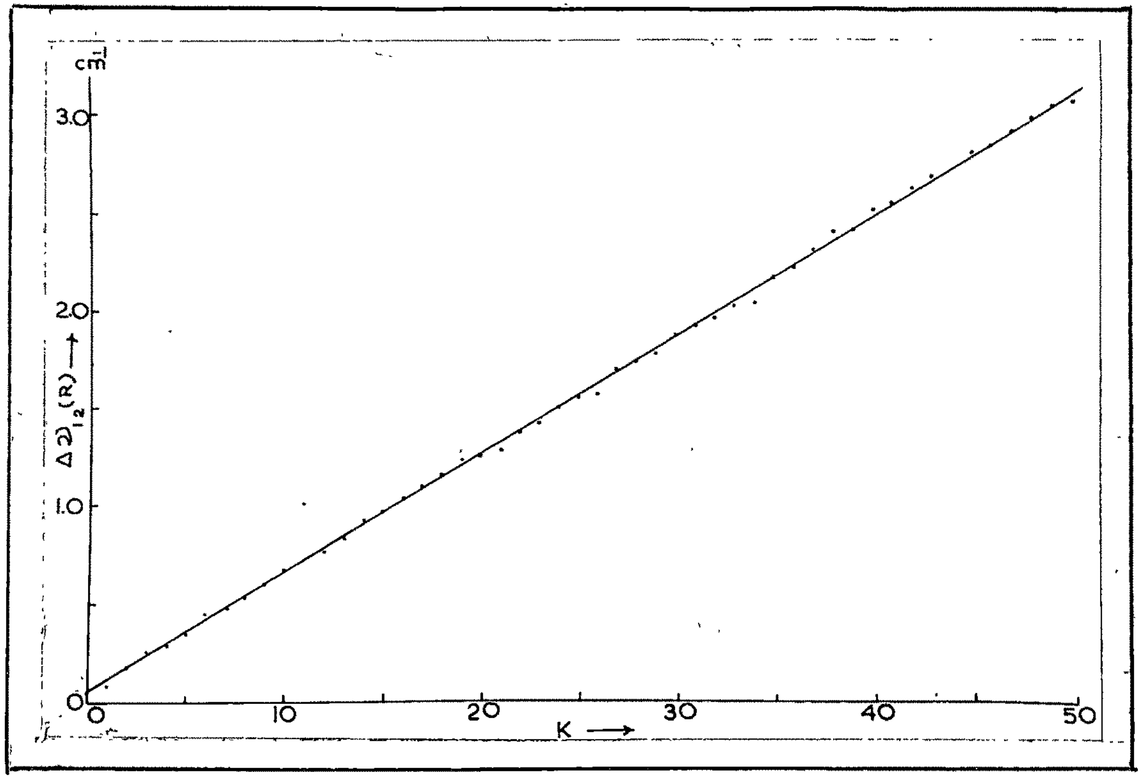

Fig. 9

Graph of rotational quantum no.K versus spin splitting of lines of R branch $\Delta\nu_{12}(R)$ due to spin effect equation:

$$\gamma = \frac{2A\ B_v\ \ell(\ell+1)}{\nu(\Pi, \Sigma)}$$

For CaCl the coupling constant $A = 71\ cm^{-1}$, $B = 0.1530\ cm^{-1}$, $\nu(\Pi, \Sigma) = 721.5\ cm^{-1}$ and $\ell = 1$, the γ value calculated using these values gives

$$\gamma = 0.0602\ cm^{-1}$$

which agrees nicely with the value obtained from the present rotational analysis (viz. 0.061 cm^{-1}).

Rotational constants obtained from the present analysis for $X^2\Sigma^+$ and $B^2\Sigma^+$ are given below:

	ν_e cm^{-1}	B_o cm^{-1}	$10^7 D_o$ cm^{-1}	Spin splitting constant γ cm^{-1}	Inter-nuclear distance r_o A°
$B^2\Sigma^+$	16856.24	0.1550	1.12	0.061	2.414
$X^2\Sigma^+$	0	0.1515	1.0	-	2.4405