CHAPTER - II

HISTORICAL SURVEY

Study of the spectra of diatomic Lead chloride and Lead monoxide molecules has been carried out by several workers. In this chapter a historical survey of the work done on these molecules by previous workers is described.

LEAD CHLORIDE

Spectrum of PbCl molecule has been studied by various workers. Absorption spectrum of

PbCl was first reported by Barrett (1929) without offering any analysis. Popov and Neujmin (1932) studied the fluorescence spectrum of PbCl molecule at low dispersion in the region λλ 4100-5900 Å in which bands are degraded towards longer wavelength side. Rochester (1936) studied the spectrum in absorption and showed that Popov and Neujmin's analysis of PbCl is incorrect. He derived the following quantum equation to fit all the observed bands.

$$\nu = 21863.1 + 228.8(v' + \tfrac{1}{2}) - 0.795(v' + \tfrac{1}{2})^2 - 303.6(v'' + \tfrac{1}{2}) + 0.875(v'' + \tfrac{1}{2})^2 \quad .....(56)$$

Morgan (1936) also analysed the spectrum of PbCl molecule in the region λλ 4100-5900 Å. Vibrational constants obtained by him are in close agreement with those of Rochester. Following quantum equations were obtained by Morgan.

For $PbCl^{35}$,

$$\nu = 21866.9 + 228.6\,u' - 0.76\,u'^2 + 0.006\,u'^3 - 304.2u'' + 0.89\,u''^2. \quad .....(57)$$

For $PbCl^{37}$,

$$\nu = 21866.9 + 223.3\,u' - 0.72\,u'^2 + 0.006\,u'^3 - 297.1\,u'' + 0.85\,u''^2 \qquad .....(58)$$

where $u' = (v' + \frac{1}{2})$ and $u'' = (v'' + \frac{1}{2})$.

Wieland (1949) studied the B <—— X system of PbCl molecule, in absorption, in the region $\lambda\lambda$ 2591-2956 Å. Bands are double headed and are degraded towards shorter wavelength side. Following quantum equation was obtained by him

$$\nu = 35199.0 + 382.1\,u' - 1.05\,u'^2 - 304.2\,u'' + 0.89\,u''^2 \qquad .....(59)$$

Wieland (1952) reanalysed B ⟵ X system of PbCl molecule revealing isotope effect due to chlorine. He obtained dissociation energy of the molecule as 24600 cm^{-1}. Available spectroscopic data (Vibrational) for PbCl molecule is given in Table 1.

Rotational analysis of $A \longrightarrow X_1$ system of PbCl molecule has been carried out by Rao and Rao (1964). They observed single P and R branches in the rotational spectrum of $A \longrightarrow X_1$ system. (4,0),

TABLE - 1

AVAILABLE SPECTROSCOPIC DATA OF PbCl MOLECULE (VIBRATIONAL)

System Designation	Region Å	Occurrence	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
$A \longrightarrow X_1$	5170-4100	Absorption	Red degraded	21863.1	228.8	0.795	303.6	0.875	Rochester (1936)
	5900-4100	Emission	Red degraded	21866.9	228.6	0.7600	304.2	0.890	Morgan (1936)
	6100-4200	Emission	Red degraded	21863.1	228.6	0.795	306.6	0.890	Singh (1970)
$A \longrightarrow X_2$	8820-6260	Emission	Red degraded	13546.2	228.6	0.7600	321.6	0.300	Rosen (1970)
$B \longleftarrow X_1$	2956-2591	Absorption	Violet degraded	35199.0	382.1	1.05	304.2	0.890	Wieland (1949)
$B \longleftarrow X_1$	2956-2591	Absorption	Violet degraded	34977.5	386.3	1.36	304.2	0.890	Cordes (1966)

(6,0), (1,1) and (3,1) bands were analysed by them. The transition for A $\longrightarrow X_1$ system was proposed to be the case c ($\frac{1}{2}$ - $\frac{1}{2}$) type and rotational constants evaluated by them are given in Table 2.

The band spectrum of PbCl in the visible region was investigated in emission by Rochester and Morgan in absorption and was known to consist of an extensive series of bands degraded towards the red in the region $\lambda\lambda$ 4100-5900 Å. A vibrational analysis of the system designated as A —— X_1 was carried out for $PbCl^{35}$. The vibrational assignments of the bands have been well supported by a study of chlorine isotope effect.

Wieland and Newburgh (1952) reported the vibrational analysis of another system designated as B $\longleftarrow X_1$ of PbCl in the ultraviolet region ($\lambda\lambda$ 2960-2590 Å). The common lower state X_1 of the A $\longrightarrow X_1$ and B $\longleftarrow X_1$ systems is very well known as ground state of PbCl molecule. Rao and Rao (1964) described that the A $\longrightarrow X_1$ system of PbCl appears to be analogue of A $\longrightarrow X_1$ system of PbF and suggested to be arising due to the transition of type $^2\Sigma \longrightarrow {}^2\Pi_{\frac{1}{2}}$.

TABLE - 2

AVAILABLE SPECTROSCOPIC DATA OF PbCl MOLECULE (ROTATIONAL)

State	Band	Band Origin ν_o cm^{-1}	B_e cm^{-1}	$D_e \times 10^{-7}$ cm^{-1}	r_e A	$I_e \times 10^{40}$ gm cm^2	Reference
1	2	3	4	5	6	7	8
$A\ ^2\Sigma^+$	(1,1)	21750.23	0.102_5	-			Rao and Rao(1964)
		-	0.21550	3.1	1.6118		Philip (1979)
	(2,1)	-	0.2142	3.0			Philip (1979)
	(3,1)	22199.34	0.102_0				Rao and Rao(1964)
	(4,0)	22727.67	0.11862				Singh and Singh (1968)
		22725.70	0.101_7	0.60			Rao and Rao(1964)
			0.103	0.60^*	2.338	271.4^*	
	(6,0)	23166.70	0.11862		2.179	235.904	Singh and Singh (1968)
			0.10716		2.293^*	261.132^*	
		23165.42	0.100_5	0.60			

Contd.....

Contd.....Table-2

1	2	3	4	5	6	7	8
	(1,1)		0.116_3				Rao and Rao(1964)
			0.23825	1.5	1.5329		Philip (1979)
	(2,1)		0.2383	1.3			Philip (1979)
$X_1\ ^2\Pi_{\frac{1}{2}}$	(3,1)		0.116_3				Rao and Rao(1964)
	(4,0)		0.116_7	0.73			Rao and Rao(1964)
			0.10375				Singh and Singh (1968)
	(6,0)		0.10270				Singh and Singh (1968)
			0.116_7	0.73			Rao and Rao(1964)
			0.117	0.73	2.195*	239.4*	Rao and Rao(1964)

* Indicates B_e, D_e, r_e and I_e values in columns 4, 5, 6, and 7 respectively.

We may assume that Hund's case (c) applies to both, the ground state and the first excited state, i.e. the transition of the A ——> X_1 system is the case (c) ($\frac{1}{2}$ - $\frac{1}{2}$). This assignment is in agreement with the fact that only two branches P and R have been experimentally observed in all the bands of this system.

Singh and Singh (1968) have done rotational analysis of A ——> X_1 system of PbCl molecule. They obtained well resolved structure in which quite sharp and clear isotopic lines due to $^{208}Pb^{35}Cl$, $^{207}Pb^{35}Cl$, $^{206}Pb^{35}Cl$ were observed in the (6,0) band. Because of the greater isotopic separation, (6,0) and (4,0) bands were analysed. Both the bands show only two branches, single R and single P. The two branches are exactly superposed at low J values and separated only at very high J values.

The study of A ——> X_1 band system of PbCl molecule was extended upto 6100 Å towards longer wavelength side by Singh (1970). About 120 bands were observed in the region λλ4200-6100 Å. The bands were sharp and red degraded. The sequences were well formed and distinct. The isotopes of ^{37}Cl could not be resolved due to low dispersion and intensity. They were represented by

$$\nu = 21863.1 + [228.8(v' + \tfrac{1}{2}) - 0.795(v' + \tfrac{1}{2})^2] - [306.6(v'' + \tfrac{1}{2}) - 0.890(v'' + \tfrac{1}{2})^2] \quad .....(60)$$

In order to study the fine structure of A ——> X_1 system of PbCl molecule, Philip Mathew (1979) photographed the spectrum in the 5th order of the two meter plane grating spectrograph with a reciprocal dispersion of 0.9 Å/mm. (1,1) and (2,1) bands were found suitable for a detailed rotational analysis. Spectrograms reveal Q branch lines in addition to P and R branches, unlike the observations made by Rao and Rao (1964). Satellite branches were found weak in intensity. Analysis of (1,1) and (2,1) bands of A ——> X_1 system reveals that the amount of Λ - doubling for the lower state and spin splitting for the upper states are negligibly small and hence it was not possible to calculate it at the resolution and dispersion obtained in the spectrograms. Nature of the bands reveals that the transition is not the case c ($\frac{1}{2}$ - $\frac{1}{2}$) type as reported by earlier workers. Additional Q branch observed in the analysis supports the fact that the transition is a typical $^2\Sigma — ^2\Pi_{1/2}$ one. The rotational constants evaluated by him are collected in Table 2.

LEAD OXIDE

Spectrum of PbO molecule has been extensively studied in emission and absorption by various workers. A large number of band systems in the region extending from visible to vacuum ultra-violet has been reported. Eder and Valenta (1924) photographed, for the first time, the bands excited upon the introduction of lead chloride into an oxygen illuminating gas flame and believed the emitter to be lead monoxide.

Using the same method of excitation Lamprecht (1911) photographed the visible region at moderate as well as higher dispersions but did not succeed to resolve the fine structure.

Grebe and Konen (1921) used carbon arc containing ordinary lead chloride for exciting these bands. They photographed bands in the blue region only and noticed small isotopic shifts and difference in the degree of sharpness of the bands.

Mecke (1929) performed a partial vibrational analysis using Lamprecht's incomplete data. Since the spectrum appeared in an arc source with compounds of lead subjected to a variety of conditions, there was a great deal of speculation concerning the identity of the emitter.

Bloomenthal (1930), therefore photographed these bands again in an arc using uranium lead as well as ordinary lead in the first and second orders of a 21 ft Rowland grating and found that the calculated and observed isotopic shifts were in fair agreement confirming PbO as the emitter of the spectrum. Each strong line of ^{206}PbO in the band spectrum emitted by a the uranium lead arc in air is represented by three lines (^{206}PbO, ^{207}PbO and ^{208}PbO) with relative intensities in agreement with that in the band spectrum from an ordinary lead arc. The first and second orders of 21 ft Rowland grating were used to make this comparison. New measurements of the wavelength of the band heads were made using moderate dispersion spectrograms of the ordinary lead arc in air. The bands in the near ultra-violet were analysed to form a new system represented by

$$\nu = 30197.0 + [530.6\,(v' + \tfrac{1}{2}) - 0.05(v' + \tfrac{1}{2})^2] - [722.3(v'' + \tfrac{1}{2}) - 3.73(v'' + \tfrac{1}{2})^2] \quad .....(61)$$

Three systems in the visible have been discussed by Mecke (1929) showing that all of them have a common lower state.

Fine structure analysis of the bands in the A and D systems of lead oxide was carried out by Christy and Bloomenthal (1930). The bands of these systems are composed of single R and P branches only. Using combination relations, the rotational constants of the molecule have been determined. The internuclear distance of the common final state is found to be 1.9207×10^{-8} cm and that of the upper state is 2.0424×10^{-8} cm. No Q branch has been found in the structure of the bands of the two systems suggesting that all the electronic levels involved have the same value of $\Lambda = 0$. It is shown that the electronic levels of the two systems investigated are singlets.

Absorption spectrum of lead oxide has been photographed by Shawhan and Morgan (1935) and a new system designated as the E-system has been found. It is nearly coincident with the D-system. A number of previously unclassified bands together with some new are assigned to a new system replacing Mecke's (1929) C system. The D-system has been extended and the new value of $\omega'_e x'_e$ is changed from 1.05 to 3.13. The new system has the lower level in common with that of the A and B systems.

Later on, absorption spectrum of lead monoxide was studied in detail by Howell (1936) who recognised five band systems and suggested the existence of the sixth one also in the shorter wavelength side named as F <—— X system containing only seven bands, which was then analysed as E <—— X system by Vago and Barrow (1947) with different interpretation. Howell (1936) produced the band spectrum of PbO in absorption by using carbon arc furnace. The spectrum stretches from λ2600 to λ6000 Å and contains five systems of which three are found to exist in emission also.

The spectra of the related molecules like PbS, SnS, SnO, GeO, etc. show many similarities and in particular it is found that the vibrational frequency varies from state to state in a similar manner for oxide and sulphide molecules.

Christy and Bloomenthal (1930) carried out the rotational analysis of A and D systems and showed that all the electronic states involved have the value $\Lambda = 0$ and are singlet in nature. Resolution employed in this work was not enough to resolve the rotational structure properly, therefore, these workers could not detect Q branch lines in either of the two systems. From the analogy of the molecules of this group, electronic transitions predicted by these authors were not convincing. Therefore Barrow, Deutsch and Travis (1961) were led to revise the analyses. Torring (1964) has studied the geometry of ground state of PbO from microwave spetra.

Ram et al (1973) carried out the study of the structure of (1,0) and (1,1) bands of the B ——> X system and (0,1) and (0,2) bands of the D ——> X system in emission by photographing at sufficiently high resolution with a view to improve molecular constants and to study perturbations in the band structure. The nature and geometry of perturbing states have also been studied. In addition, several perturbations observed in the v' = 1 level of the B state and v' = 0 level of the D state have been studied. With the help of the Schmid and Yero relation (1935) and from the appearance of the perturbed structure, it has been concluded that the perturbing states have $\Omega = 1$ and their rotational constants are reported to be 0.2595 cm^{-1} and 0.2683 cm^{-1} respectvely.

Rotational analysis of the bands of both the systems reveal the presence of P, Q and R branches of which Q is intense thereby indicating a transition of the type $1 \longrightarrow 0^+$ predicted by Barrow et al (1961). Available spectroscopic data of PbO molecule is given in Tables 3 and 4.

ROTATIONAL TEMPERATURE

The thermal intensity distribution in a band can be employed for determining the temperature of the source of emission or absorption. The maximum of intensity in a branch of rotation or vibration-rotation band shifts towards higher

TABLE - 3

AVAILABLE SPECTROSCOPIC DATA ON PbO MOLECULE (VIBRATIONAL)

State		T_e cm^{-1}	ω_e cm^{-1}	$\omega_e x_e$ cm^{-1}	References
G		51661	540.5	6	Barrow (1970)
F		51153	558.5	3	Barrow (1970)
E	o^+	34454	454	7	Vago and Barrow (1947)
D	1	30198.7	530.5	2.92	Howell (1936)
C'	1	24947	494	3.0	Howell (1936)
C	o^+	23820	532	3.9	Howell (1936)
B	1	22285	498.0	2.20	Howell (1936)
A	o^+	19862.6	444.3	0.54	Bloomenthal (1930)
b	o^-	19454	441	-	Oldenborg et al (1975)
a	1	16024.9	481.5	2.45	Oldenborg et al (1975)
X	1^+	0	721.0	3.54	Torring (1964)

TABLE - 4

AVAILABLE SPECTROSCOPIC DATA ON PbO MOLECULE (ROTATIONAL)

State	ν_{oo} cm^{-1}	B_e cm^{-1}	$D_e \times 10^7$ cm^{-1}	α_e cm^{-1}	r_e cm^{-1}	References
E o^+	34320	0.239	-	0.0014	2.18	Barrow (1961)
D 1	30103.5	0.2711	0.28	0.0031	2.046	Ram et al (1973)
C' 1	24833	0.248	0.25	0.0018	2.14	Barrow (1970)
C o^+	23725	0.254	0.25	0.002	2.11	Barrow (1970)
B 1	22173.4	0.2646	0.30	0.0026	2.071	Ram et al (1973)
A o^+	19725.0	0.25869	0.33	0.00138	2.0946	Linton and Broida (1976)
a 1	15905.4	0.252	-	-	2.12	Linton and Broida (1976)
X $^1\Sigma^+$	-	0.3073056	0.223	0.0019148	1.921813	Torring (1964)

J values with increasing temperature according to the equation

$$J_{max} = \sqrt{\frac{kT}{2Bhc}} - 1/2$$

$$= 0.5896\sqrt{\frac{T}{B}} - 1/2$$

where c, k, h and B are constants.

Thus from the position of the maximum, the temperature of the source can be determined. More accurate and reliable value is obtained when the whole intensity distribution is measured. In the case of $\Sigma - \Sigma$ bands, from equation (55), the observed values of $\log \left\{ I_{em} / (K' + K'' + 1) \right\}$ against $K'(K' + 1)$ are plotted and a straight line is obtained, whose slope is used to calculate the value of the temperature.

Another method has been suggested and used by Knauss and McCay (1937). They determine for which values of J (or K) the intensity in two overlapping branches of a band is the same for equal or nearly equal wave number. This position shifts to larger J (or K) values with increasing temperature. Even if the fine structure of the bands is not resolved the shape of the band profile varies as a function of temperature and may be used for a determination of the temperature. This method was used by Smit-Miessen, Spier, and Smit (1942) for violet CN bands. They have used the peak intensities of the band heads to calculate rotational temperature. The logarithms of the sums of the strengths of all bands with a given initial state plotted against the vibrational energy of the initial state fall on a straight line whose slope is hc/kT from which temperature can be calculated. This method was first applied to the CN bands in the carbon arc by Ornstein and Brinkman (1931).

The band spectroscopic methods for the determination of temperature are naturally of high importance when the usual methods cannot be used; e.g. for determination of temperature of the electric Arc. Ornstein and Brinkman (1931) were the first to apply this method to the arc using the CN and A10 bands and Lochte, Holtgreven and Maecker (1937) obtained a temperature of 7600°K from the study of 3883 Å band of CN molecule.

It must be emphasized that the

temperatures thus obtained are the effective temperatures. They represent true temperatures only if either the excitation is strictly thermal or is of such a type that it does not affect the thermal distribution. However, in flames, frequently the rotational distribution indicates a higher effective temperature than the true temperature, since the excitation is due to chemical elementary reaction rather than the thermal collisions. This is suggested by Gaydon and Wolfhard (1939).

In recent years molecular spectra have become of increasing importance in the investigation of astrophysical problems.

PROBLEM

Spectroscopic properties of atoms and molecules depend upon their valence electrons. Atoms and molecules having same number of valence electrons will have similar optical spectra. Thus spectrum of one molecule can be compared to those of other homologous molecules. A study of spectra of molecules of different groups will help us to understand the effect of change in a number of electrons on energy levels and nature of the spectrum.

A detailed study of the historical survey of PbCl and PbO molecules described as above reveals that various workers have made fairly extensive study of these molecules only at low dispersion.

It has been observed by earlier workers (Rao and Rao, 1964) that $A \longrightarrow X_1$ system of PbCl molecule consists of bands having P and R branches using which they have calculated vibrational and rotational constants of the molecule. However, Philip Methew (1979) observed three branches identified as

P, Q and R and calculated vibrational and rotational constants which do not agree with the constants reported by previous workers. The observation of P, Q and R branches proves that the electronic transition case c (½ - ½) assigned by Rao and Rao (1964) is wrong. Thus it is thought worthwhile to reinvestigate the A ——> X_1 system of PbCl molecule at high resolution to evaluate accurate rotational constants and assign the correct electronic transition. The (2,1), (0,3), (0,4) and (0,5) bands of A ——> X_1 system of PbCl have been found suitable for the study of their rotational stucture. The (0,1), (0,2) and (1,0) bands of D ——> X system of PbO were employed for the determination of rotational temperature from the relative intensity measurements.

The work reported so far on the spectrum of PbO molecule has been nicely described by Ram et al. (1973). Though study of this molecule is extensive, it has been found that there is no report on the intensity measurements of the vibrational bands and rotational lines. No one has yet employed intensity measurements to study the vibrational and rotational temperature of the PbO molecule. Hence the author desired to make an attempt to caculate the rotational temperature along with rotational analysis of some of the suitable bands at high dispersion.

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