

Emission spectra of E—X and F—X systems of CaF

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PLATE 2

Bands of  $E^2\Sigma - X^2\Sigma$  and  $F^2\Pi - X^2\Sigma$  system of CaF lying in the region 3000-2600 Å have been observed for the first time in emission at a dispersion of about 12 Å/mm at 2800 Å, using the flame of C-arc fed with CaF<sub>2</sub> suitably mixed with Na<sub>2</sub>CO<sub>3</sub> and operated at 220 V D. C. mains and 5 to 6 amp. current. In all, 12 bands of  $\Delta V=0, +1$  and  $+2$  sequences of E-X and 10 bands of  $\Delta V = -1, 0$  and  $+1$  sequences of F-X systems have been observed. Most of these bands were reported earlier in absorption. New vibrational constants for both E-X and F-X systems have been obtained and the reported mean vibrational constants of the ground state of the molecule have been accordingly modified. Transitions for both E-X and F-X systems reported in absorption have been supported and we feel that in E-X system, there is predominance of P<sub>2</sub>-heads in emission compared to the P<sub>1</sub>-heads reported in absorption. Predominance of P-heads both in emission and absorption, reasonably indicates that the reported F<sup>2</sup>Π state cannot belong strictly to Hund case (b). Comparing the observed bands in emission with those reported in absorption, an attempt has been made to give the qualitative estimate of the rotational constants for both E-X and F-X systems.

INTRODUCTION

Six band systems of CaF arising due to the transitions from the excited  $A^2\Pi$ ,  $B^2\Sigma$ ,  $C^2\Pi$ ,  $D^2\Sigma$ ,  $E^2\Sigma$  and  $F^2\Pi$  states to the ground  $X^2\Sigma$  state in each case, are known and no intercombination system has been reported to this date. The systems A-X and B-X are known both in emission (Datta, 1921) and absorption (Walters & Barrett 1928; Fowler 1941) and have also been studied in details by different investigators (Johnson 1929; Harvey 1931; Mohanty & Upadhyaya 1967). The system C-X which was first reported by Datta (1921) in emission and reinvestigated by Johnson (1929) has been extended by Fowler (1941) in absorption. The systems D-X, E-X and F-X were reported by Fowler (1941) in absorption at a furnace-temperature of about 2000°C and the vibrational analysis of them was also carried out by him, but no further work on these systems has ever been reported.

In the present investigation, the bands of E-X and F-X systems reported in absorption by Fowler (1941) have been observed for the first time in emission, using the technique similar to that employed by Datta (1921) with some modifications.

## EXPERIMENTAL

The usual C-arc with electrodes in vertical position was employed at 220 V, D. C. mains and 5 to 6 amp. current. The arc was fed with  $\text{CaF}_2$  mixed with  $\text{Na}_2\text{CO}_3$ . The addition of  $\text{Na}_2\text{CO}_3$  was found suitable for increasing the separation between the electrodes in order to have the wider flame of the arc purposely required and also to reduce the possibility of occurrence of unwanted atomic lines. But it was necessary to mix  $\text{Na}_2\text{CO}_3$  with  $\text{CaF}_2$  in such a proportion that the flame formed in the gap of widely separated electrodes, was sufficiently rich in greenish colour for, with the flame of such colour the bands under investigation could be satisfactorily observed. The image of this flame was allowed to fall on the slit of a spectrograph through a suitable quartz-lens and its spectrum was photographed on a Hilger-Medium-Quartz-Spectrograph. The bands of  $E-X$  and  $F-X$  systems appeared in the region 3000-2600 Å at a dispersion of about 12 Å/mm at 2800 Å. An exposure of about 8 minutes on Ilford N-30 plate was found suitable for the purpose. Iron-arc lines were used as standard.

## RESULTS

The enlarged reprint (plate 2) shows the observed emission bands with their vibrational assignments for both  $E-X$  and  $F-X$  systems. Table 1 gives the Deslandres scheme for the observed emission bands of  $E-X$  system while table 2 shows that for  $F-X$  system. Table 3 contains the new vibrational constants for both  $E-X$  and  $F-X$  systems obtained by us and for the sake of comparison, the constants reported by Fowler (1941) in absorption, are also given in it. This table further includes the reported (Herzberg 1950) mean vibrational constants of the ground state of the molecule, which have been modified by us in the light of new constants for the common lower state of  $E-X$  and  $F-X$  systems. These modified constants of the ground state, similar to those reported by Herzberg (1950), also represent the average of the constants (Johnson 1929, Harvey 1931, Herzberg 1950) of the lower states of all the known systems except those of the  $B-X$  system. The constants of the lower state of the  $B-X$  system have been excluded for the same reasons as suggested by Herzberg (1950). Table 4 gives the details of our measurements for the observed emission bands of both  $E-X$  and  $F-X$  systems including the eye-estimate of their relative intensities in the scale of 10 for each of the two systems. The wavenumbers calculated from the newly derived (table 3) and the reported (Fowler 1941) constants (since the latter values are not mentioned in the published paper (Fowler 1941) are also given in this table and the agreements of the observed emission bands both with respect to the newly derived (table 3) and the reported (Fowler 1941) constants, are, for the sake of comparison, included

in it. Table 5 shows the comparative agreements of the modified (table 3) and the reported (Herzberg 1950) mean vibrational constants of the ground state of the molecule with respect to the (0,0) bands of the different known systems and for the reasons stated above, the B-X system has been excluded. For calculating the wavenumbers of the (0,0) bands of the different systems (table 5), the corresponding constants of the upper state of the respective system reported by Herzberg (1950), have been used.

TABLE 1. (E-X SYSTEM OF CaF)

$v'$	$v''$	0	1	2	3	4	
0		34165.2	—				
		639.9					$\Delta G_{v'+\frac{1}{2}}$ 639.9
1		34805.1	583.8	34221.3			$2W_e'X_e'$ 7.2
		632.9		632.4			632.7
2		35438.0	584.3	34853.7	—		6.4
				628.3			628.3
3			35482.0	577.2	34904.8	—	6.9
				621.4			621.4
4				35526.2	571.4	34954.8	—
					615.6		615.6
5					35570.4	563.0	35007.4
						608.6	608.6
6						35616.0	
		$\Delta G_{v'+\frac{1}{2}}$	584.1	577.2	571.4	563.0	
		$2W_e''X_e''$		6.9	5.8	8.4	

TABLE 2. (F-X SYSTEM OF CaF)

$v'$	$v''$	0	1	2	3	
0		37597.0	581.9	37015.1		
		675.0		674.0		$\Delta G_{v'+\frac{1}{2}}$ 674.5
1		38272.0	582.9	37689.1	573.7	37114.0
				668.0	667.7	
						$2W_e'X_e'$ 6.6
2			38357.1	575.4	37781.7	569.6
					37212.1	
				659.5	658.3	658.9
3				38441.2	570.8	37870.4
		$\Delta G_{v'+\frac{1}{2}}$	582.4	574.6	570.2	
		$2W_e''X_e''$		7.8	4.4	

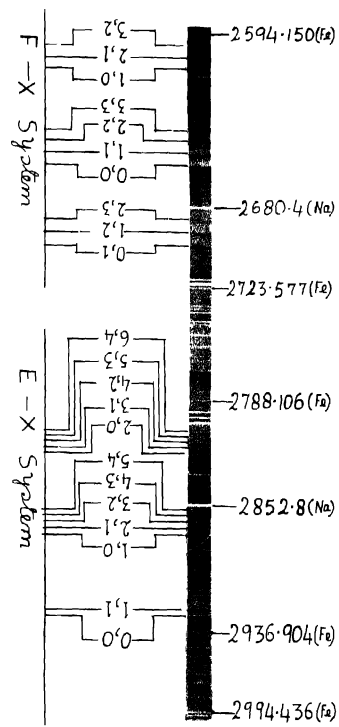
TABLE 3. COMPARISON OF NEWLY DERIVED AND REPORTED CONSTANT OF CAF

System	New constants (Present Authors) cm <sup>-1</sup>	Reported constants (Fowler 1941) cm <sup>-1</sup>	N-R cm <sup>-1</sup>
E-X	$W_e'$ = 645.52	$W_e'$ = 646.3	-0.78
	$W_e'X_e'$ = 3.12	$W_e'X_e'$ = 3.24	-0.12
	$W_e''$ = 587.86	$W_e''$ = 587.8	+0.06
	$W_e''X_e''$ = 2.94	$W_e''X_e''$ = 2.90	+0.04
	$T_e$ = 34136.2	$T_e$ = 34135.2	+1.00
E-X	$W_e'$ = 682.2	$W_e'$ = 681.7	+0.50
	$W_e'X_e'$ = 3.68	$W_e'X_e'$ = 3.55	+0.13
	$W_e''$ = 587.86	$W_e''$ = 586.9	+0.96
	$W_e''X_e''$ = 2.94	$W_e''X_e''$ = 2.82	+0.11
	$T_e$ = 37549.7	$T_e$ = 37547.9	+1.80
	Modified (Present Authors)	Herzberg (1950)	Mo-R
Mean constants of ground state.	$W_e'$ = 587.3	$W_e'$ = 587.1	+0.2
	$W_e'X_e'$ = 2.77	$W_e'X_e'$ = 2.74	+0.03

Note :—The letters N, R and Mo stand respectively for the words : New, Reported and Modified.

## DISCUSSION

It can be seen from tables 1 and 2 that the observed bands in emission are represented quite satisfactorily in separate Deslandres schemes. The new vibrational constants (table 3) derived from these tables (1 & 2) and which have been modified in order to get the best fit to represent (table 4) the observed emission bands for the two systems, agree (table 3) fairly with those reported for E-X and F-X systems by Fowler (1941) in absorption. Moreover, the nature of the observed emission bands of both the systems, particularly with regard to their degradation to shorter wavelengths (plate 2), is quite similar to those of E-X and F-X system



Emission spectrum of CaF



of Fowler (1941). These facts taken together conclusively confirm that the observed emission bands of table 1 belong to the E-X system and those of table 2 belong to the F-X system of CaF.

TABLE 4 DETAILS OF THE MEASUREMENT OF E-X AND F-X SYSTEM OF CaF

System	V', V''	Bands observed in emission			ν-calculated with (cm <sup>-1</sup> )		ν <sub>0</sub> -ν <sub>0</sub> with (cm <sup>-1</sup> )	
		λ <sub>air</sub> Å	Int.	ν <sub>0</sub> cm <sup>-1</sup>	New const's (Pr. Auth.)	Reported const's (Fowler) 1941	New const's (Pr. Auth.)	Reported const's (Fowler) 1941
E X	0,0	2926.1	10	34165.2	34165.0	34164.6	+0.2	+0.8
	1,1	2921.3	3	34221.0	34222.0	34222.2	-1.0	-0.9
	1,0	2872.3	6	34805.1	34804.3	34804.2	+0.8	+0.9
	2,1	2868.3	7	34853.7	34854.3	34855.5	-0.6	-1.8
	3,2	2864.1	8	34904.8	34906.0	34906.2	-1.2	-1.4
	4,3	2860.0	5	34954.8	34956.4	34956.2	-1.6	-1.4
	5,4	2855.7	2	35007.4	35006.3	35005.5	+1.1	+1.9
	2,0	2821.0	5	35438.0	35437.3	35437.5	+0.7	+0.5
	3,1	2817.5	7	35482.0	35482.1	35482.4	-0.1	-0.4
	4,2	2814.0	7	35526.2	35526.6	35526.6	-0.4	-0.4
5,3	2810.4	5	35570.4	35570.7	35570.1	-0.3	+0.3	
6,4	2806.9	3	35616.0	35614.4	35612.9	+1.6	+3.1	
F X	0,1	2700.8	5	37015.1	37014.7	37013.9	+0.4	+1.2
	1,2	2693.6	6	37114.0	37113.4	37112.8	+0.6	+1.2
	2,3	2686.5	3	37212.1	37210.7	37210.4	+1.4	+1.7
	0,0	2659.0	10	37597.0	37596.7	37595.1	+0.3	+1.9
	1,1	2652.5	7	37689.1	37689.5	37688.5	-0.4	+0.6
	2,2	2646.0	3	37781.7	37780.9	37780.4	+0.8	+1.3
	3,3	2639.0	1	37870.4	37870.8	37870.8	-0.4	-0.4
	1,0	2612.1	5	38272.0	38271.5	38269.7	+0.5	+2.3
	2,1	2606.3	5	38357.1	38357.0	38356.0	+0.1	+1.1
	3,2	2600.6	2	38441.2	38441.0	38440.7	+0.2	+0.5

TABLE 5 COMPARATIVE AGREEMENT OF MODIFIED AND REPORTED MEAN CONSTANT OF GROUND STATE OF CAF

System	$V', V''$	$\nu$ -reported cm <sup>-1</sup>	$\nu$ -calculated with (cm <sup>-1</sup> )		$\nu_0 - \nu_c$ with (cm <sup>-1</sup> )		Remarks
			R.M.G.S.C.	Mo. M.G.S.C.	R-M G.S.C.	Mo. M.G.S.C.	
A-X	0,0 (Q <sub>1a</sub> )	16485.1 (3)	16484.4	16484.3	+0.7	-0.8	
	0,0 (Q <sub>2</sub> )	16560.2 (3)	16560.3	16560.2	-0.1	0.0	
C-X	0,0 (Q <sub>1</sub> )	30202.8 (5)	30203.4	30203.3	-0.6	-0.5	
D-X	0,0	30803.9 (5)	30804.1	30804.0	-0.2	-0.1	
	0,0	34164.4 (5)	34164.7	34164.6	-0.3	-0.2	With R.U.S.C.
E-X	0,0	34165.2 (A)	34165.3	34165.2	-0.1	0.0	With N.U.S.C.
	0,0	37595.1 (5)	37595.0	37594.9	+0.1	+0.2	With R.U.S.C.
F-X	0,0	37597.0 (A)	37597.1	37597.0	-0.1	0.0	With N.U.S.C.

Note :—The letters A, R, M, Mo, G, U, S and C stand respectively for the words :  
Authors, Reported, Mead, Modified, New, Ground, Upper, State and Constants.

Table 3 shows that the new constants for the common lower state of *E-X* and *F-X* systems, unlike those reported by Fowler (1941) in absorption, are just the same as theoretically expected.

For *E-X* system the observed bands in emission are found to be of single-headed nature (plate 2) and support the reported view (Fowler 1941) that the system belongs to the  $E^2\Sigma-X^2\Sigma$  transitions. The relative intensity-distribution of the observed bands in emission is approximately the same as that reported (Fowler 1941) in absorption. Moreover, particularly in the region of this system, there are a number of unaccounted bands and band-like features (plate 2) and are most likely those unclassified bands of Fowler (measurements not given by him) which were found by him also to lie in the region of *E-X* system.

For *F-X* system reported to belong to a  $^3\Pi-^2\Sigma$  transition, it can be seen (table 4) that the agreement of the observed heads in emission with new constants (table 3) compared to the constants reported by Fowler (1941) in absorption is not of the same order as found in the case of *E-X* system indicating that the observed heads in emission and those reported in absorption may not be just the same. The values of  $\nu_0 - \nu_c$  with the constants of Fowler (1941) (reported by him for  $P_1$  - heads), for all the heads



observed in emission except that for the weakest (3,3) band, are positive and it appears that the heads observed in emission are shifted, in general, slightly to the higher wave number (shorter  $\lambda$ ) side of the corresponding  $P_1$ -heads reported (Fowler 1941) in absorption. We consequently, feel that there is predominance of  $P_2$ -heads in emission compared to the  $P_1$ -heads reported (Fowler 1941) in absorption, for, comparing the observed value ( $\nu_e=37597.0 \text{ cm}^{-1}$ ) for the (0,0) band with that ( $\nu_e = 37595.1 \text{ cm}^{-1}$ ) reported (1941) in absorption, the  $\nu_e - \nu_r = 1.9 \text{ cm}^{-1}$  also agrees with the separation ( $\approx 2.0 \text{ cm}^{-1}$ ) estimated by Fowler (1941) in absorption between  $P_1$ -and  $P_2$ -heads for the same (0,0) band. The  $Q_3$ -heads indicated by Fowler (1941) in absorption (measurements not given by him) whose separation in the case of (0,0) band from  $P_1$ -head has been estimated by him of the order of  $11.7 \text{ cm}^{-1}$  are, however, not observed in emission. Predominance of  $P$ -heads observed in emission in the present case and also reported earlier in absorption by Fowler (1941), quite reasonably show that the reported (1941)  $F^2II$  state cannot belong strictly to the Hund case (b), for, in that case  $Q$ -heads should be the strongest (Herzberg (1950), page 257) and like the most cases (Herzberg (1950), page 261), the  $F^2II$  state appears to belong to a case intermediate between (a) and (b). Moreover, the relative intensity-distribution of bands observed in emission is nearly the same as that reported (Fowler 1941) in absorption.

A further comparison of the observed bands in emission with those reported (Fowler 1941) in absorption for both E-X and F-X systems, shows that the (0,0) band (plate 2) of each of the two systems is the strongest member of the system, indicating quite reasonably that  $r_e$ -values and consequently the  $B_e$ -values of the upper and lower states for both E-X and F-X systems, are not very unequal. Using to relation (Herzberg (1950) page 179),

$$B_e = B_v + \alpha_e (V + \frac{1}{2}) + \dots\dots\dots,$$

we get for the (0,0) band,

$$B_e' = B_v' + \frac{1}{2}\alpha_e'$$

and

$$B_e'' = B_v'' + \frac{1}{2}\alpha_e''$$

Hence,  $B_e' + \frac{1}{2}\alpha_e' \approx B_e'' + \frac{1}{2}\alpha_e''$  for  $B_e' \approx B_e''$ .

Since for both systems bands are degraded to shorter wavelengths,  $B_e' > B_e''$  and the above relation clearly indicates that  $\alpha_e'$  of each of E-X and F-X systems must be less than  $\alpha_e''$ . We thus get the qualitative estimate of the rotational constants for both E-X and F-X systems. However, a rotational analysis is essential for the confirmation of the conclusions arrived at.

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