CHAPTER - VI

ELECTRON CONFIGURATION, RESULTS AND DISCUSSION

This chapter deals with the discussion of theoretically derived possible electronic states of PbCl and PbO molecules and their correlation with the experimentally obtained results during the course of present study.

Our knowledge of electronic states from their observed molecular spectra is complete only for few diatomic molecules and for many molecules, electronic states observed are not more than two or three. It is obvious that an understanding of the electronic states of molecules must be built upon a prior knowledge of electronic states of their constituent atoms. Wigner and Witmer (1928) have derived rules for determining what type of molecular states result from the given states of the separated atoms on the basis of quantum mechanics. These rules have been discussed in detail by Mulliken (1930, 1932) and Herzberg (1950).

The manifold of the electronic state can be obtained by bringing together the component atoms of a molecule or by splitting up of the hypothetical united atom. The two atoms that form the monochloride of Lead and monoxide of lead belong to different periods of the periodic table and thus have different nuclear charge. In such a case the closed shells of the separated atoms need not be considered (Lennard and Jones 1929) while determining electron configuration of the molecules.

ELECTRON CONFIGURATION AND ELECTRONIC STATES OF PbCl

It is sufficient for the practical purpose to consider only those electrons which are in the outermost incomplete shells. The ground state electron configuration of Pb and Cl atoms can be written as

$_{82}Pb$: $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^2$ $4p^6$ $4d^{10}$ $4f^{14}$
$5s^2$ $5p^6$ $5d^{10}$ $6s^2$ $6p^2$
$(K\ L\ M\ N\ O_{spd})\ 6s^2\ 6p^2$

and

$_{17}Cl$: $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^5$
$(K\ L)\ 3s^2\ 3p^5$

The possible low lying electronic levels of PbCl molecule can be derived from the low lying electronic levels of the separated atoms of Pb and Cl. In other words the PbCl molecule may be expected to dissociate into Pb (^3P_o) and Cl ($^2P_{3/2}$) atoms which are in their ground states respectively. For the total outer 11 electrons ($6s^2$ $6p^2$ of Pb and $3s^2$ $3p^5$ of Cl), the following distribution may be considered to obtain possible molecular states of PbCl. According to Mulliken's notation, the ground state electron configuration can be written as $(z\sigma)^2\ (y\sigma)^2\ (w\pi)^4\ (x\sigma)^2\ (v\pi)$ giving rise to the ground state X $^2\pi$. Then the first excited state of PbCl is obtained when $(v\pi)$ orbital electron is excited to the $(u\sigma)$ orbital, thereby giving rise to $A\ {}^2\Sigma^+$ state of PbCl i.e.

$(z\sigma)^2\ (y\sigma)^2\ (w\pi)^4\ (x\sigma)^2\ (u\sigma)\ :\ A\ {}^2\Sigma^+$.

Similarly $B\ {}^2\Sigma^+$ arises when $(v\pi)$ orbital electron is excited to the $(t\sigma)$ orbital i.e.

$(z\sigma)^2\ (y\sigma)^2\ (w\pi)^4\ (x\sigma)^2\ (t\sigma)\ :\ B\ {}^2\Sigma^+$.

The ground state $X\ {}^2\pi$ splits into two sub-states $X_1\ {}^2\pi_{1/2}$ and $X_2\ {}^2\pi_{3/2}$ due to spin - orbit coupling. Thus the bands of PbCl molecule existing in the regions λλ 8820 - 6260 Å, λλ 5900 - 4200 Å and λλ 2960 - 2590 Å are reported to be arising due to the electronic transitions

$A\ {}^2\Sigma^+ \longrightarrow X_2\ {}^2\pi_{3/2}$, $A\ {}^2\Sigma^+ \longrightarrow X_1\ {}^2\pi_{1/2}$ and

$B\ {}^2\Sigma^+ \longrightarrow X_1\pi_{1/2}$ respectively.

While dealing with the possible molecular states of PbCl, theoretical principle to understand the changes in shape and size of the molecule during the electronic excitation will now be discussed.

The molecular shape in an excited state is a property of the whole molecule and not of one part. This needs the adoption of molecular orbital (MO) view point. The MO method leads to a series of molecular orbitals into which we are to "feed" the electrons in an "aufbau" process. There are many electronic excitations that we call Rydberg type. In these, an electron is excited either from a bonding orbital or from a lone-pair orbital that goes into an orbital which closely resembles an excited hydrogenic orbital. Thus this outer electron is almost independent of the rest of the molecule and we have one electron excitation. Even when the Rydberg electron is in a huge outer orbital, its interaction with the remaining core part of the molecule is not purely electronic but also an exchange and a coulomb interaction (Murrel, Cool, Mulliken, Rice, Stamper and Coulson). The Rydberg electron does not see merely the effective positive charge at the centre of the core but it also sees a complicated electronic charge cloud with which it experiences exchange and coulomb interactions.

In any geometrical position of the atoms of a molecule, the force acting on any chosen nucleus may be computed by purely classical electrostatics. This theorem is due to Hellmann and Feynmann. If one electron is excited from MOψ to MOχ there will be a change in electron density represented by $\Delta\rho = \chi^2 - \psi^2$.

During the excitation the nuclei will not have enough time to move, and so suddenly, there are forces exerted on them. The Hellmann and Feynmann theorem will lead us to Berlin's bonding and antibonding regions.

Any small element of the charge cloud of the electrons exerts its own force on all nuclei, and will therefore, tend to increase or decrease the bond length and valance angles. We can divide the space into the so called bonding and antibonding regions. The idea of bonding and antibonding regions enables us to understand the changes taking place in the molecule during excitation. When an electron is excited from a bonding orbital to an antibonding orbital, vibrational frequency of the molecule will be lowered. Bonding properties of any electronic orbital depend on the number of electrons present, as we go from lighter to heavier molecules, effect of inter-electronic repulsion will become more predominant and there will be a change in the nature of bonding.

From the study of (4,0), (6,0), (1,1) and (3,1) bands of PbCl in the visible region Rao and Rao (1964) suggested that these bands are arising due to the electronic transition (½ ——> ½) in Hund's Case (c) which is analogous to the transition $A\ ^2\Sigma \longrightarrow {}^2\Pi_{1/2}$ of the similar molecule PbF, both the states belonging to Hund's Case (c). However Philip Mathew (1979) carried out the rotational analysis of (1,1) and (2,1) bands of $A \longrightarrow X_1$ system at a better dispersion. He observed three branches in the structure of both the bands, which he identified as P, Q and R branches. This was the presumption in anticipation that the two similar molecules PbCl and PbF may have analogous electronic transitions $A\ ^2\Sigma \longrightarrow X\ ^2\Pi$. Considering this, he performed rotational analysis of the above bands. Obviously the rotational constants evaluated by him did not agree with those reported by Rao and Rao (1964). Thus the electronic transition and rotational constants reported by above mentioned workers differ absolutely, demanding for the reinvestigation.

From the present work on the rotational analysis of (2,1), (0,3), (0,4) and (0,5) bands of A ——> X_1 system of PbCl it has been observed that the presumption of Philip Mathew (1979) is absolutely wrong. He was misled to identify the three branches as P, Q and R probably because of the poor resolution of the rotational structure. The spectrograms obtained during the present study reveal the presence of main P and R branches accompanied by other weak branch lines which may be attributed to isotopes of Pb and Cl. The lines are too close to account for isotopic shifts. Thus the present work confirms the work reported by Rao and Rao (1964). The study of intensity distribution in the rotational structure of the above bands was of great help to arrive at the conclusion that the transition involved in the emission of the above bands is ($\frac{1}{2}$ ——> $\frac{1}{2}$), both the states being in Hund's Case (c).

ELECTRON CONFIGURATION AND ELECTRONIC STATES OF PbO

The electron configuration of oxygen atom can be written as

$_8O$: $1s^2$ $2s^2\ 2p^4$

(K) $2s^2\ 2p^4$.

The possible electronic levels of PbO molecule can be derived from separated atoms of Pb and O by considering

(1) Both in ground state.

(2) Pb in ground state and O in an excited state.

(3) Pb in excited state and O in the ground state.

(4) Both in excited states.

The configuration of total outer 10 electrons ($6s^2\ 6p^2$ of Pb and $2s^2\ 2p^4$ of O) in the formation of PbO molecule is equivalent to that of CO molecule.

Now the lowest configuration in CO may be written as

.........$(z\sigma)^2\ (y\sigma)^2\ (w\pi)^4\ (x\sigma)^2$ .....(a)

..........$(z\sigma)^2\ (y\sigma)^2\ (w\pi)^4\ (x\sigma)\ (v\pi)$ .....(b)

and ....$(z\sigma)^2\ (y\sigma)^2\ (w\pi)^3\ (x\sigma)^2\ (v\pi)$ .....(c)

These configurations in Hund's Case (a) or (b) give rise to the following molecular states.

$^1\Sigma^+$

$^3\Pi_r$, $^1\Pi$ and

$^1\Sigma^+$, $^1\Sigma^-$, $^3\Sigma^+$, $^3\Sigma^-$, $^1\Delta$ and $^3\Delta$

respectively. In Hund's Case (c), the corresponding molecular states are

0^+

0^+, 0^-, 1, 1, 2 and

0^+, 0^+, 0^-, 0^-, 1, 1, 1, 2, 2, 3.

For PbO, the number of observed molecular states is greater than that predicted in Hund's Case (a) and (b). This indicates that some of the states arise due to Hund's Case (c). Qualitative observations on the intensity measurements of the electronic band spectra of PbO molecule in emission as well as absorption and the determination of characters of low lying states of this molecule confirm the above prediction.

Thus the ground state X is identified to be 0^+, the state arising due to the lowest electron configuration. From the configurations (a),(b) and (c) three 0^+ states have been observed at 19862 cm^{-1}, 23820 cm^{-1} and 34454 cm^{-1} designated as A, C and E states. Further, out of five 1 states corresponding to configurations (b) and (c), only three states at 22285 cm^{-1}, 24947 cm^{-1} and 30198 cm^{-1} designated as B, C' and D states are observed. The two unaccounted states of $\Omega = 1$ are predicted to be the perturbing states B and D. Similarly occurence of 0^- and 2 states may be possible through the interactions with the $\Omega = 1$ states. a(1) and b(0^-) levels are reported to be at 16024 cm^{-1} and 16454 cm^{-1}.

Thus the wellknown band systems of PbO molecule are reported to be arising due to the electronic transitions A (0^+) <——> X (0^+), B (1) <——> X (0^+), C (0^+) <—— X (0^+), D (1) <——> X (0^+) and E (0^+) <——> X (0^+).

The presence of P, Q and R branch lines of which Q and R forming heads clearly provides confirmative proof that the electronic transition giving rise to the bands of D ——> X system is 1 ——> 0^+. In otherwords change of the last antibonding $(x\sigma)$ electron from the configuration

$$(x\sigma)^2\ (y\sigma)^2\ (w\pi)^4\ (x\sigma)^2\ :\ {}^1\Sigma^+$$

to the $(v\pi)$ bonding electron in

$$(x\sigma)^2\ (y\sigma)^2\ (w\pi)^4\ (x\sigma)\ (v\pi)\ :\ {}^3\Pi_r,\ {}^1\Pi$$

configuration takes place. As a result corresponding decrease in the vibrational frequency $(\omega'_e < \omega''_e)$ of the molecule takes place. The nature of red degraded bands of D <——> X system is in accordance with theoretical expectations. Thus theoretically derived molecular states of PbO molecule can be verified with the help of experimental observations. Not only this but the experimental results explain very well the nature and behaviour of electronic levels.

DISCUSSION ON ROTATIONAL TEMPERATURE

As described earlier there is no work reported on the vibrational and rotational temperature of the PbO molecule. Author has obtained well defined and sharp single lines of P and Q branches of (1,0), (0,1) and (0,2) bands of D ⟶ X system by employing sufficiently high resolution. Relative intensity measurements of large number of rotational lines are done using microdensitometer and planimeter. Using the rotational constants and J numbering of rotational lines, rotational temperature of the source emitting D ⟶ X system of PbO has been calculated. The average value of this effective temperature turns out to be 4738.5° ± 126.3 °K. It is believed that the value of effective temperature remains fairly constant. This is supported by the fact that the position of intensity maximum in P and Q branches of the above bands remains fixed when the experimental conditions such as the slitwidth, time of exposure, intensity of the discharge, time of processing the plates are varied.

FURTHER PLAN OF WORK

The work on PbCl and PbO molecules carried out by author and described in this thesis is unfinished. It is planned to determine the vibrational temperature of PbO molecule from the study of relative intensity measurement of the vibrational band structure of various band systems. It is also proposed that the emission and absorption spectra of the halides and oxide of lead should be studied at very high resolution, using the techniques such as Laser Rotational Raman spectroscopy and Laser - induced fluorescence for the molecules existing in the distant hot stars and interstellar clouds. The study of interstellar molecule is very young field even today. This study has developed enormously ever since radio astronomical methods were applied to the observation of molecular spectra of interstellar clouds. The band spectroscopic methods of determining rotational and vibrational temperatures of a source is of great interest and important tool in the present context.