CHAPTER II

HISTORICAL SURVEY

Spectroscopic studies of the Iodides of Calcium, Zinc and Indium are extensively carried out by several workers. C. M. Olmsted (1906); O. H. Walters and Barrat (1928); Wieland (1929); Hedfeld (1931); M. Wehrli (1934); M. Wehrli and E. Miescher (1934); Oeser (1935); Mesnage (1939); Howell (1943); Rao and Rao (1946); Wieland (1946); Ramasastry (1948, 1949); A. Barrett and M. Mandel (1958); P. S. Murty, Y. P. Reddy and P. T. Rao (1970); L. K. Khanna, V. S. Dubey (1973); M. N. Kamalasanan and S. G. Shah (1975).

A brief review of the work reported so far on the spectra of Iodides of Calcium, Zinc and Indium is given here.

2.1 CALCIUM IODIDE

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

	ν_0 cm^{-1}	ω'_e cm^{-1}	ω''_e cm^{-1}	Degradation
Olmsted	23740	206	241	Red

	ν_0 cm^{-1}	ω'_e cm^{-1}	ω''_e cm^{-1}	Degradation
Hedfeld	15589	243	239	Violet
	15748	242	239	
	15616	240	240	

Mesnage (1939) reported a group of bands in region $\lambda\lambda$4400-4100 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 vibrational quantum ~~equantum~~ equations reported were

$$\nu_{Q1} = 23315.51 + 229.75\,(v'+\tfrac{1}{2}) - 0.633\,(v'+\tfrac{1}{2})^2 - 238.70\,(v''+\tfrac{1}{2}) + 0.628\,(v''+\tfrac{1}{2})^2 \quad ..... \quad (25)$$

$$\nu_{R_2} = 23743.96 + 224.72\,(v'+\tfrac{1}{2}) - 0.530\,(v'+\tfrac{1}{2})^2 - 238.70\,(v''+\tfrac{1}{2}) + 0.628\,(v''+\tfrac{1}{2})^2 \quad ..... \quad (26)$$

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 in 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 λλ3343-3151 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 $\Delta v = -5, -4, -3, \pm 2, \pm 1$ and 0. Each sequence consists of a large number of bands. For this system the quantum equation reported was

$$\nu_D = 31011.43 + 256.0\,(v'+\tfrac{1}{2}) - 0.8\,(v'+\tfrac{1}{2})^2 - 239.0\,(v''+\tfrac{1}{2}) + 0.628\,(v''+\tfrac{1}{2})^2 \;\ldots\ldots \quad (27)$$

Khanna and Dubey (1973 a) also reanalysed the A_1-X , A_2-X and C-X 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 (λλ6354 – 5977 A°). The system was weak and consisted of single headed bands degraded towards the violet. The band system was overlapping with A – X 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.

$$\nu_p = 16022.9 + 237.0\,(v'+\tfrac{1}{2}) - 0.96\,(v'+\tfrac{1}{2})^2 - 239.0(v''+\tfrac{1}{2}) + 0.628(v''+\tfrac{1}{2})^2 - 0.008(v''+\tfrac{1}{2})^3 \;\ldots\ldots \quad (28)$$

The spectrum was photographed on a steinheil three prism large glass spectrograph having a dispersion of about

14.7 A°/mm at 6200 A°.

It was in the course of an attempt to study the spectrum of CaI molecule in this laboratory that M. N. Kamalasanan and S. G. Shah(1975) recorded a new system of bands in the region $\lambda\lambda$4950-4600 A°. In the spectrogram a number of violet degraded bands were observed. The most intense band at 21149.2 cm^{-1} was taken as 0,0 band. Bands corresponding to $\Delta v = 0$, ± 1, ± 2 and -3 were observed with strong Q and corresponding weak P heads. The bands were analysed to form two subsystems arising from a transition of the type $^2\Delta - {}^2\Pi$. For the $^2\Delta - {}^2\Pi_{3/2}$ component the higher members could not be clearly recognised due to the overlapping with the members of $^2\Delta - {}^2\Pi_{\frac{1}{2}}$ components. The difference between the system origins was found to be 57 (cm^{-1}) wave numbers which is quite close to the doublet splitting of a A level (59 cm^{-1}) observed by earlier workers.

The Q heads of the bands were satisfactorily fitted in the quantum equations given below.

$$\nu_{Q_2} = 21070.1 + 287.2(v'+\tfrac{1}{2}) - 0.80(v'+\tfrac{1}{2})^2$$
$$- 241.7(v''+\tfrac{1}{2}) + 0.50(v''+\tfrac{1}{2})^2$$

$$\nu_{Q_1} = 21127.1 + 287.2(v'+\tfrac{1}{2}) - 0.80(v'+\tfrac{1}{2})^2$$
$$- 242.7(v''+\tfrac{1}{2}) + 0.50(v''+\tfrac{1}{2})^2.$$

The analysis reveals that the bands observed belong to two sub-systems of a $^2\Delta - ^2\Pi$ transition. The lower state vibrational frequency does not agree with the ground state frequency of CaI molecule (238.2 cm^{-1}) reported by earlier workers. However it nicely agrees with the vibrational frequency of the A level (241.69 cm^{-1} and 242.65 cm^{-1}) observed by previous workers. The separation between the band origins observed in the present analysis nearly agrees with the reported doublet separation of the A levels. Hence it is suggested that the lower level involved in this transition is not the ground state but the first excited state viz. $A^2\Pi$ state. The upper state frequency of 287.2 cm^{-1} is much higher than any of the observed levels in this molecule. If one takes $A^2\Pi$ state as the lower state of this system, the upper state may lie at about 36715 cm^{-1}. The structure of these bands shows that the upper level may be a $^2\Delta$ state analogous to the $^2\Delta$ state of CaCl molecule. The doublet separation in the Δ state may be about 2 cm^{-1}. Our present knowledge on the spectra of Calcium Iodide is compiled in Table 1.

2.2 ZINC IODIDE

The spectroscopic studies on halides of Zinc were extensively carried out by Wieland (1929) along with the halides of Cadmium and Mercury. These molecules were subjected to detailed investigation later by several workers. (Walter and Barratt, 1929; Wieland, 1946; Oeser, 1935).

Wieland (1929) in his extensive studies on the spectra of halides of Zinc, Cadmium and Mercury

TABLE 1

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
$A^2\Pi_{1/2} \rightleftarrows X^2\Sigma$	Absorption Emission	6615-6220	Violet degraded	15585.1	243.4	0.8	238.3	0.61	Spectroscopic data book edited by Rosen (1957)
$A^2\Pi_{3/2} \rightleftarrows X^2\Sigma$	Absorption Emission	6690-6200	Violet degraded	15645.9	241.1	0.66	238.3	0.61	Rosen-data book
$B^2\Sigma \rightleftarrows X^2\Sigma$	Absorption Emission	6665-6270	Violet degraded 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 and Dubey (1973)
$C^2\Pi_{1/2} \rightleftarrows X^2\Sigma$	Absorption Emission	4440-4250	Red degraded	23314.0	230.2	0.69	238.3	0.61	Rosen-data book
				23315.5	229.75	0.633	238.7	0.628	Murty and Reddy(1970)
$C^2\Pi_{3/2} \longleftarrow X^2\Sigma$	Absorption	4310-4100	Red degraded	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 and Rao(1970)
$D^2\Sigma \longrightarrow X^2\Sigma$	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 and Dubey (1973)
$E^2\Delta \longrightarrow A^2\Pi$	Emission	4950-4600	Violet degraded	21070.1	287.2	0.80	241.7	0.50	Kamalasanan and Shah (1975)
				21127.1	287.2	0.80	242.7	0.50	

observed three groups of bands of Zinc Iodide in emission. One group of bands, degraded to red, in the visible region and another in the near ultraviolet region have been reported. The analysis of the bands in the visible region was not given. The bands in the ultraviolet region were quite intense and are degraded to violet. They lie between λλ 3393-3258 A°. Wieland derived the following vibrational constants from the analysis of this system.

$$\omega'_e = 248.2 \text{ cm}^{-1} \qquad \omega'_e x'_e = 0.70 \text{ cm}^{-1}$$

$$\omega''_e = 223.4 \text{ cm}^{-1} \qquad \omega''_e x''_e = 0.75 \text{ cm}^{-1}$$

and $\nu_e = 30117.6 \text{ cm}^{-1}$.

The third group of bands observed by Wieland was in the vicinity of 2400A°; but no measurement of it was given. He, however, made the important observation that the bands show much simplified structure if they were excited in the presence of an excess of an inert gas.

Oeser (1935) studied the spectra of the halides of Zinc and Cadmium in absorption and also in fluorescence. In absorption, it showed several distinct maxima but no bands were observed. He could, however, observe about thirteen fluorescence bands in the visible region.

Later, Rao and Rao (1946) reinvestigated the spectrum of Zinc Iodide in emission and detected a brief system of about ten diffuse bands in the region λλ3278-3193 A°. The vibrational analysis of these bands revealed that the final state involved in the transition is same as that of the near ultraviolet Wieland system and they obtained the following vibrational constants for the upper state :

$$\omega'_e = 211.7 \text{ cm}^{-1} \qquad \omega'_e x'_e = 2.5 \text{ cm}^{-1}$$

$$\text{and} \qquad \nu_e = 30506.3 \text{ cm}^{-1}$$

Thus it was interpreted that the Wieland system and the system observed by Rao and Rao are the two components of a doublet electronic transition $^2\Pi - {}^2\Sigma$

with a doublet interval of 370 cm^{-1}. This conclusion was in complete confirmity with the suggestion made by Howell (1943).

Rao and Rao also confirmed the occurrence of a group of bands for Zinc Iodide in the region of 2400A°.

Ramasastry (1948) obtained these bands in high frequency discharge and analysed them. They were degraded to red and extend from λ 2458A° to λ 2252A°. The vibrational constants calculated for this system, which is designated as E - X are :

$$\omega'_e = 142.0\ cm^{-1} \qquad \omega'_e x'_e = 3.0\ cm^{-1}$$

$$\omega''_e = 225.6\ cm^{-1} \qquad \omega''_e x''_e = 1.0\ cm^{-1}$$

$$\text{and} \quad \nu_e = 44114.5\ cm^{-1} .$$

Each band of this system consisted of three component heads, which were shown to be due to the isotopes of Zinc (Zn^{64}, Zn^{66} and Zn^{68}). Predissociation of the upper electronic state was suggested between the vibrational level $v' = 2$ and $v' = 3$ because of the sudden diffuseness of all the bands after the vibrational level, $v' = 2$.

Ramasastry (1949) observed another band system for ZnI, designated as $D_1 - X$ using high frequency discharge. Large number of bands degraded to red were obtained in the region λλ 2990-2700 A°. He noticed that these bands have the same general characteristic features as the system E - X, such as the Zinc isotope heads and pre dissociation. The following are the vibrational constants derived from the analysis of this system :

$$\omega'_e = 80.0 \text{ cm}^{-1} \qquad \omega'_e x'_e = 1.25 \text{ cm}^{-1}$$

$$\omega''_e = 220.1 \text{ cm}^{-1} \qquad \omega''_e x''_e = 0.825 \text{ cm}^{-1}$$

$$\text{and} \quad \nu_e = 39911.4 \text{ cm}^{-1}$$

Our present knowledge on the spectra of Zinc Iodide compiled in Table 2.

TABLE 2

AVAILABLE SPECTROSCOPIC DATA ON ZINC 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
$B^2\Sigma \longrightarrow X^2\Sigma$	Emission Fluorescence	6140-3500	Bands appear as line like on a continuum probably degraded to red	-	-	-	-	-	Wieland (1929)
$C^2\Pi_{1/2} \longrightarrow X^2\Sigma$	Emission	3398-3258	Violet degraded	30117.6	248.2	0.70	223.4	0.75	Wieland (1929)
$D^2\Pi_{3/2} \longrightarrow X^2\Sigma$	Emission	3278-3193	Diffuse bands probably degraded to red	30506.3	211.7	2.5	220.0	-	Rao and Rao (1946) Howell (1943)
$D_1 \longrightarrow X^2\Sigma$	Emission	2990-2715	Degraded to red Isotop heads due to Zn observed	39911.4	80.0	1.25	224.5	0.875	C.Ramasastry (1949)
$E \longrightarrow X^2\Sigma$	Emission	2458-2252	Degraded to red	44114.5	142.5	3.0	225.6	1.0	C.Ramasastry (1948)

2.3 INDIUM IODIDE

The spectrum of Indium Iodide molecule was studied by M. Wehrli (1934) and M. Wehrli and E. Miescher (1934) at low dispersion in absorption and in emission. Single and double headed bands in the region λλ3948-4293 A° were vibrationally classified as belonging to A - X and B - X systems respectively and the electronic transitions A $^3\Pi_0$ - X $^1\Sigma^+$ and B $^3\Pi_1$- X $^1\Sigma^+$ were assigned to them. Third system C - X was again observed by M. Wehrli and E. Miescher (1934) in absorption and was assigned to an electronic transition of the type C $^1\Pi \leftarrow$ X $^1\Sigma^+$. This system was observed on a continnum with maximum at 3180 A°. The vibrational constants of A - X, B - X and C - X system obtained from work of M. Wehrli and M. Wehrli and E. Miescher are given in Table 3.

A.Barrett and M. Mandel (1958) studied the spectrum of InI molecule in the microwave region in absorption and obtained the rotational constants for

TABLE 3

AVAILABLE SPECTROSCOPIC DATA ON INDIUM 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}	$\omega_e''x_e''$	Reference
$A^3\Pi_0 \rightleftarrows X^1\Sigma^+$	Emission Absorption	4293–3948	Single headed violet degraded	24401.6	158.5	1.7	177.1	0.4	M.Wehrli(1934)
$B^3\Pi_1 \rightleftarrows X^1\Sigma^+$	Emission Absorption	4293–3948	Double headed violet and red	25050.5	146.7	2.3	177.1	0.4	M.Wehrli and E.Miescher (1934)
$C^1\Pi \longleftarrow X^1\Sigma^+$	Absorption	Maximum at 3180	Observed on a continuum degradation uncertain	∼31500	–	–	177.1	0.4	M.Wehrli and E.Miescher (1934)

In case of calcium iodide molecule, the spectrum in the red region λλ6175–6600 A° consisting of systems A $^{2}\Pi$ —— X $^{2}\Sigma^{+}$ and B $^{2}\Sigma^{+}$ —— X $^{2}\Sigma^{+}$ have been studied for vibrational analyses in view of the fact that the vibrational constants of the levels involved have been derived on measurements of a few bands only by the earlier workers. The B levels of halides of Calcium exhibit considerable amount of spin splitting. However in case of CaI molecule the earlier workers have not observed any such spin splitting. The spin splitting in the B $^{2}\Sigma^{+}$ level of the analogous molecules (CaCl, CaF and SrCl) arises from an interaction with the A $^{2}\Pi$ state. It was therefore thought desirable to reinvestigate A – X and B – X systems of the CaI molecule in the red region.

In case of Zinc Iodide molecule the near ultraviolet bands in the region λλ3258–3393 A° belonging to C $^{2}\Pi$ – X $^{2}\Sigma$ system were selected for vibrational isotopic analysis owing to the fact that Zinc has three isotopes Zn^{64}, Zn^{66}, and Zn^{68} with percentage natural abundance 48.89, 27.81 and 18.57 respectively. Since the study of the isotopic 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 case of Indium Iodide molecule the rotational analysis of none of the bands of A $^3\Pi_0$ - X $^1\Sigma^+$ and B $^3\Pi_1$ - X $^1\Sigma^+$ system is reported by the earlier workers. Hence it was thought worth while to analyse some of the bands of these systems, if they could be resolved for such an analysis and obtain the rotational constants. For the same group molecules (TlI, TlBr, and TlCl) band systems have been observed in the ultraviolet and near visible in which the ground state is not involved. However in InI molecule no such system has been observed by earlier workers. It was decided to reinvestigate the emission spectrum of this molecule to search for such system.