# CHAPTER 2

## HISTORICAL SURVEY

Several workers reported the spectroscopic studies of the molecules of the halides of cadmium. [ Terenin (1927), Walter and Barratt (1929), Wieland (1929, 1946), Oeser (1935), Subbaraya, Rao and Rao (1935), Cornell (1938), Howell (1943), Ramasastry and Rao (1946) and Ramasastry (1947, 1949). ]. In what follows the previous works of these workers on the molecules cadmium chloride, cadmium bromide and cadmium iodide are separately reviewed.

### (1) CADMIUM CHLORIDE

The band spectrum of cadmium chloride was first investigated by Wieland (1929) in the course of his extensive study of the halides of zinc, cadmium and mercury. During this study the spectra were mainly excited by a high-frequency oscillator. Even though the halides of mercury were found to give several systems, comparatively a few systems were reported by Wieland for the halides of cadmium. For cadmium chloride, he has reported the existence of two groups of bands. The first of these groups lies between λλ6400-3600 A.U. and consists of diffuse bands, degraded towards the longer wavelength side. The second one of these groups of bands was reported to occur between λλ 3400-3300 A.U. and consisted of sharp bands, degraded towards the shorter wavelength side. Cornell (1938) obtained the ultra-violet band spectra of the chlorides of zinc, cadmium and mercury excited by a high-frequency discharge. For cadmium chloride, he reported a brief system consisting of seven bands degraded towards the red and lying between λλ 2240-2185 A.U. Cornell made an important observation that all the ultra-violet spectra studied by him occur near the resonance lines of the respective metal atoms. The cadmium resonance line lies at 2288 A.U. and the system extends towards the shorter wavelength side of this line. This fact enabled him to correlate the various molecular states with probable dissociation products. The detailed discussion of the molecular states will be given in chapter (6).

A systematic attempt to regularize the band systems of zinc, cadmium and mercury halides was made by Howell (1943). Howell arranged the three groups of bands of cadmium chloride reported by Walter and Barratt (1929) and lying in the region λλ 3181-3080 A.U. into a doublet system represented by the transition $^2\Pi \rightarrow {}^2\Sigma$ and having a $^2\Pi$ interval of 1115 $cm^{-1}$.

The investigation on the spectrum of cadmium chloride was again undertaken by Ramasastry (1947), who reported altogether nineteen bands for the Cornell system (1938) lying between λλ2240-2181 A.U. In addition to extending the system of bands he also determined accurately the vibrational constants for the ground and excited states. They are as under :

$$\omega_e'' = 330.9 \ cm^{-1}, \qquad \omega_e''x_e'' = 1.0 \ cm^{-1}.$$
$$\omega_e' = 264.0 \ cm^{-1}, \qquad \omega_e'x_e' = 7.5 \ cm^{-1}.$$

Isotopic components for (0,1) and (1,2) bands were also reported by him. He further observed the absence of emission bands, recorded by Walter and Barratt (1929) in the region λλ3181-3018 A.U. during their studies on the absorption spectra of cadmium chloride molecule. He also reported the bands in the regions $\lambda\lambda$ 4800-4000 A.U. and $\lambda\lambda$6400-5400 A.U. In the former region he found twenty three diffuse bands degraded towards the red side. These were measured but their analysis was not given whereas in the latter region no measurements were made.

The above findings in the case of cadmium chloride molecule are ~~elegantly~~ summarised in table 1 (Page 20).

Very little work appears to have been done on the absorption spectra for the cadmium chloride molecule. In course of the extensive study on the absorption spectra associated with the metals, zinc, cadmium and mercury, Walter and Barratt (1929) first reported three groups of bands for the cadmium chloride molecule lying in the regions (i) $\lambda\lambda$ 3181-3135 A.U., (ii) $\lambda\lambda$3104-3077 A.U. and (iii) $\lambda\lambda$3074-3018 A.U. More systematic study on the absorption and fluorescence spectra of the halides of zinc and cadmium was made by Oeser (1935) who confirmed the assignment of the bands in the region $\lambda\lambda$3181-3018 A.U. to the cadmium chloride molecule. Measurements of about twelve absorption

## TABLE 1

## AVAILABLE SPECTROSCOPIC DATA ON CdCl MOLECULE.

| System | Region in A.U. | Probable transition | Occurance | Degradation and nature of the bands. |
|---|---|---|---|---|
| | 2163-1774 | – | In absorption only. | |
| Cornell (E) | 2240-2181 | $^2\Sigma - {}^2\Sigma$ | In emission only. | Sharp red-deg. bands. |
| Howell (D) | 3181-3115 | $^2\Pi - {}^2\Sigma$ | In absorption only. | Violet degraded bands. |
| (C) | 3104-3018 | | | |
| | 3400-3300 | – | In emission only. | Violet degraded bands. |
| | 4700-4050 | – | In emission only. | Diffuse Red Deg. bands. |

bands in the far ultra-violet region lying between λλ2163-1774 A.U. were also reported by him. It must be remarked here that the bands reported by Walter and Barratt and Oeser as lying in the region λλ3181-3018 A.U. could not be observed by Ramasastry during his work on emission spectra as reported above.

## (2) CADMIUM BROMIDE

Using high-frequency discharge Wieland (1929) obtained the band spectra of the cadmium bromide molecule in the region λλ3250-3120 A.U. It consisted of sharp and intense bands degraded towards violet with six sequences of which (0,0) band was lying at λ3176.65 A.U. He also listed three unclassified bands at λ3395.1 A.U., λ3092.5 A.U. and 3075.4 A.U. From an analogy with the band systems of the halides of zinc, cadmium and mercury, Howell (1943) suggested that the bands obtained by Wieland form one of the component of the transition $^2\Pi - {}^2\Sigma$ but could not succeed in observing the other one. Some additional bands were obtained by Ramasastry (1949). These were attributed to the missing component of the Wieland system. Wieland (1929) also mentioned the occurance of the diffuse bands extending from $\lambda\lambda$6400-3300 A.U. Using high-frequency source, Ramasastry obtained these visible bands extending from $\lambda\lambda$4800-3900 A.U. Measurements of about fifty bands were reported and regularity of intervals was indicated which was of the order of about 110 $cm^{-1}$. No measurements in the red region were made by him. Table 2 (Page 23) gives the present state of knowledge regarding the band spectra of the cadmium bromide molecule, covering the range from red to ultra-violet region.

Walter and Barratt (1929) studied the absorption spectra of various compounds of zinc, cadmium and mercury. They reported about twelve bands in the region $\lambda\lambda$ 3351-3070 A.U. These were attributed to cadmium bromide molecule. However the measured wavelengths of these bands agree closely with TlBr absorption band heads (Butkow 1929). This led Pearse and Gaydon (1963) to suggest that these bands were due to TlBr molecule and not due to cadmium bromide molecule.

## TABLE 2

## AVAILABLE SPECTROSCOPIC DATA ON CdBr MOLECULE

| System | Region in A.U. | Probable transition | Occur~~a~~ence | Degradation and nature of the bands |
|---|---|---|---|---|
| Wieland's system | 3250-3120 | $^2\Pi - {}^2\Sigma$ | In emission only. | Violet degraded and sharp intense bands. |
| Visible system | 4900-3850 | — | In emission only. | Red degraded diffuse bands. |

## (3) CADMIUM IODIDE

Wieland (1929) also studied the emission spectra of cadmium iodide. His analysis indicated that the spectra emitted by the diatomic molecule cadmium iodide could be divided into three groups. According to him, the spectrum emitted by the halides of zinc, cadmium and mercury salts can be divided into three groups denoted by I, II and III. Group I consists of bands in the ultra-violet region with recognizable heads, which can be ascribed to diatomic molecules. Bands of this group have been analysed by Wieland in the case of Hgcl, HgBr and HgI, CdBr and CdI and ZnI. Group II is made up of bands which show little regularity and are ascribed to triatomic molecules. Bands of group III, are very faint, diffuse and without sharp heads. A complete vibrational analysis of group I was given by him, and the visible system (Group III) was first ascribed to the triatomic molecule of cadmium iodide but his later work on this molecule indicated that this system too was due to diatomic molecule.

The study of the band spectra of the halides of group II(b) elements was made by Howell (1943), Rao and others (1944a, 1944b, 1946). They established that these molecules (including cadmium iodide) gave rise to band systems corresponding to the electronic transition $^2\Pi-^2\Sigma$ and electronic width of the $^2\Pi$ term was related to the corresponding atomic interval of the metal atom and that transition was between non-binding or atomic orbitals. Howell suggested that the system analysed by Wieland in the region $\lambda\lambda$3500-3250 A.U. was one of the components of the predicted $^2\Pi-^2\Sigma$ systems, the other missing component should be searched from among the fragmentary group in the vicinity of $\lambda$3550 A.U. mentioned by Wieland.

Later work on this molecule was reported by Subbaraya, Rao and Rao (1935) in the extreme red region. Using a 1/2 Kw, 10 Kv transformer and with the electrodes cooled by a stream of water, they excited the molecule. The photographs were taken with a Hilger $E_1$ spectrograph and 10 ft. concave grating spectrograph in a Rowland mounting in the first order. They analysed the spectrum in the region $\lambda\lambda$6350-5693 A.U. but the vibrational constants obtained by them, for the ground state do not agree with those obtained for ultra-violet systems.

The system of bands in the ultra-violet ( λλ 2473-2364 A.U.) recorded by Wieland (1929) was extended further and their vibrational formula was derived by Ramasastry (1946). It was interpreted as probably due to the transition $^2\Sigma - ^2\Sigma$ the lower $^2\Sigma$, state being the ground state of the molecule. Table (3) (page 27) incorporates the present state of knowledge of the cadmium iodide molecule with reference to the regions, probable transitions, occurance, nature and degradation of the various band systems.

## PROBLEM

From the above historical survey, on the investigations of the spectra of halides of cadmium and data given in tables (1), (2) and (3) one concludes that for the molecules cadmium chloride and cadmium iodide the band systems occur corresponding to metal resonance line $^1P - ^1S$. These band systems are related to the resonance line in the same way as $^2\Pi - ^2\Sigma$ systems to the $^3P - ^1S$ lines. These systems are assigned to a transition $^2\Sigma - ^2\Sigma$. No such system, however, has been found in the case of cadmium bromide. Such a

## TABLE 3

## AVAILABLE SPECTROSCOPIC DATA ON CdI MOLECULE

| System | Region in A.U. | Probable transition | Occurance | Degradation and nature of bands. |
|---|---|---|---|---|
| E | 2550-2350 | $^2\Sigma - {}^2\Sigma$ | In emission | Red degraded bands. |
| D | 3500-3250 | $^2\Pi_{3/2} - {}^2\Sigma$ | In emission, in absorption, and in fluorescence | Violet degraded bands |
| C | 3600-3500 | $^2\Pi_{1/2} - {}^2\Sigma$ | In emission | Violet degraded bands |
|  | 6600-3600 | – | Low pressure discharge tube and in fluorescence | Diffuse and line like bands; degraded to longer wave length. |

system should be present for the cadmium bromide molecule, and may be displaced more towards red as compared to that of cadmium chloride and more towards violet as compared to cadmium iodide. A reinvestigation of the spectrum of cadmium bromide as compared to that of cadmium chloride and cadmium iodide in this region was therefore taken up.

Besides these ultra-violet systems, there is evidance of a system, probably ${}^2\Sigma - {}^2\Sigma$ occurring near to ${}^2\Pi - {}^2\Sigma$ system. Such a system has been observed to be mixed up with $\lambda\lambda$ 2700-2900 A.U. system of mercury chloride (Krishnamurthy 1958) and the perturbation observed in the case of mercury fluoride may be due to the presence of a ${}^2\Sigma$ state. It is also observed by Rochester and Olsson (1939) that a similar system exists in the case of zinc fluoride and there is definate evidence of interaction between ${}^2\Sigma$ and ${}^2\Pi$ upper states. In any case there is definite evidence of the existance of ${}^2\Sigma$ state having nearly the same energy as that of ${}^2\Pi$ state. It is therefore imperative to reinvestigate the regions in which C and D systems of these molecules occur and the present work reports the D' systems in the case of cadmium bromide and cadmium iodide but due to fragmentary nature of the systems, complete analysis could not be given.

In the light of later work reported by Wieland on the spectra of halides of mercury and the work reported by Ramasastry on the halides of cadmium, it has been established beyond doubt that the diffuse bands in the visible region for all these molecules belong to respective diatomic molecules only. It has been suggested that these bands appear better in the inert atmosphere and in low vapour pressure high-frequency discharges. No attempt so far has been made towards the analysis of the bands in the visible region for these molecules. A systematic approach towards the study of the bands of these molecules in the visible region was therefore desirable, mainly because, low lying states have been involved in the transitions. The present author has successfully analysed the bands of the halides of cadmium (except CdF) in the lower visible region. The study of the visible systems in the case of cadmium chloride and cadmium bromide molecules is already reported (Patel and Patel 1966).