CHAPTER II

HISTORICAL SURVEY

The spectroscopic studies on the halides of mercury were extensively carried out by Wieland (1929, 1939) along with the halides of zinc and cadmium. The band spectra of these molecules were investigated in various details by several workers (Lohmeyer, 1906; Franz et al., 1925; Mulliken, 1925; Ternin, 1927; Wieland, 1929, 1932, 1937, 1939, 1941, 1946, 1948, 1949, 1960; Prileshajewa, 1932; Duschinskya, 1935; Subbaraya, 1937; Cornell, 1938; Sastry, 1941, 1942; Rao A.L.S., 1942; Howell, 1943; Rao K.R., 1944, 1946, 1947; Rao V.R.,1944; Ramsastry, 1946, 1947, 1948, 1952; Krishnamurthy, 1958, 1960; Patel M.M. et al.,1967). A brief review of the work reported so far on the spectra of mercury chloride, mercury bromide and mercury iodide is given here.

(i) MERCURY CHLORIDE:

The spectrum of mercury chloride in the visible region was first observed by Lohmeyer (1906), Franz (1925) and Ternin (1927). Wieland (1929) made a detailed report on the spectrum of the molecule in the region 7000 A° to 2300 A° using Geisslar discharge tubes and prism spectrograph having a maximum dispersion of 10 A°/mm. He conveniently classified the observed bands under three heads - class I bands in the region 2650-2400 A°, class II bands in the region 2900-2700 A° and class III bands in the region 5700-3000 A°.

The class I bands degraded to shorter wavelengths were analysed by him completely. The system was ascribed to diatomic mercury chloride molecule. The isotope effects due to chlorine and mercury were observed. Cornell (1938) in his high dispersion studies also observed the isotope effect and the bands were resolved into P and Q heads. The system was considered as one of the components of a $^2\pi - {}^2\Sigma$ transition with the (0,0) band at 39728 cm^{-1}.

The class II bands in the region 2900-2700 A° were described by Wieland (1929) to be degraded to shorter wavelengths and were supposed to be due to triatomic mercury chloride molecule because of their complex appearance. In a subsequent paper (1932) he referred to a poorly established interval of 290 cm^{-1} but no systematic analysis was attempted. Later on, Cornell (1938) photographed these bands along with the OH impurity bands. The bands were assumed to form close sequences of Q heads. However, the vibrational constants derived by him did not show any level in common with the down ultraviolet system. The system was considered to be diatomic in origin. Sastry (1941) reanalysed the above mentioned bands as Q_1 heads. In addition to them he obtained a few more bands which were arranged to form the sequence of Q_2 heads. He attributed all the bands to a $^2\pi — {}^2\Sigma$ transition with a doublet interval of 90 cm^{-1}. But like Cornell he also did not take into account some of the intense bands. Howell (1943) during his extensive studies on the halides of zinc, cadmium and mercury suggested that the bands in the region 2900-2700 A° may form one of the components of the $^2\pi — {}^2\Sigma$ transition, the other component being in the region 2650-2400 A° with a doublet separation of 3200 cm^{-1}. In view of this discrepancy, Krishnamurthy (1958) reinvestigated these bands at a dispersion of 3.5 A°/mm. What Cornell and Sastry had taken as the close sequences were considered by him as the rotational structure of the individual bands. He suggested the possibility of regarding all the bands in the region 2900-2700 A° to form a single system with the (0,0) band at 36392.2 cm^{-1}. But as a somewhat abrupt increase in the interval and intensity was observed among the bands, he was inclined to suggest another possibility of considering some of them to form a different band system with (0,0) and (0,1) bands at 35553.5 cm^{-1} and 35261.8 cm^{-1} respectively. This group of bands was then assumed to form the second component of the $^{2}\pi - {}^{2}\Sigma$ transition and thus a doublet interval of 838.7 cm^{-1} could be observed. The isotope effect due to chlorine could not be observed because of the presence of rotational structure and the weaker P heads.

The class III bands of mercury chloride molecule described by Wieland extend from 5700 A° to 3000 A° and were obtained in emission, chemiluminescence and fluorescence (Wieland, 1929 and 1941). Bands were described to be complex and diffuse and they were degraded on either side with intensity maxima at 5550 A°. A detailed vibrational analysis was carried out for large number of bands and the change of degradation amongst them was interpreted by including a cubic term in the vibrational quantum formula. Presence of isotope effect of chlorine was observed for a large number of bands and the system was assigned to a transition $^{2}\Sigma - {}^{2}\Sigma$. In the later work by Wieland (1960), the products of dissociation and dissociation energy of the molecule were discussed in detail.

The available spectroscopic data of the mercury chloride molecule is collected in table I.

(ii) MERCURY BROMIDE:

The spectrum of mercury bromide was first observed by Lohmeyer (1906) in the visible region. The molecule was subjected to detailed investigation by Wieland (1929), the experimental set up being the same as in the case of mercury chloride. The bands ranging from 7000 A° to 2300 A° were divided into three classes as follows:

Class I : 2665 - 2430 A°
Class II : 2900 - 2700 A°
Class III : 5000 - 3200 A°

An exhaustive vibrational analysis of the class I bands was reported and the bands were considered to be due to a triatomic molecule. Isotope effect due to bromine and mercury was established for a large number of bands. Sastry (1941) in his studies on the spectrum observed a few more bands and the group of bands in the region 2650-2400 A° was considered by him to be diatomic in origin and an electronic transition $^2\pi$ — $^2\Sigma$ was suggested.

The class II bands described by Wieland (1929) were shaded to shorter wavelengths and were attributed to triatomic mercury bromide molecule. Sastry (1941) obtained these bands

TABLE I

AVAILABLE SPECTROSCOPIC DATA ON MERCURY CHLORIDE 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) $^2\Sigma - (X)^2\Sigma$	Emission, absorption, fluorescence and chemiluminiscence	5700-3000	Complex, diffuse and shaded on either side	23421	192.0	0.5	292.61	1.6025	Wieland (1941, 1960)
(C) $^2\pi_{\frac{1}{2}}-(X)^2\Sigma$	Emission, absorption and photo-dissociation	2900-2750	Broad and diffuse on shorter wave-lengths and violet degraded	36472.5	285.1	0.4	279.7	0.6	Cornell (1938)
				36473.6	285.6	0.5	280.2	0.5	Sastry (1941)
				36564.2	287.8	0.5	281.0	0.5	
				36546	385		292.5		Krishnamurthy (1958)
(D) $^2\pi_{\frac{3}{2}}-(X)^2\Sigma$	Emission	2637-2380	Violet degraded	39700.5	341.4	1.71	292.5	1.69	Wieland (1929)
				39725.0	339.68	1.724	290.80	1.704	Wieland (1932)
				39703.5	341.8	1.87	293.4	1.82	Cornell (1938)

in uncondensed discharge and photographed them on a quartz Littrow spectrograph. A vibrational analysis was reported for these bands and isotope effect due to bromine was accounted. The bands were attributed by him to diatomic molecule and the probable electronic transition was suggested to be $^2\Sigma - {}^2\Sigma$. As in the case of HgCl, Howell (1943) assumed it reasonable to consider this group of bands as one of the components of a $^2\pi - {}^2\Sigma$ transition, giving a doublet separation of 3900 cm^{-1}, the other component being in the region 2665-2400 A°. In view of this, Krishnamurthy (1958) reinvestigated these bands at a dispersion of 3.5 A°/mm. The bands in the range 2930-2835 A° were found intense, simple and normal in appearance and the (0,0) band may lie within this region. These bands were analysed under the assumption that the structure accompanying the intense heads was the rotational structure of the individual bands. Isotope effect of bromine could not be observed on account of the rotational structure and the weaker P heads. A group of bands lying in the limit 2835-2770 A° was observed to be crowded and complex in appearance and they could not be arranged along with the group of bands on the longer wavelength side. These two groups of bands were ascribed to an electronic transition $^2\pi - {}^2\Sigma$ with a $^2\pi$ interval of 969.4 cm^{-1}. Krishnamurthy (1958) also reported the existence of another group of bands in the range 2792-2770 A° which were broad and weak in intensity. They were reported to show double headed nature with about 15 cm^{-1} as an almost constant separation between the two components. The vibrational frequencies of 177 cm^{-1} and 226 cm^{-1} for the lower and upper levels respectively were suggested and the system was assumed to be due to a transition $^2\Sigma — ^2\Sigma$.

The visible spectrum of mercury bromide molecule extending from 5000 A° to 3200 A° was first observed by Lohmeyer (1906). The wavelengths of the bands were known from the unpublished data of Wieland (B. Rosen et al.,1951). The bands were complex and diffuse and lying over a general continuum. Wieland (1939) carried out in detail a vibrational analysis for these bands. A reversal of shading among some bands was observed and was interpreted by including a cubic term in the quantum formula representing the bands. The system was ascribed to a transition $^2\Sigma — ^2\Sigma$. In a later work (1960) he discussed the products of dissociation and the energy of dissociation of the molecule.

Rao et al. (1944) reported a new group of bands in the range 2470-2430 A°. A vibrational analysis for these bands was carried out by considering them as close sequences with the (0,0) band at 40711 cm^{-1}. The system was assigned to a probable transition $^2\Sigma — ^2\Sigma$. However, Rosen (1954) has expressed some doubt about the vibrational constants derived by them.

The available spectroscopic data on the mercury bromide molecule is given in table II.

(iii) MERCURY IODIDE:

The spectrum of mercury iodide was subjected to detailed investigations in emission by various workers and a large number of band systems were found to exist for the molecule. An extensive study of this molecule was carried out by Wieland (1929) along with the other halides of mercury and again the bands were classified under three heads:

Class I : 2700-2530 A°
Class II : 3100-2800 A°
Class III : 5000-3400 A°

Prilheshejeva (1932) obtained a group of bands degraded to red for mercury iodide molecule in the region 2400-2100 A°. A complete analysis of these bands was not known until Ramsastry et al. (1947) photographed them in emission at a dispersion of 5 A°/mm. The vibrational analysis of the bands revealed that the bands arise due to two different electronic transitions. The bands in the region 2170-2110 A° were ascribed to a $^2\Sigma$ — $^2\Sigma$ transition and the other group of bands lying in the region 2230-2165 A° to a $^2\pi$ — $^2\Sigma$ transition. The

TABLE II

AVAILABLE SPECTROSCOPIC DATA ON MERCURY BROMIDE 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) $^2\Sigma$ - $(X)^2\Sigma$	Emission, fluorescence and chemi-luminiscence	5080-3200	Complex, diffuse and shaded on either side	23485	135.3	0.3	186.25	0.975	Wieland (1939)
				23485	135.075	0.275	186.47	0.9665	Wieland (1960)
(C) $^2\pi_{\frac{1}{2}}$-$(X)^2\Sigma$	Emission, absorption	2940-2700	Broad and diffuse on shorter wave-lengths and violet degraded	34537.8	459	3.6	372.8	3.8	Sastry (1941)
				34724.5	275.8	2.1	186.1	0.6	Krishna-murthy (1958)
				35702.6	254.6	1.3	183.0	1.0	
(D) $^2\pi_{\frac{3}{2}}$-$(X)^2\Sigma$	Emission and photo-dissociation	2665-2470	Violet degraded	38574.4	228.5	0.95	186.25	0.975	Wieland (1929)
				38595.5	227.5	0.95	185.3	0.975	Wieland (1932)
(E) $^2\Sigma \rightarrow (X)^2\Sigma$	Emission	2470-2438	Red degraded	40720	166	1.1	183	2.0	Rao et al. (1944)

bands belonging to the other component of this $^2\pi$ — $^2\Sigma$ transition were later on observed by Ramsastry (1948) in the region 2534-2450 A° and a doublet separation of 5490 cm^{-1} was noticed. Two more groups of bands lying in the range 2437-2381 A° and 2350-2265 A° were studied by him (1948,1952). The former of these two groups was considered more probable to be resulting from the transition between two excited states.

A brief group of four headed bands degraded to red was observed by Sastry (1942) around 2540 A° and a $^2\pi$ — $^2\Sigma$ transition with a $^2\pi$ interval of 126 cm^{-1} was suggested. Another group of bands shaded to red in the range 2610-2530 A° was observed by him and was assigned to a $^2\pi$ — $^2\Sigma$ transition with an electronic separation of 766 cm^{-1}. However, the vibrational frequency for the lower state was reported to be 55 cm^{-1} for this system. Krishnamurthy (1960) reinvestigated this group of bands and considered the lower state to be the ground state and upper state to be the $^2\pi$ state with an electronic separation of 858.9 cm^{-1}.

A large number of violet degraded bands lying in the ranges 2800-2650 A° and 3100-2850 A° were obtained by Wieland (1929). In a later work (1932) he considered the origin of the bands as due to diatomic mercury iodide and approximate vibrational formulae for the two group of bands were derived.

Rao et al. (1944) reinvestigated the two group of bands and attributed them to the two components of a $^2\pi$ — $^2\Sigma$ transition with a $^2\pi$ interval of 3538 cm^{-1}. The ν_e value for the shorter wavelength component was preferred to fix at 36295.5 cm^{-1} which was 160 cm^{-1} far from that considered by Wieland.

The visible spectrum of HgI molecule was first observed by Lohmeyer (1906). Mulliken (1925) obtained the spectrum in an N_2 after-glow of a discharge passing through the vapour of mercury iodide. Ternin (1927) reported the wavelengths for these bands. Wieland (1929) described these bands to be complex, diffuse and lying over a general continuum. Subbaraya et al. (1937) first suggested a vibrational analysis for them. The vibrational constants derived by them did not show any level in common with the lower levels for the other systems of this molecule. Wieland (1948, 1960) carried out a detailed vibrational analysis for a large number of bands and the products and the heats of dissociation for the molecule were also discussed.

The available spectroscopic data on the mercury iodide molecule is displayed in table III.

TABLE III

AVAILABLE SPECTROSCOPIC DATA ON MERCURY 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}
(B) $^2\Sigma$-(X) $^2\Sigma$	Emission, fluorescence and absorption	4520-3600	Complex, diffuse and lying over a continuum	24293	110	0.25
				24187.1	110.45	0.15
(C) $^2\Pi_{\frac{1}{2}}$-(X) $^2\Sigma$	Emission, Absorption and fluorescence	3095-2800	Extensive and violet degraded	32784	233.3	2.25
				32730	235.6	2.16
(D) $^2\Pi_{3/2}$-(X) $^2\Sigma$	Emission, absorption and fluorescence	2809-2647	Extensive and violet degraded	36130	175	-
				36269.2	178.0	1.14
(E) $^2\Pi$- $^2\Sigma$	Emission	2657-2606 and 2601-2545	Red degraded	38022.1	44.2	0.4
				38786.7	47.7	0.8
				38507.5	100.4	1.14
				39369.1	97.9	0.9

PROBLEM:

From the above description of the work reported by the earlier workers on the spectra of halides of mercury in the ultraviolet region it can be noticed that the mercury iodide molecule exhibits about seven band systems, while the molecules mercury chloride and mercury bromide reveal not more than three systems each. It was hence of interest to search for the missing analogues in these molecules. Further, Howell (1943) made the important suggestion that the C and D systems observed for the halides of mercury occurring in the regions 2800-2600 A° and 3100-2800 A° correspond to the $^3P - {}^1S$ resonance line of mercury at 2536.5 A° and they should be assigned to an electronic transition $^2\pi - {}^2\Sigma$ having a doublet separation which is related to the ^3P width of the corresponding metal (Hg) atom. A theoretical value for coupling constant 'a' for the 6p electron of 6s6p, ^3P mercury was shown to be $\frac{2}{3} \times 6398 = 4295$ cm^{-1}. The corresponding molecular constant giving rise to a $^2\pi$ state was given to be A = 3940 cm^{-1}. It was shown that a little change in the doublet splitting may occur with the change of a halogen atom of the molecule. The analogous systems in the halides of zinc and cadmium were also found to be related to their respective $^3P - {}^1S$ resonance lines and the doublet splitting observed also agree quite well with the theoretically calculated values. Although the doublet intervals observed for mercury fluoride (Howell, 1943) and for mercury iodide (Rao et al. 1944) are consistent with the theoretically predicted value, the intervals observed for HgCl and HgBr (Krishnamurthy,1958) are altogether different. Moreover, Deslandres tables reported by Krishnamurthy for mercury chloride and mercury bromide indicate irregularity of interval and intensity. In view of this ambiguity it was felt fruitful to reinvestigate the ultraviolet spectra of HgCl and HgBr.

In the analyses of the C and D systems for the halides of mercury the only decisive test while assigning them to a $^2\pi$ — $^2\Sigma$ transition was the presence of Q heads in the bands which in most of the cases overlap with the isotopic heads. It was therefore thought desirable to use maximum available dispersion to resolve some of the intense heads and study their rotational structure, thereby one could fix the nature of the electronic transition without any ambiguity. The D system of the molecule HgCl was selected for this purpose.

Zinc chloride (Cornell, 1938), cadmium chloride (Ramsastry, 1947) and cadmium iodide (Ramsastry, 1948) reveal band systems corresponding to the ^1P - ^1S line of their respective metal atoms; all of which were suggested to be due to an electronic transition $^2\Sigma - {}^2\Sigma$. The analogous group of bands studied by Sastry (1942) and Krishnamurthy (1960) for mercury iodide occurring in the range 2650-2550 A° has been ascribed to a transition $^2\pi - {}^2\Sigma$. A reinvestigation of this group of bands in the lower ultraviolet region was desirable in view of the ambiguity regarding the upper state involved in the transition.