CHAPTER II

HISTORICAL SURVEY

Spectroscopic studies of the halides of calcium, strontium and barium are extensively carried out by several workers. C.M. Olmsted (1906); S. Datta (1921); O.H. Walters and Barhatt (1928); R.C. Johnson (1929); A. Harvey, K. Hedfeld, A.E. Parker and R.K. Asundi (1935); C.A. Fower, R.E. Harrington (1942); M. Schutte (1954); E. Morgan and R.F. Barrow (1960); B.S. Mahanti and K.N. Upadhya (1967); G.V. Kovalenok and Sokolov (1969); P.S. Murty, Y.P. Reddy, P.T. Rao, M.M. Shukla, M.M. Patel, N.R. Shah (1970); L.K. Khanna, V.S. Dubey, A.B. Darji, S.P. Vadiya, Ashrafunnisa, Rao (1973); M.N.Kamalasanan(1974)

A brief review of the work reported so far on the spectra of halides of calcium is given here. Along with it a brief survey on the work done on iodides of barium and strontium is also included.

(1) CALCIUM FLUORIDE

The band spectrum of calcium fluoride was studied systematically for the first time by S. Datta (1921). He photographed two groups of bands in the ultraviolet region and five groups of bands in the visible region. The groups A_1, A_2, A_3 and A_4 in the visible region are similar in structure having degradation towards red and consist of double headed bands. The bands in the groups B_1 and B_2 fade off towards violet. The bands in the group C_1 have violet degradation. He attempted to form homologous series of different alkaline earth fluorides and to connect them by empirical relations using the constants of series equation and molecular weights of respective compounds. Later in the year 1929, R.C. Johnson reported a number of sequencies in the spectra of CaF and SrF which exhibited the phenomenon of 'a tail'. This occurs when the convergence of the sequence is sufficiently rapid and intensity of higher members is appreciable.

A. Harvey (1931) carried out the rotational analysis of CaF bands in the visible region (λλ 5291 to 5152 A°) and assigned them to a transition of the type $^2\Pi - {}^2\Sigma$

C.A. Fowler (1941) carried out careful vibrational analysis of a number of systems of this molecule in ultraviolet as well as visible region and reported number of new excited states viz. C, D, E and F. The electronic transitions assigned by him are respectively $^2\Pi - X^2\Sigma$, $^2\Sigma - X^2\Sigma$, $^2\Sigma - X^2\Sigma$ and $^2\Pi - X^2\Sigma$. The quantum equations reported by him for these systems are:

$C^2\Pi$ — $X^2\Sigma$ (Q_1)

$$\nu = 30255.9 + 481.7(v'+\tfrac{1}{2}) - 2.02(v'+\tfrac{1}{2})^2$$
$$- 588.2(v''+\tfrac{1}{2}) + 2.75(v''+\tfrac{1}{2})^2$$

$D^2\Sigma$ —— $X^2\Sigma$

$$\nu = 30772.3 + 650.7(v'+\tfrac{1}{2}) - 2.89(v'+\tfrac{1}{2})^2$$
$$- 587.5(v''+\tfrac{1}{2}) + 2.85(v''+\tfrac{1}{2})^2$$

$E^2\Sigma$ —— $X^2\Sigma$

$$\nu = 34135.2 + 646.3(v'+\tfrac{1}{2}) - 3.24(v'+\tfrac{1}{2})^2$$
$$- 587.8(v''+\tfrac{1}{2}) + 2.90(v''+\tfrac{1}{2})^2$$

$F^2\Pi$ — $X^2\Sigma(P_1)$

$$\nu = 37547.9 + 681.7(v'+\tfrac{1}{2}) - 3.55(v'+\tfrac{1}{2})^2$$
$$- 586.9(v''+\tfrac{1}{2}) + 2.82(v''+\tfrac{1}{2})^2$$

Mahanti and Upadhya in 1967 obtained molecular constants from the rotational analysis of (0,0) bands of $A^2\Pi$ — $X^2\Sigma$ and $B^2\Sigma$ — $X^2\Sigma$ systems. Values of rotational constants corresponding to the two systems reported by them are given below:

	$A^2\Pi$ — $X^2\Sigma$		$B^2\Sigma$ — $X^2\Sigma$
	$^2\Pi_{1/2}$ — $^2\Sigma$	$^2\Pi_{3/2}$ — $^2\Sigma$	
B'_0	0.3634 cm^{-1}	0.3647 cm^{-1}	0.3474 cm^{-1}
B''_0	0.3510 cm^{-1}	0.3510 cm^{-1}	0.3510 cm^{-1}
ν_{00}	16489.91 cm^{-1}	16564.55 cm^{-1}	18857.51 cm^{-1}
$\gamma' - \gamma''$	-	-	0.06727

G.V. Kovalenok and V.A. Sokolov (1967) carried out the vibrational analysis of the bands in the emission spectrum of CaF in the region 6500 to 5900 A°. The vibrational analysis reported by them is however incorrect. The same workers carried out rotational analysis also, but the results reported are not reliable (Ref. Diatomic molecules - a critical bibliography of spectroscopic data - Chief editor: Simone Bourcier).

S.C. Prasad and M.K. Narayan (1969) have photographed $E^2\Sigma$ — $X^2\Sigma$ and $F^2\Sigma$ — $X^2\Sigma$ systems in emission at a dispersion of about 12 A°/mm. They have observed a few new bands and have modified the analysis offered by Fowler.

K.V. Subbaram and D. Ramchandra Rao (1969) reinvestigated the $A^2\Pi$ — $X^2\Sigma$ system of CaF lying in the region λλ 6300-5830A°. They also reported a few new bands in addition to those reported by the previous workers.

The available spectroscopic data for CaF molecule are collected in Table 1.

(2) CALCIUM CHLORIDE

Band spectrum of calcium chloride molecule was first reported by C.M. Olmsted in the year 1906. O.H. Walters and S. Barratt (1928) using a prism instrument observed bands of CaCl in the region λλ 6350 - 2918 A°. The bands in the regions λλ 6350 - 5810 A° and 3238 - 2918 A° were reported to be degraded to shorter wave length. While the bands in the region λλ 3994 - 3671 A° were degraded to longer wave length side.

TABLE 1

AVAILABLE SPECTROSCOPIC DATA ON CALCIUM FLUORIDE MOLECULE

System designation and transition	Occurrence	Region A°	Nature of the bands	ν_e cm^{-1}	ω'_e cm^{-1}	$\omega'_e x'_e$ cm^{-1}	ω''_e cm^{-1}	$\omega''_e x''_e$ cm^{-1}	Reference
$A^2\Pi_{\frac{1}{2}} \rightleftarrows X^2\Sigma^+$	Arc, Absorption (t > 1300°C)	6297-5830	Violet as well as red degraded	16483.0	591.9	3.427	587.4	2.84	R.C.Johnson (1929) M.A. Harvey (1931)
$A^2\Pi_{3/2} \rightleftarrows X^2\Sigma^+$	"	"	"	16558.0	593.4	3.113	587.4	2.84	B.S. Mahanty & Upadhya(1967)
$B^2\Sigma \rightleftarrows X^2\Sigma^+$	Arc, Absorption (t > 1300°C)	5422-5145	Red degraded	18857.5	566.7	2.82	587.4	2.84	B.S. Mahanty & Upadhya(1967)
$C^2\Pi \rightleftarrows X^2\Sigma^+$	"	3525-3220	"	30285.2 30255.9	481.7	2.02	588.2	2.75	C.A.Fowler(1941) R.C.Johnson (1929)
$D^2\Sigma \rightleftarrows X^2\Sigma^+$	Absorption (t > 1700°C)	3245-3066	Violet degraded	30772.3	650.7	2.89	587.5	2.85	C.A.Fowler(1941)
$E^2\Sigma \rightleftarrows X^2\Sigma^+$	Absorption (t > 1700°C) Emission	3035-2754	"	34135.2 34136.2	646.3 645.5	3.24 3.12	587.80 587.86	2.90 2.94	C.A.Fowler(1941) S.C. Prasad & Narayan (1969)
$F^2\Pi \rightleftarrows X^2\Sigma^+$	"	2701-2557	"	37547.9 37549.7	681.7 682.2	3.55 3.68	586.90 587.86	2.82 2.94	C.A.Fowler(1941) Prasad & Narayan (1969)
$G — X^2\Sigma$	Absorption (t $\gtrsim$ 2000°C)	$<$ 2500	Continum						

K. Hedfeld in 1931 reinvestigated the spectrum of CaCl in the same region. The values of vibrational frequencies calculated by him differed from those obtained by Olmsted. The constants reported by both of them are given below to get a comparative idea.

	ν_o cm^{-1}	ω_e' cm^{-1}	ω_e'' cm^{-1}	Degradation
Olmsted	26556	330	358	Red
Hedfeld	16095	359.25	356.25	Violet
	16164	362.70	358.50	
	16142	357.50	361.00	
	16060			
	16847			

Doublet splitting		Ground state frequency	
Olmsted	Hedfeld	Olmsted	Hedfeld
76.3 cm^{-1}	75.5 cm^{-1}	360 cm^{-1}	358.75 cm^{-1}

A.E. Parker (1935) photographed a number of band systems in the emission spectrum of CaCl in the 2nd order of a concave grating spectrograph at a dispersion of about 2.2 A°/mm and a systematic vibrational analysis was carried out. Amongst the observed band systems three were well developed. Two systems in the red were observed with the

$\Delta v = 0, \pm 1$ sequences and one system in the ultraviolet with the $\Delta v = 0, \pm 1, \pm 2$ and ± 3 sequences. The band system farthest to red degrades to the violet and has four heads. It was assigned to a $^2\Sigma - {}^2\Pi$ transition and the head forming branches are P_1, Q_1, P_2 and Q_2 branches. Several bands which were not reported by Hedfeld were observed in the $\Delta v = \pm 1$ sequences. The equations reported for the Q heads are

$$\nu = 16093.5 + 367.1(v'+\tfrac{1}{2}) - 0.91(v'+\tfrac{1}{2})^2 - 364.4(v''+\tfrac{1}{2}) + 0.80(v''+\tfrac{1}{2})^2$$

$$\nu = 16164.0 + 355.3(v'+\tfrac{1}{2}) - 0.45(v'+\tfrac{1}{2})^2 - 352.2(v''+\tfrac{1}{2}) - 0.33(v''+\tfrac{1}{2})^2$$

Beside this system there is another system in the red as reported by Hedfeld. Each band had a single head and he concluded that it is due to a transition $^2\Sigma - {}^2\Sigma$ or due to a $^2\Pi - {}^2\Sigma$ transition. The observed bands are degraded towards the violet and the heads are formed by P_1 and P_2 branches. The following quantum equation was derived from the heads.

$$\nu = 16850.6 + 361.0(v'+\tfrac{1}{2}) - 1.2(v'+\tfrac{1}{2})^2 - 364.0(v''+\tfrac{1}{2}) + 1.0(v''+\tfrac{1}{2})^2$$

A band system of CaCl has also been reported by Olmsted in the ultraviolet region. These bands exhibit four heads and are degraded to the red. The system has been assigned to a transition of the type ${}^2\Sigma - {}^2\Pi$ having R_1, Q_1, R_2 and Q_2 heads. The vibrational assignments for these bands were done and the following equation representing the stronger Q heads was reported.

$$\nu = 26498.9 + 336.0(v'+\tfrac{1}{2}) - 1.4(v'+\tfrac{1}{2})^2$$
$$- 368.3(v''+\tfrac{1}{2}) + 1.5(v''+\tfrac{1}{2})^2$$

The most interesting feature of these bands was the open rotational structure. The rotational analysis of (0,0) band was done and the reported constants are as follows:

$B'' = 0.26\ \mathrm{cm}^{-1}$ $\qquad$ $B' = 0.24\ \mathrm{cm}^{-1}$

$I'' = 106(10)^{-4}\mathrm{g\ cm}^2$ $\qquad$ $I' = 115(10)^{-4}\mathrm{g\ cm}^2$

$r'' = 1.86(10)^{-8}\ \mathrm{cm}$ $\qquad$ $r' = 1.93(10)^{-8}\ \mathrm{cm}$

$\omega r''^3 = 2340\ \mathrm{cm}^2$ $\qquad$ $\omega r'^3 = 2430\ \mathrm{cm}^2$

In the same year (1935) R.K. Asundi worked on the same molecule. Three band systems A-X, B-X and C-X were reported in red, orange and ultraviolet region respectively. He calculated the energies of four electronic levels X, A, B and C and they are respectively, 0, 1.99, 2.08 and 3.82 eV.

The measurements of the band heads of the two systems were made at higher dispersions. These systems were assigned to $^2\Pi - {}^2\Sigma$ and $^2\Sigma - {}^2\Sigma$ transitions, but were found to have no vibrational energy function in common. Some of the bands in the red region which were attributed to CaCl are due to CaO.

R.E. Harrington (1942, Berkley Thesis) has reported four systems in the regions λλ 6370-6050 A°, 6080-5820 A°, 3950-3640 A° and 3290-2930 A° in absorption which have been identified as $A^2\Pi - X^2\Sigma$, $B^2\Sigma - X^2\Sigma$, $C^2\Pi - X^2\Sigma$ and $D^2\Sigma - X^2\Sigma$.

Von Marianne Schutte (1954) excited CaCl bands with the help of a discharge tube in which helium at a pressure of about 5 mm of mercury was kept as a carrier gas. Ca-metal in presence of $CaCl_2$ was heated to a suitable high temperature. The discharge was operated at about 2 KV, 300-400 mA. He reported new systems in the region λλ 5500-4600 A°. The assigned transitions of these system were $F^2\Pi - A^2\Pi$, $G^2\Delta - A^2\Pi$ and $F^2\Pi - B^2\Sigma$. These systems do not appear in absorption. The reported new transitions are

$F^2\Pi - A^2\Pi$ with ν_{00} at 19597, 19612 cm^{-1}
$F^2\Pi - B^2\Sigma$ with ν_{00} at 18858, 18880 cm^{-1}
$G^2\Delta - A^2\Pi$ with ν_{00} at 20578, 20643 cm^{-1}

The values of ω_e' and $\omega_e'x_e'$ for the states F and G are respectively 432.5 and 0.8, 434 and 1.1 cm^{-1}.

E. Morgan and R.F. Barrow (1960) observed the $C^2\Pi$ — $X^2\Sigma^+$ system in absorption. The rotational analysis of (0,0) band and shorter wave length sub-bands (1,0) and (0,1) were carried out. Constants reported by Morgan and Barrow are given below:

State	Te cm^{-1}	$\Delta G_{0,1}$ cm^{-1}	Be cm^{-1}	$10^4\alpha$ cm^{-1}	$10^7 D$ cm^{-1}	r_e A°
$C^2\Pi_{3/2}$	26557.80	333.86	0.14268	7.47	1.0	2.516
$C^2\Pi_{1/2}$	26481.82		0.14216		1.0	
$X^2\Sigma$	0	367.53	0.15156	7.8	1.0	2.439

In 1967 and 1968 Kovalenok and Sokolov studied emission spectrum of CaCl in the region λλ 6500-5900 A°. Vibrational analyses as well as rotational analyses of orange bands were carried out. The data reported by them are however not correct.

The available spectroscopic data for CaCl molecule are collected in Table 2.

TABLE 2

AVAILABLE SPECTROSCOPIC DATA ON CALCIUM CHLORIDE MOLECULE

System designation and transition	Occurrence	Region A°	Nature of the band	T_e cm^{-1}	ω'_e cm^{-1}	$\omega'_e x'_e$ cm^{-1}	ω''_e cm^{-1}	$\omega''_e x''_e$ cm^{-1}	Reference
$A_1^2\Pi_{\frac{1}{2}} \rightleftarrows X^2\Sigma$	Arc, Flame	6370-6050	Violet degraded	16093.5	372.6	-	369.3	1.4	Harrington(1942, Thesis Berkely)
				"	367.1	0.91	364.4	0.8	Parker (1935)
$A_2^2\Pi_{3/2} \rightleftarrows X^2\Sigma$	Absorption (t 900-1200°C)	"	"	16164.0	372.3	1.2			Harrington(1942, Thesis)
				"	355.3	0.45	352.2	0.33	Parker(1935)
$B^2\Sigma \rightleftarrows X^2\Sigma$	Arc, Flame Absorption (t 900-1200°C)	6080-5820	"	16850.6	366.3	1.2	369.3	1.4	Harrington(1942)
				"	361.0	1.2	364.0	1.0	Parker (1935)
$C_1^2\Pi_{\frac{1}{2}} \rightleftarrows X^2\Sigma$	"	3950-3640	Red degraded	26498.9	336.0	1.4	369.3	1.4	Harrington(1942)
$C_2^2\Pi_{3/2} \rightleftarrows X^2\Sigma$	"	"	"	26574.7	336.0	1.4	368.3	1.5	Parker (1935)
$D^2\Sigma \leftarrow X^2\Sigma$	Absorption (t ∽ 1750°C)	3290-2930	Violet degraded	31107.8	423.4	1.61	369.3	1.4	Harrington(1942)
$E^2\Sigma \leftarrow X^2\Sigma$	"	3050-2770	"	34266.4	413.3	1.68	369.0	1.4	"
$F^2\Pi_{\frac{1}{2}} \rightarrow A^2\Pi$	Dech.	5520-4780	"	35675.0	432.5	0.8			M. Shutte(1954)
$F^2\Pi_{3/2} \rightarrow A^2\Pi$				35700.0					
$G^2\Delta_{\frac{1}{2}} \rightarrow A^2\Pi$	Dech.	5020-4620	"	36705.0	434	1.1			M. Shutte(1954)
$G^2\Delta_{3/2} \rightarrow A^2\Pi$				36710.0					
$F^2\Pi \rightarrow B^2\Sigma$	Dech.	5410-5250	"						M. Shutte(1954)

(3) CALCIUM BROMIDE

In 1906 Olmsted reported the spectrum of CaBr by exciting the molecule in a flame. Walters and Barratt (1928) obtained the absorption spectrum. They recorded a group of five very weak bands in the region λλ 2967-2890 A°, but no detailed analysis has been attempted. Only wave lengths of the bands heads were reported by them. Hedfeld (1931) repeated the same work done by Olmsted and vibrational constants were revised. The constants reported by them are given below in the tabular form.

	ν_o cm^{-1}	ω_e' cm^{-1}	ω_e'' cm^{-1}	Degradation
Olmsted	25527	261	281	Red
Hedfeld	15925	282.00	280.00	Violet
	15988	281.50	280.40	

Harrington (1942) investigated the spectrum of CaBr and found that it consists of four discrete band systems in the region λλ 6400-3050 A°. Harrington has designated them as A-X, B-X, C-X and D-X. B and D systems were obtained only in absorption while A and C systems were obtained both in emission as well as in absorption. After carrying out the detailed vibrational analysis of all these four systems, it was concluded that the lower state X is common to all systems and has been identified as a $^2\Sigma$ state. From the observed vibrational structure the band systems have been attributed to $^2\Pi - {}^2\Sigma$, $^2\Sigma - {}^2\Sigma$, $^2\Pi - {}^2\Sigma$ and $^2\Sigma - {}^2\Sigma$ electronic transitions respectively.

In 1968 Y.P. Reddy and P.T. Rao reported a new group of bands in the region λλ 3025-2900 A°. It is designated as E-X. Looking to the nature of the bands the system was attributed to $^2\Sigma - {}^2\Sigma$ transition. The system consists of five groups of single headed bands degraded to violet. Three sequences $\Delta v = -1,-2,-3$ were easily identified on the longer wavelength side and on the shorter wavelength side only $\Delta v = +1$ sequence was identified. The observed P heads could be fitted into the quantum equation:

$$\nu = 33942.2 + 318.6(v'+\tfrac{1}{2}) - 1.2(v'+\tfrac{1}{2})^2 - 285.3(v''+\tfrac{1}{2}) + 0.9(v''+\tfrac{1}{2})^2$$

The isotopic separation of $Ca^{81}Br$ heads from those of the $Ca^{79}Br$ heads were calculated on the basis of the well-known formulae and reported separation varies from about 1.1 to 4.1 cm^{-1}.

In 1970 B.R.K. Reddy, Y. Prabhakar Reddy and P.T. Rao observed the emission spectrum of CaBr by passing bromine and argon over heated calcium metal, in a quartz discharge tube. The bands of this system were degraded to shorter wavelength in the region λλ 4950-4600 A°. The observed system was weak and consisted of five groups of double-double headed bands. Hence the system was attributed to a $^2\Sigma - {}^2\Pi$ transition. The two groups of bands on the longer wavelength side were identified as $\Delta v = -1, -2$ sequences. While the two groups on the shorter wavelength side were identified as $\Delta v = +1$ and $+2$ sequences. The analysis of this system showed that the lower state involved is the $A^2\Pi$ state of the molecule. The following vibrational quantum formula represents the inner P_2 and Q_1 heads.

$$\nu = \begin{matrix} 20812.3 \\ 20876.7 \end{matrix} + 343.4(v'+\tfrac{1}{2}) - 1.0(v'+\tfrac{1}{2})^2$$
$$- 287.6(v''+\tfrac{1}{2}) + 0.9(v''+\tfrac{1}{2})^2$$

The rotational analysis of the (0,0) band of C system of the molecule in the region λλ 3960-3910 A° has been carried out by M.N. Kamalasanan (1974). The reported constants are given below.

$CaBr^{81}$	$CaBr^{79}$
$B'_0 = 0.0764 \pm 0.0005\ cm^{-1}$	$B'_0 = 0.0758 \pm 0.0005\ cm^{-1}$
$D'_0 = 2.4 \times 10^{-6}\ cm^{-1}$	$D'_0 = 2.4 \times 10^{-8}\ cm^{-1}$
$r'_0 = 2.88$ A°	$r'_0 = 2.88$ A°
$B''_0 = 0.0816 \pm 0.0005\ cm^{-1}$	$B''_0 = 0.0811 \pm 0.0005\ cm^{-1}$
$D''_0 = 2.4 \times 10^{-8}\ cm^{-1}$	$D''_0 = 2.4 \times 10^{-8}\ cm^{-1}$
$r''_0 = 2.78$ A°	$r''_0 = 2.78$ A°

However the r_e values reported are much higher than expected.

Available spectroscopic data of CaBr molecule is given in Table 3.

(4) CALCIUM IODIDE

In year 1906 Olmsted reported the spectrum of calcium iodide molecule for the first time. Walters and Barratt (1928) observed the spectrum of CaI in absorption. Three groups of bands in the regions λλ 6690-6270 A°, 4440-4410 A° and 3290-3075 A° were reported. The dispersion was low and no detailed analysis was offered. Hedfeld (1931) investigated the spectrum of CaI in emission (in flame) in red region (λλ 6690-6270 A°) and vibrational analysis was carried out. The constants reported by Olmsted and Hedfeld are given here.

TABLE 3

AVAILABLE SPECTROSCOPIC DATA ON CALCIUM BROMIDE MOLECULE

System designation and transition	Occurrence	Region A°	Nature of the band	T_e cm^{-1}	ω_e' cm^{-1}	$\omega_e'x_e'$ cm^{-1}	ω_e'' cm^{-1}	$\omega_e''x_e''$ cm^{-1}	Reference
$A_1^2\Pi_{\frac{1}{2}} \rightleftarrows X^2\Sigma$	Arc, flame	6400-6270	Violet degraded with 4 heads	15985.8	288.1	0.92	285.3	0.82	Harrington(1942)
$A_2^2\Pi_{3/2} \rightleftarrows X^2\Sigma$	Absorption (t 1000-1500°C)	6380-6140		15922.5			285.7	0.86	Herzberg - Spectra of diatomic molecule.
$B^2\Sigma \leftarrow X^2\Sigma$	Absorption (t 1300-1500°C)	6130-6000	Violet degraded double head	16380.0	284.6	0.92	284.2	0.82	"
$C_1^2\Pi_{\frac{1}{2}} \leftarrow X^2\Sigma$	"	4110-3800	Red degraded with 4 heads	25537.5	265.2	0.97	285.9	0.90	"
$C_2^2\Pi_{3/2} \leftarrow X^2\Sigma$				25314.0			286.9	1.01	
$D^2\Sigma \rightleftarrows X^2\Sigma$	Absorption (t 1300-1500°C)	3290-3050	Violet degraded	31190.8	326.6	1.02	285.3	0.77	"
				31190.91	326.5	1.02	285.27	0.77	Reddy & Rao (1968)
$E^2\Sigma \rightarrow X^2\Sigma$	Emission	3025-2900	"	33942.2	318.6	1.2	285.3	0.9	"
$^2\Sigma \rightarrow A^2\Pi$	"	4600-4950	"	20812.3 20876.7	343.4	1.0	287.6	0.9	" (1970)

	ν_o cm^{-1}	ω'_e cm^{-1}	ω''_e cm^{-1}	Degradation
Olmsted	23740	206	241	Red
Hedfeld	15589	243	239	Violet
	15748	242	239	
	15616	240	240	

Mesnage (1939) reported a group of bands in region $\lambda\lambda$4400-4100 A° of which some of the bands were double-headed and some were diffused. Later Murty, Reddy and Rao (1970) reinvestigated the spectrum of CaI in the same region. They photographed the spectrum in the 1st order of a 21 ft concave grating spectrograph. The source was high frequency discharge through a mixture of heated calcium metal and iodine vapour. They observed a doublet system consisting of a number of well marked sequences. The bands were degraded to red. $\Delta G(v)$ intervals of the lower state of each of the two sub-system agree with the three other systems reported by Hedfeld in the red region. The system consists of double-double headed bands and is attributed to a $C^2\Pi$ — $X^2\Sigma$ transition with a doublet interval of about 428 cm^{-1}. The quantum equations reported were -

$$\nu_{Q_1} = 23315.51 + 229.75\,(v'+\tfrac{1}{2}) - 0.633(v'+\tfrac{1}{2})^2$$
$$- 238.70(v''+\tfrac{1}{2}) + 0.628(v''+\tfrac{1}{2})^2$$

$$\nu_{R_2} = 23743.96 + 224.72(v'+\tfrac{1}{2}) - 0.530(v'+\tfrac{1}{2})^2$$
$$- 238.70(v''+\tfrac{1}{2}) + 0.628(v''+\tfrac{1}{2})^2$$

The double-headed bands of the third system analysed by Hedfeld were attributed to $B^2\Sigma - X^2\Sigma$ transition.

In 1973 Lalit K. Khanna and V.S. Dubey photographed in emission the spectrum of CaI molecule by exciting it in carbon arc. The system reported consists of single headed bands degraded towards the shorter wavelength side in the region λλ 3343-3151 A°. After a careful vibrational analysis, the system was assigned to a transition $D^2\Sigma - X^2\Sigma$. The system is classified into a large number of well separated sequences with $\Delta v = -5, -4, -3, \pm 2, \pm 1$ and 0. Each sequence consists of a large number of bands. For this system the quantum equation reported was

$$\nu_D = 31011.43 + 256.0(v'+\tfrac{1}{2}) - 0.8(v'+\tfrac{1}{2})^2$$
$$- 239.0(v''+\tfrac{1}{2}) + 0.628(v''+\tfrac{1}{2})^2$$

Khanna and Dubey (1973a) also reanalysed the A_1, A_2 and C systems and revised the vibrational analysis offered by earlier workers.

In the same year Khanna and Dubey (1973b) reported another system in emission in the region ($\lambda\lambda$ 6354-5977 A°). The system was weak and consisted of single headed bands degraded towards the violet. The band system was overlapping with A system. This system was assigned to an electronic transition $B^2\Sigma — X^2\Sigma$. It consists of a number of closed sequences with $\Delta v = -1, 0, +1, +2$ and $+3$ and is fairly well represented by the expression

$$\nu_B = 16022.9 + 237.0(v'+\tfrac{1}{2}) - 0.96(v'+\tfrac{1}{2})^2 - 239.0(v''+\tfrac{1}{2}) + 0.628(v''+\tfrac{1}{2})^2 - 0.008(v''+\tfrac{1}{2})^3$$

The spectrum was photographed on a Steinheil three prism large glass spectrograph having a dispersion of about 14.7 A°/mm at 6200 A°.

Darji A.B. and Vaidya S.P. (1973) photographed the emission spectrum of CaI in 6175-6610 A° region, in the 2nd order of a two meter plane grating spectrograph at a reciprocal dispersion of 3.38 A°/mm. The bands have been analysed into two different systems which have been attributed to electronic transitions $A^2\Pi — X^2\Sigma$ and $B^2\Sigma — X^2\Sigma$. Both the groups are reported to be violet degraded. One of them has sub-heads (P_1 and P_2) with equal intensities and then separation between them was about

3.4 cm^{-1}. While the other having intense Q-heads and corresponding weak P head had a separation of 9 cm^{-1} between them. The quantum equation which satisfactorily represents P_1 and P_2 heads is

$$\nu = \begin{matrix} (P_1)\ 15711.8 \\ \\ (P_2)\ 15715.2 \end{matrix} \quad + 239.95(v'+\tfrac{1}{2}) - 0.62(v'+\tfrac{1}{2})^2$$

$$- 238.8(v''+\tfrac{1}{2}) + 0.55(v''+\tfrac{1}{2})^2$$

The upper state shows a splitting of 3.4 cm^{-1} which was considered to be spin splitting in the upper state $B^2\Sigma$. After carrying out the systematic vibrational analysis of the $A^2\Pi - {}^2\Sigma$ system it was observed that the following quantum equations satisfactorily represent their Q heads.

$A^2\Pi_{3/2} - X^2\Sigma$

$$\nu_Q = 15645.57 + 241.69(v'+\tfrac{1}{2}) - 0.83(V'+\tfrac{1}{2})^2$$
$$- 238.40(V''+\tfrac{1}{2}) - 0.79(v''+\tfrac{1}{2})^2$$

$A^2\Pi_{1/2} - X^2\Sigma$

$$\nu_Q = 15586.20 + 242.65(v'+\tfrac{1}{2}) - 0.62(v'+\tfrac{1}{2})^2$$
$$- 238.26(v''+\tfrac{1}{2}) + 0.73(v''+\tfrac{1}{2})^2$$

The available spectroscopic data for CaI molecule are collected in Table 4.

TABLE 4

AVAILABLE SPECTROSCOPIC DATA ON CALCIUM IODIDE MOLECULE

System designation and transition	Occurrence	Region A°	Nature of the bands	ν_e cm^{-1}	ω'_e cm^{-1}	$\omega'_e x'_e$ cm^{-1}	ω''_e cm^{-1}	$\omega''_e x''_e$ cm^{-1}	Reference
$A^2\Pi_{\frac{1}{2}} \rightleftarrows X^2\Sigma$	Absorption Emission	6615-6220	Violet degraded	15585.1	243.4	0.8	238.3	0.61	Spectroscopic data book edited by Rosen(1957)
				15586.2	242.6	0.62	238.26	0.73	Darji and Vaidya (1973)
$A^2\Pi_{3/2} \rightleftarrows X^2\Sigma$	Absorption Emission	6690-6200	"	15645.9	241.1	0.66	238.3	0.61	Rosen- Data book
				15645.5	241.6	0.83	238.40	0.79	Darji & Vaidya (1973)
$B^2\Sigma \rightleftarrows X^2\Sigma$	"	6665-6270	" weak single headed	15711.2	239.8	0.65	238.3	0.61	Rosen -Data book
				16022.9	237.0	0.96	239.0	0.628	Khanna & Dubey (1973)
$C^2\Pi \rightleftarrows X^2\Sigma$	"	4440-4250	Red degraded	15711.8	239.95	0.62	238.8	0.55	Darji & Vaidya (1973)
				23314.0	230.2	0.69	238.3	0.61	Rosen- Data book
				23315.5	229.75	0.633	238.7	0.628	Murty-Reddy(1970)
$C^2\Pi \leftarrow X^2\Sigma$	Absorption	4310-4100	"	23741.9	227.6	1.49	238.3	0.61	Rosen- Data book
				23743.9	224.72	0.53	238.7	0.628	Murty, Reddy & Rao (1970)
$D^2\Sigma \rightarrow X^2\Sigma$	Emission	3290-3075	Violet degraded	31062.0	275.1	1.30	238.3	0.61	Rosen- Data book
				31011.43	256.0	0.80	239.0	0.628	Khanna & Dubey (1973)

(5) BARIUM IODIDE

In 1906 Olmsted reported the spectrum of BaI by exciting the molecule in flame. A few bands were reported in the region λλ 5610-5310 A°. Walters and Barratt(1928) observed the spectrum in absorption. The groups of bands observed in the region λλ 3830-3760 A°. were reported to be degraded to shorter wavelength. The wavelengths and intensities of the band heads were reported but no analysis was offered.

Mesnage (1939) photographed the emission spectrum in the region λλ 5650-5250 A°. Two intense sequences with a separation of 755 cm^{-1} were observed. B.R.K. Reddy and P.T. Rao (1970) excited BaI molecule in a high frequency discharge through a mixture of heated barium metal and iodine. The spectrum showed the existence of a number of well developed single headed bands in the region λλ 3950-3650 A° degraded to shorter wavelength. They were identified as the P heads. The central group of bands at $\nu = 26101$ cm^{-1} was identified as $\Delta v = 0$ sequence. Other groups of bands on the longer wavelength side were identified as $\Delta v = -1, -2$ and -3 sequences. Those on the shorter wavelength side were identified as $\Delta v = +1, +2, +3$ sequences. The bands were attributed to the electronic transition $D^2\Sigma$ — $X^2\Sigma$.

The reported quantum formula was

$$\nu = 26091.5 + 175.2(v'+\tfrac{1}{2}) - 0.4(v'+\tfrac{1}{2})^2 - 163.5(v''+\tfrac{1}{2}) + 0.6(v''+\tfrac{1}{2})^2$$

However, a few weaker bands in the region λλ 3760-3680 A° could not be fitted in the above quantum formula. They are reported to belong to another system which is designated as $E^2\Sigma — X^2\Sigma$ transition. For this weaker system the vibrational quantum formula reported was

$$\nu = 26759.0 + 176.0(v'+\tfrac{1}{2}) - 0.35(v'+\tfrac{1}{2})^2 - 163.5(v''+\tfrac{1}{2}) + 0.6(v''+\tfrac{1}{2})^2$$

Patel M.M. and Shah N.R. (1970) photographed emission spectrum of BaI molecule using a high frequency discharge, at a dispersion of about 7.3 A°/mm with a plane grating in the region λλ 3950-3700 A°. The reported bands are clearly degraded towards the violet. The bands on the longer wavelength side have sharp single heads. Careful study of the spectrogram revealed that there are two groups of bands in this region. The longer wavelength group has its (0,0) band at 25781.8 cm^{-1}. The shorter wavelength group has been analysed taking the (0,0) band at 26766.4 cm^{-1}. The green

TABLE 5

AVAILABLE SPECTROSCOPIC DATA ON BARIUM IODIDE MOLECULE

System designation and transition	Occurrence	Region A°	Nature of the bands	ν_e cm^{-1}	ω'_e cm^{-1}	$\omega'_e x'_e$ cm^{-1}	ω''_e cm^{-1}	$\omega''_e x''_e$ cm^{-1}	Reference
$C^2\Pi \rightarrow X^2\Sigma$	Emission	5705-5280	V(R)	17819.5	156.88	0.48	150.90	0.40	Patel & Shah (1970)
				18572.6	156.82	0.31	151.16	0.35	
	Absorption		V(R)	17816.3	156.7	0.28	152.2	0.29	Mesnage(1939)
				18568.8	158.4	0.34			Rosen- Data book
$D^2\Sigma \leftrightarrows X^2\Sigma$	Emission	3970-3800	Violet degraded single headed	26091.5	175.2	0.4	163.5	0.6	Reddy and Rao (1970)
	"			25777.3	160.81	0.31	151.87	0.62	Patel and Shah (1970)
	Absorption			25764.4	161.1	0.26	152.2	0.29	Rosen- Data book
$E^2\Sigma \rightarrow X^2\Sigma$	Emission	3800-3565	Violet degraded	26759.0	176.0	0.35	163.5	0.6	Reddy and Rao (1970)
	"			26755.3	173.95	0.65	151.75	0.45	Patel and Shah (1970)
	Absorption			26753.3	176.0	0.30	152.2	0.29	Rosen- Data book

spectrograph at a dispersion of 9 A°/mm. About 35 bands have been reported in the region λλ 6932-6683 A°. The bands were degraded to shorter wavelength side. The bands form well defined sequences ($\Delta v = 0, +1$ and -1). From the nature of the band heads he assigned the bands an electronic transition $^2\Pi - {}^2\Sigma$. Within reasonable accuracy the reported quantum formula for Q heads was

$$\nu = \begin{matrix} 14420.2\ (Q_{12}) \\ \\ 14744.7\ (Q_2) \end{matrix} \quad + 175.12(v'+\tfrac{1}{2}) - 0.72(v'+\tfrac{1}{2})^2$$

$$- 169.44(v''+\tfrac{1}{2}) + 0.64(v''+\tfrac{1}{2})^2$$

B.R.K. Reddy, Y.P. Reddy and P.T. Rao (1974) photographed the band system of SrI by exciting it in a radio-frequency discharge through a mixture of heated strontium metal and iodine vapour in the presence of argon. The spectrum was photographed under high dispersion (1.25 A°/mm). It revealed the existance of a doublet system of bands degraded to longer wave-length in the region λλ 4500-4200 A°. The assigned transition is $C^2\Pi - X^2\Sigma$. The head forming branches are

R_1 and Q_1 in $C^2_1\Pi_{1/2} - X^2\Sigma$

and R_{21} and R_2 in $C^2_2\Pi_{3/2} - X^2\Sigma$

The following quantum formula was found to represent the Q_1 and R_2 heads of the two sub-systems.

$C_1^2\Pi_{1/2} — X^2\Sigma$

$$\nu_{(Q_1)} = 22666.1 + 170.9(v'+\tfrac{1}{2}) - 0.36(v'+\tfrac{1}{2})^2$$
$$- 174.1(v''+\tfrac{1}{2}) + 0.37(v''+\tfrac{1}{2})^2 - 0.0009(v''+\tfrac{1}{2})^3$$

$C_2^2\Pi_{3/2} — X^2\Sigma$

$$\nu_{(R_2)} = 23223.4 + 168.5(v'+\tfrac{1}{2}) - 0.40(v'+\tfrac{1}{2})^2$$
$$- 174.1(v'+\tfrac{1}{2}) + 0.37(v''+\tfrac{1}{2})^2$$

Reddy et al. (1971) reinvestigated the spectrum of SrI. In addition to the visible C-X system, the spectrum revealed the existence of number of bands degraded to shorter wavelength in the infra-red region λλ 7100-6500 A°. It was found that bands belonging to systems $A^2\Pi — X^2\Sigma$ and $B^2\Sigma — X^2\Sigma$ were overlapping. From the similarity of their appearance the two bands at $\nu = 14428$ cm^{-1} and 14752 cm^{-1} could be easily identified as the (0,0) bands of the sub-systems - $A_1 - X$ and $A_2 — X$. For the A system the constans reported were

$\nu_e = 14420$ cm^{-1} $\quad$ $\omega'_e = 190.0$ cm^{-1} $\quad$ $\omega'_e x'_e = 0.5$ cm^{-1}

$\nu_e = 14744$ cm^{-1} $\quad$ $\omega'_e = 174.0$ cm^{-1} $\quad$ $\omega'_e x'_e = 0.4$ cm^{-1}

In addition to these, the spectrum of SrI reveals one strong diffused band at $\nu = 14643 \text{ cm}^{-1}$ and two weak bands at $\nu = 14818 \text{ cm}^{-1}$ and 14992 cm^{-1}. This band system was assigned a $B^2\Sigma — X^2\Sigma$ transition. The reported constants were

$$\nu_e = 14642 \text{ cm}^{-1} \qquad \omega'_e = 176 \text{ cm}^{-1} \qquad \omega'_e x'_e \doteq 0.5 \text{ cm}^{-1}$$

In 1973 Ashrafunisa, D.V.K. Rao and P.T. Rao reinvestigated the spectrum of SrI in the region λλ7200-6500 A°. Several groups of bands degraded to shorter wavelength side with the overlapping systems were assigned to $A^2\Pi — X^2\Sigma$ and $B^2\Sigma — X^2\Sigma$ transitions. The sub-system on the longer wavelength side was assigned to $A^2\Pi_{1/2} — X^2\Sigma$ and that on the shorter wavelength side to $A^2\Pi_{3/2} — X^2\Sigma$ transitions. The vibrational quantum formulae reported for the P_1 and Q_2 heads of the two sub-systems were

$$\nu_{P_1} = 14422.71 + 182.3(v'+\tfrac{1}{2}) - 0.54(v'+\tfrac{1}{2})^2$$
$$- 173.75(v''+\tfrac{1}{2}) + 0.395(v''+\tfrac{1}{2})^2 - 0.00015(v''+\tfrac{1}{2})^3$$

$$\nu_{Q_2} = 14815.91 + 182.2(v'+\tfrac{1}{2}) - 0.37(v'+\tfrac{1}{2})^2$$
$$- 173.8(v''+\tfrac{1}{2}) + 0.285(v''+\tfrac{1}{2})^2 - 0.00015(v''+\tfrac{1}{2})^3$$

Another system revealed a few sequences of double headed bands. The reported electronic transition was $B^2\Sigma — X^2\Sigma$. The double heads are identified as P_1 and P_2 heads of $^2\Sigma — {}^2\Sigma$ transition. The observed separation was about 3.7 cm^{-1} between P_1 and P_2 heads and is due to the large spin splitting in the upper state. The P_1 heads were represented by the formula

$$\nu_{P_1} = 14748.83 + 179.5(v'+\tfrac{1}{2}) - 0.315(v'+\tfrac{1}{2})^2 - 173.8(v''+\tfrac{1}{2}) - 0.285(v''+\tfrac{1}{2})^2 - 0.00015(v''+\tfrac{1}{2})^3$$

Kamalasanan M.N. (1975) photographed the spectrum of SrI in the region λλ5250-4900 A° in the 1st order on a two meter plane grating spectrograph at a reciprocal dispersion of 7.3 A°/mm. The observed groups of bands were analysed as two sub-systems. For the longer wavelength component, bands corresponding to $\Delta v = 0, \pm 1, \pm 2$ and -3 were reported with strong Q heads accompanied by weak P heads. Whereas for the shorter wavelength component bands corresponding to $\Delta v = 0, \pm 1$ and ± 2 were reported with strong Q heads accompanied by very weak P heads. The Q heads of the observed bands were fitted in the following quantum equations.

$F^2\Pi_{1/2} — B^2\Sigma$

$$\nu_{(Q_1)} = 19584.1 + 210.4(v'+\tfrac{1}{2}) - 0.40(v'+\tfrac{1}{2})^2 - 180.0(v''+\tfrac{1}{2}) + 0.38(v''+\tfrac{1}{2})^2$$

$F^2\Pi_{3/2} — B^2\Sigma$

$$\nu_{(Q_2)} = 19886.6 + 210.4(v'+\tfrac{1}{2}) - 0.40(v'+\tfrac{1}{2})^2 - 179.1(v''+\tfrac{1}{2}) + 0.38(v''+\tfrac{1}{2})^2.$$

The available spectroscopic data for SrI molecule are collected in Table 6.

PROBLEM

From the above survey of the work reported by the earlier workers on the spectra of halides of calcium and iodides of barium and strantium it would be noticed that the B levels of most of these molecules exhibit considerable amount of spin splitting. However in CaCl molecule the earlier workers have not observed any such spin splitting. The spin splitting in the $B^2\Sigma$ level of the analogous molecules arises from an interaction with the $A^2\Pi$ state. In CaCl molecule one observes that the $A^2\Pi$ level is lying close enough to the B level and it is

TABLE 6

AVAILABLE SPECTROSCOPIC DATA ON STRONTIUM IODIDE MOLECULE

System designation and transition	Occurrence	Region A°	Nature of the band	T_e cm^{-1}	ω'_e cm^{-1}	$\omega'_e x'_e$ cm^{-1}	ω''_e cm^{-1}	$\omega''_e x''_e$ cm^{-1}	Reference
$A^2\Pi_{\frac{1}{2}} \rightleftarrows X^2\Sigma$	Absorption & Emission	7094-6177	Violet degraded	14420.2	175.12	0.75	169.44	0.64	Shukla (1970)
				14420.0	190.0	0.50	-	-	Reddy,Reddy,Rao (1970)
				14422.7	182.3	0.54	173.75	0.395	Ashrafunisa, Rao,Rao (1973)
$A^2\Pi_{3/2} \rightleftarrows X^2\Sigma$	"	"	"	14744.7	175.12	0.72	169.44	0.64	Shukla (1970)
				14744.0	174.0	0.4	-	-	Reddy-Reddy,Rao (1970)
				14815.1	182.3	0.54	173.75	0.395	Ashrafunisa, Rao,Rao (1973)
$B^2\Sigma \rightarrow X^2\Sigma$	Emission		Overlapping with A-X system	14642.0	176.0	0.5	-	-	Reddy,Rao,Rao (1970)
				14748.8	179.5	0.315	173.8	0.285	Ashrafunisa, Rao,Rao (1973)
$B \rightleftarrows X^2\Sigma$	Absorption & Emission	4485-4375	Red degraded	22666.0	170.5	0.42	173.9	0.42	Mesnage (1939)
$C^2\Pi_{\frac{1}{2}} \rightarrow X^2\Sigma$				22666.1	170.9	0.36	174.1	0.37	Reddy,Reddy, Rao (1970)
$C \rightleftarrows X^2\Sigma$	"	4344-4250	"	23226.0	168.6	0.5	173.9	0.42	Mesnage (1939)
$C^2\Pi_{3/2} \rightarrow X^2\Sigma$				23223.4	168.5	0.4	174.1	0.37	Reddy,Rao(1971)
$D^2\Sigma \rightarrow X^2\Sigma$	Emission	3350-3560		28943.9	200.4	0.50	174.9	0.35	Shah,Patel and Darji (1973)
$F^2\Pi_{\frac{1}{2}} \rightarrow B^2\Sigma$	"	4900-5250	Violet degraded	19584.1	210.4	0.4	180.0	0.38	Kamalasanan(1975)
$F^2\Pi_{3/2} \rightarrow B^2\Sigma$	"	"	"	19886.6	210.4	0.4	179.1	0.38	

expected that the B level should exhibit an appreciable amount of spin splitting. It was therefore thought worthwhile to reinvestigate the B system of CaCl molecule and to compare the amount of spin splitting with the value of spin splitting calculated for the case of precession.

The rotational analysis of none of the bands of B system is reported by the earlier workers. Hence it was thought worthwhile to analyse some of the bands of B system, if they could be resolved for such an analysis and obtain the rotational constants.

In the D system of CaBr molecule the isotopic splitting of the bands has not been observed by the earlier workers even though Br has two isotopes of nearly equal natural abundance. Since the study of isotope separation of the band heads of a molecule is a confirmative test for the correctness of the band assignments in the vibrational analysis, the study of the vibrational spectrum at a higher dispersion of this molecule was undertaken.

In most of the group II molecules a number of band systems have been observed in which the ground state is not involved. Such systems usually appear in the visible region or in the infra-red region. However, in CaI molecule no such system has been observed. It was decided to reinvestigate the visible region of this molecule to search for such systems.

In comparison to other halides of Sr and Ca only a few systems have been reported for the iodide of Sr. The study on the spectrum of strantium iodide was under taken with a view to search for the corresponding systems if any and compare them with those of the analogous molecules.

In BaI molecule there are two intense groups of bands in the green region which were observed by the earlier workers. Compared to similar systems which are observed for other molecules in the same group, this group may arise due to a transition $C^2\Pi — X^2\Sigma$ and the two groups observed may be (0,0) sequences of the components. However since the other sequence members were not observed by the earlier workers it was not possible to give a proper vibrational analysis and to derive the vibrational constants. It was therefore desired that the spectrum of this molecule may be reinvestigated in this region with a better source so as to get more intense bands to provide a correct vibrational analysis. The D and E systems of BaI molecule have been investigated by the previous workers, however, the analysis reported by them is not convincing. A re-investigation of these band systems was therefore under taken.

The results obtained during the present study are compiled in the second part of the thesis and the comparison of various states of the molecules are presented.