

## The $B^2\Sigma-X^2\Sigma$ system of the CaF molecule

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**Abstract.** The spectrum of the  $B^2\Sigma-X^2\Sigma$  system of the CaF molecule has been photographed in the second order of a 10.6 m concave grating spectrograph with 0.33 Å/mm dispersion. The rotational structure of the (0, 0) and (1, 0) bands has been analysed and the precise molecular constants have been obtained. Using the constants so determined the band origins of a large number of bands with  $0 < v', v'' < 10$  have been calculated and used to obtain the accurate vibrational constants for  $B$  and  $X$  states and these are presented.

**Keywords.** Concave grating spectrograph; molecular constants; vibrational constants; spin splitting; microwave optical double resonance.

### 1. Introduction

The spectrum of CaF molecule has been a subject of extensive study by several workers (Fabry 1905; Datta 1921; Hulthen 1928; Johnson 1929; Harvey 1931; Mohanty and Upadhyaya 1967; Nanda and Mohanty 1970; Field *et al* 1975 and Nakagawa *et al* 1978). The  $B-X$  system of this molecule lying in the spectral region 5145–5450 Å was established to have a  $^2\Sigma-^2\Sigma$  electronic transition by Harvey (1931). The rotational structure in the (0, 0) band of the  $A-X$  and  $B-X$  system of this molecule was first analysed by Mohanty and Upadhyaya (1967). Recent studies on the  $A-X$  system of this molecule by Field *et al* (1975), using the laser fluorescence technique and by Nakagawa *et al* 1978 using the microwave optical double resonance technique show that the earlier studies by Mohanty and Upadhyaya (1967) on the rotational structure of this molecule are incorrect. The dye laser excitation study by Field *et al* (1975) has been modified by Nakagawa *et al* (1978) and we consider the microwave optical double resonance (MODR) study to be correct. Since the ground state rotational constants reported earlier by the analysis of  $B-X$  system are very different from the constants obtained in the MODR analysis, the rotational analysis of this system earlier reported also seems to be incorrect. This discrepancy prompted us to reinvestigate the  $B-X$  system of this molecule. In the present investigation we have analysed the rotational structure in the (0, 0) and (1, 0) bands of this system and details of this study are now reported.

### 2. Experimental

Pure sample of CaF<sub>2</sub> (BDH, 99.9%) was excited in a copper arc cavity running at

220 V d.c. and 2.5–5 amp current. The spectrum was photographed in the second order of a 10.6 m concave grating spectrograph with 0.33 Å/mm dispersion. Exposures of 30 min and 12 hr duration respectively were found sufficient to record the spectrum of the (0, 0) and the (1, 0) sequences with sufficient intensity. Iron lines were used as standard for measurement. The lines were measured on a Russian EZA-2 comparator with  $10^{-4}$  mm least count.

### 3. Results and discussion

#### 3.1. Description of the spectra

We could record the spectrum of the two sequences  $\Delta v=0$  and  $+1$  starting from 5291.5 Å and 5145.43 Å respectively on high resolution instrument. The bands belonging to both the sequence are red degraded and have double heads with large separation. Both the sequences give extensive bands and we could record upto (20, 20) and (20, 19) bands in  $\Delta v=0$  and  $\Delta v=+1$  sequences respectively. The transition of this system is established to be  ${}^2\Sigma^- \rightarrow {}^2\Sigma$  (Harvey 1931). The occurrence of double heads in a  ${}^2\Sigma^- \rightarrow {}^2\Sigma$  transition, so much separated, appears unusual. A comparison of the spectrum of this system of CaF with the  $B-X$  systems of MgF and BaF (Barrow *et al* 1967) and SrF (Movikov and Gurvich 1967) indicates that this large separation is a common feature of the  $B-X$  system of the molecules of this group, and is due to large spin splitting in the  $B^2\Sigma$  state. The two heads are formed by the  $R_1$  and  $R_2$  branches. The rotational structure of the bands in both the sequences overlap over the consecutive bands severely. Therefore the rotational structure of only the first member of each sequence (i.e. (0, 0) and (1, 0) bands) was found suitable for analysis. Only two series (i.e.  $R_1$  and  $R_2$ ), converging at  $R_1$  and  $R_2$  heads are present in the structure. In fact there should have been four branches  $R_1$ ,  $R_2$ ,  $P_1$  and  $P_2$  due to the presence of large spin splitting. The absence of  $P$  branch members in the structure leads to the conclusion that either the band origin is far away from the heads or the  $P$  branch members are very weak. The rotational structure in the (0, 0) band and the contact print of the (0, 0) sequence are given in figure 1, and the vacuum wave number and  $N$  assignments in the (0, 0) and (1, 0) bands are given in table 1.

#### 3.2. Rotational analysis

Since only two branches  $R_1$  and  $R_2$  are present in the structure and the  $P_1$  and  $P_2$  branch members are probably heavily overlapped by the rotational structure of the next sequence bands, rotational analysis by the usual procedure is difficult (Herzberg 1950). We have therefore used the following method to determine the molecular constants and  $N$  assignments.

Assuming that Hund's coupling case (b) holds good for both the  ${}^2\Sigma$  states, the  $R_1$  and  $R_2$  branches in a  ${}^2\Sigma^- \rightarrow {}^2\Sigma$  transition can be given as

$$\begin{aligned} \nu_{R_1}(N) = & \nu_0 + 2B'_v + \frac{1}{2}\gamma' - 4D'_v + (3B'_v - B''_v - 12D'_v + \frac{1}{2}(\gamma' - \gamma''))N \\ & + (B'_v - B''_v + D''_v - 13D'_v)N^2 - 2(3D'_v - D''_v)N^3 - (D'_v - D''_v)N^4 \quad (1) \end{aligned}$$

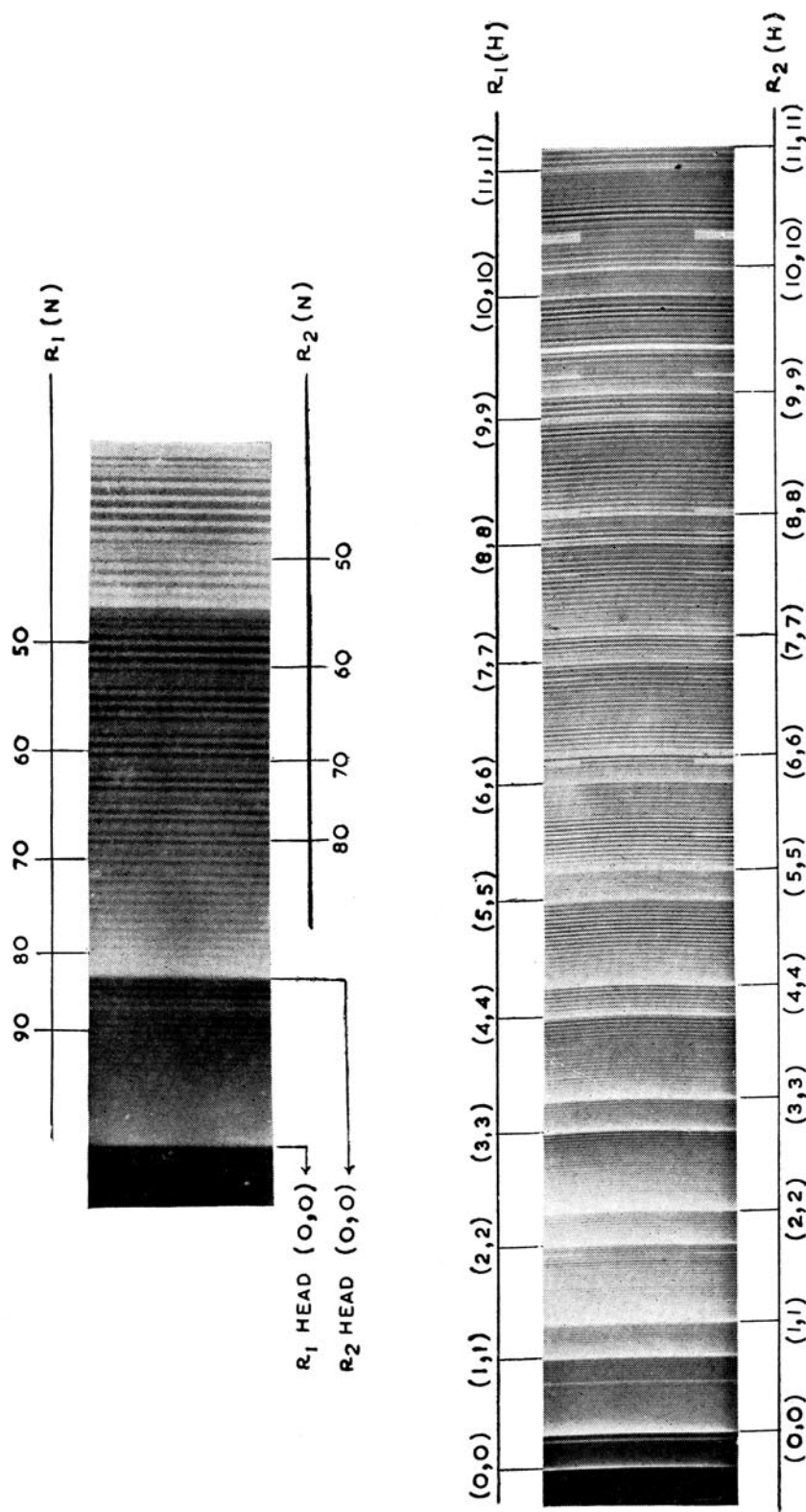


Figure 1. Rotational structure in  $(0, 0)$  band and the contact print of  $(0, 0)$  sequence of the  $B^2\Sigma-X^2\Sigma$  system of CaF molecule.

**Table 1 (a).** Vacuum wavenumber (in  $\text{cm}^{-1}$ ) and  $N$  assignments for (0, 0) band,  $\nu_{00} = 18844.19 \text{ cm}^{-1}$ .

$N$	$R_1(N)$		$R_2(N)$	
	$\nu_{\text{obs}}$	$\nu_{\text{calc}}$	$\nu_{\text{obs}}$	$\nu_{\text{calc}}$
47	—	—	18870.68	18870.73
48	—	—	71.19	71.18
49	—	—	71.65	71.61
50	—	—	71.98	72.04
51	—	—	72.44	72.48
52	—	—	72.95	72.90
53	18876.34	18876.33	73.29	73.32
54	76.87	76.80	73.79	73.74
55	77.23	77.26	74.08	74.14
56	77.76	77.72	74.49	74.55
57	78.22	78.18	74.90	74.95
58	78.64	78.62	75.31	75.34
59	79.11	79.01	75.72	75.73
60	79.48	79.51	76.12	76.12
61	79.95	79.94	76.46	76.50
62	80.39	80.37	76.86	76.86
63	80.77	80.80	77.19	77.24
64	81.25	81.22	77.60	77.60
65	81.67	81.63	77.99	77.96
66	82.02	82.04	78.34	78.32
67	82.48	82.44	78.64	78.66
68	82.82	82.84	79.00	79.01
69	83.23	83.23	79.38	79.36
70	83.62	83.62	79.70	79.68
71	84.04	84.00	80.04	80.01
72	84.38	84.38	80.35	80.32
73	84.75	84.75	80.65	80.64
74	85.11	85.12	80.98	80.96
75	85.52	85.48	81.28	81.26
76	85.85	85.84	81.58	81.56
77	86.20	86.19	81.88	81.86
78	86.55	86.53	82.10	82.15
79	86.85	86.87	82.47	82.43
80	87.21	87.21	82.71	82.71
81	87.55	87.53	82.96	82.98
82	87.86	87.86	83.24	83.25
83	88.16	88.17	83.58	83.53
84	88.49	88.49	83.70	83.77
85	88.89	88.79	84.03	84.01
86	89.09	89.09		
87	89.29	89.39		
88	89.66	89.67		
89	89.94	89.96		
90	90.22	90.24		
91	90.49	90.50		
92	90.74	90.77		
93	91.02	91.03		
94	91.27	91.28		
95	91.47	91.53		

**Table 1(b).** Vacuum wavenumber (in  $\text{cm}^{-1}$ ) and  $N$  assignments for (1, 0) band,  $\nu_{10}=19405.94 \text{ cm}^{-1}$ .

	$R_1(N)$		$R_2(N)$	
	$\nu_{\text{obs}}$	$\nu_{\text{calc}}$	$\nu_{\text{obs}}$	$\nu_{\text{calc}}$
7	—	—	19410.79	19410.79
8	—	—	11.40	11.35
9	—	—	11.93	11.92
10	—	—	12.50	12.47
11	—	—	13.01	13.01
12	—	—	13.51	13.55
13	—	—	14.10	14.08
14	19415.55	19415.50	14.55	14.60
15	16.03	16.06	15.07	15.11
16	16.69	16.62	15.58	15.61
17	17.15	17.16	16.08	16.09
18	17.73	17.69	16.58	16.57
19	18.26	18.22	17.06	17.04
20	18.75	18.73	17.45	17.50
21	19.20	19.24	17.92	17.96
22	19.80	19.74	18.35	18.40
23	20.20	20.22	18.86	18.83
24	20.76	20.70	19.35	19.25
25	21.20	21.17	—	19.67
26	21.58	21.63	20.08	20.07
27	22.08	22.08	20.53	20.46
28	22.54	22.52	20.88	20.85
29	23.00	22.95	21.23	21.22
30	23.37	23.37	21.58	21.59
31	23.76	23.77	21.98	21.94
32	24.15	24.18	22.30	22.29
33	24.58	24.57	22.65	22.62
34	24.92	24.95	23.00	22.95
35	25.30	25.32	23.30	23.27
36	25.69	25.68		

$$\nu_{R_2}(N) = \nu_0 + 2B'_v(\gamma' - \frac{1}{2}\gamma'') - 4D'_v + (3B'_v - B''_v - 12D'_v - \frac{1}{2}(\gamma' - \gamma''))N + (B'_v - B''_v + D''_v - 13D'_v)N^2 - 2(3D'_v - D''_v)N^3 - (D'_v - D''_v)N^4. \quad (2)$$

Due to the presence of large spin splitting in the excited state and the large  $N$  value at the head, the terms containing  $N^3$  and  $N^4$  and also the spin-splitting constant  $\gamma$  cannot be neglected. These equations can be treated as polynomials of fourth degree of the type,

$$\nu(N) = a + bN + cN^2 + dN^3 + fN^4. \quad (3)$$

In order to achieve the correct  $N$  numbering and to determine the constants  $a$ ,  $b$ ,  $c$ ,  $d$  and  $f$  in the above equation the least squares method was used and the  $N$  values

were adjusted in such a way that the constant term  $a$  in the above equation becomes approximately equal for both the branches. The polynomials thus obtained for  $R_1$  and  $R_2$  branches in the (0, 0) and (1, 0) bands are:

$$\nu_{R_1}(N) = 18844.90 + 0.706506 N - 0.002022 N^2 - 0.1848 \times 10^{-5} N^3 - 0.8 \times 10^{-8} N^4, \quad (4)$$

$$\nu_{R_2}(N) = 18844.82 + 0.651306 N - 0.002022 N^2 - 0.1848 \times 10^{-5} N^3 - 0.8 \times 10^{-8} N^4, \quad (5)$$

and  $\nu_{R_1}(N) = 19406.63 + 0.698588 N - 0.004628 N^2 - 0.1848 \times 10^{-5} N^3 - 0.8 \times 10^{-8} N^4, \quad (6)$

$$\nu_{R_2}(N) = 19406.50 + 0.643588 N - 0.004628 N^2 - 0.1848 \times 10^{-5} N^3 - 0.8 \times 10^{-8} N^4, \quad (7)$$

respectively. Since the molecular constants for the ground state are known from the MODR analysis (Nakagawa *et al* 1978), from the coefficients of  $N$ ,  $N^2$ ,  $N^3$  and  $N^4$  the molecular constants for the excited state (i.e.  $B'_v$ ,  $D'_v$  and  $\gamma'$ ) could be determined. The spin-splitting constant  $\gamma'$  was also estimated using the relation:

$$R_1(N) - R_2(N) = \Delta \nu_{1,2}(N) = (\gamma' - \gamma'') N + \frac{1}{2} (3\gamma' - \gamma''). \quad (8)$$

A plot of  $\Delta \nu_{1,2}(N)$  versus  $N$  is a straight line whose slope gives  $(\gamma' - \gamma'')$ . Since the value of  $\gamma''$  is very small ( $0.001 \text{ cm}^{-1}$ , Nakagawa *et al* 1978) the value of  $\gamma'$  can easily be determined and it comes out to be  $\gamma' = 0.056 \text{ cm}^{-1}$ . This value is found to be in close agreement with the value obtained in the least square procedure.

The origins of the other bands with  $v'$ ,  $v'' > 0$  were obtained by the head origin separation formula since the molecular constants  $B'_e$ ,  $\alpha'_e$ ,  $\gamma'$ ,  $B''_e$ ,  $\alpha''_e$  and  $\gamma''$  are known. These values were fitted in the Deslandres scheme and the precise vibrational constants were obtained. The molecular constants thus determined are given in table 2.

### 3.3. Electron configuration

According to molecular orbital theory the ground state of CaF molecule can be given as

$$(z\sigma)^2 (\omega\pi)^4 (y\sigma) \dots X^2 \Sigma^+ \quad (9)$$

and the first and the second excited state i.e.  $A$  and  $B$  states may be correlated to the electronic configurations

$$(z\sigma)^2 (\omega\pi)^4 (np\pi) \dots A^2 \pi_r, \quad (10)$$

$$(z\sigma)^2 (\omega\pi)^4 (np\sigma) \dots B^2 \Sigma, \quad (11)$$

Table 2. Molecular constants (in  $\text{cm}^{-1}$ ) for  $B^2\Sigma$  and  $X^2\Sigma$  states of CaF molecule.

Constant	Present	Mohanty and Upadhyia 1967
—	$B_0'$	0.340464
—	$B_1'$	0.337858
—	$B_e'$	0.341767
$B^2\Sigma$	$\alpha_e'$	0.002606
—	$D_e'$	$4.58 \times 10^{-7}$
—	$\gamma'$	0.056
—	$\omega_e'$	567.54
—	$\omega_e' x_e'$	2.897
—	$B_0''$	0.342486(a)
$X^2\Sigma$	$D_e''$	$4.5 \times 10^{-7}$ (a)
—	$\gamma''$	0.001(a)
—	$\omega_e''$	586.33
—	$\omega_e'' x_e''$	2.81

(a) These constants are the same as obtained from the MODR analysis of the  $A-X$  system by Nakagawa *et al* (1978).

respectively. In both these configurations an electron goes from a non-bonding orbital ( $\gamma\sigma$ ) to a non-bonding orbital ( $np\pi$ ) or ( $np\sigma$ ) resulting in a minor change in  $\omega_e$  values [ $X^2\Sigma$  ( $\omega_e=586.33 \text{ cm}^{-1}$ ),  $B^2\Sigma$  ( $\omega_e=567.54 \text{ cm}^{-1}$ ) and  $A^2\pi$  ( $\omega_e=592.7 \text{ cm}^{-1}$ )]. The two states arising from  $np\sigma$  and  $np\pi$  configurations lie very close to each other; therefore a case of pure precession is expected to occur. Under such a condition the spin-splitting constant in the  $B^2\Sigma$  state must be approximately equal to the  $\Lambda$ -doubling constant in the  $A^2\pi$  state. In fact the value of the  $\Lambda$ -doubling constant for the  $A^2\pi$  state is  $0.0438 \text{ cm}^{-1}$  (Nakagawa *et al* 1978) which is in good agreement with the spin-splitting constant  $\gamma$  for  $B^2\Sigma$  state ( $0.056 \text{ cm}^{-1}$ ).

#### 4. Conclusion

Mohanty and Upadhyia (1967) analysed the structure of only (0, 0) band of this system. They have completely neglected the last two terms in equation (3) containing the  $D_v'$  and  $D_v''$  in their analysis which becomes much appreciable near the head (because of the large  $N$  value at the head). This leads to an inaccuracy in their  $N$  numbering and the rotational constants. The constants obtained by them have been compared with the constants obtained in our study and are given in table 2. We have also calculated the  $\alpha_e'$  value using the relation

$$R(1, 0) - R(0, 0) = \Delta G' (1/2) - \alpha_e' N(N+1) \quad (12)$$

The slope of the plot of  $R(1, 0) - R(0, 0)$  versus  $N(N+1)$  gives  $\alpha_e'$  value whereas the intercept on  $y$  axis gives  $\Delta G' (1/2)$ . The  $\alpha_e'$  and  $\Delta G' (1/2)$  values thus determined are found to be in excellent agreement with the  $\alpha_e'$  (i.e.  $B_0' - B_1'$ ) and  $\Delta G'$

(1/2) (i.e.  $\nu_{10} - \nu_{00}$ ) values obtained by rotational analysis. Our analysis shows that the origin in (0, 0) and (1, 0) bands lies near (2, 2) and (2, 1) bands respectively. Harvey (1931) in his absorption experiment had also detected that the origin of the (0, 0) band lies somewhere after (2, 2) band. Therefore the  $P$  branch members of (0, 0) and (1, 0) bands which lie beyond the origin are heavily overlapped by the  $R_1$  and  $R_2$  branch members of (1, 1), (2, 2) or (2, 1) bands respectively and could not be marked.

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