CHAPTER VII

ELECTRON CONFIGURATION AND CONCLUSIONS

In this chapter possible electronic states for diatomic molecules CaI, ZnI and InI along with the other monohalides will be discussed on theoretical basis and will be correlated with the experimental observations.

The knowledge about a large number 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 the electronic states of their constituent atoms. Wigner and Witmer (1928) on the basis of quantum mechanics, have derived rules for determining what types of molecular states result from given states of the separate atoms. 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 (building - up principle) or by splitting up of the hypothetical united atom. The two atoms that form CaI molecule belong to different periods of the periodic table and thus have different nuclear charges. In such a case the closed shells of the separated atoms need not be considered (Lennard and Jones 1929) while deriving electronic configurations of the molecule. It is thus sufficient for practical purpose to consider only those electrons which are in the outermost orbits.

7.1 ELECTRON CONFIGURATION FOR HALIDES OF CALCIUM

The electron configurations for atoms in Calcium halide molecules can be given as :

Ca : $K\ L\ M_{sp} 4s^2$

F : $K\ 2s^2\ 2p^5$

Cl : $K\ L\ 3s^2\ 3p^5$

Br : $K\ L\ M\ 4s^2\ 4p^5$

I : $K\ L\ M\ N\ 5s^2\ 5p^5$

Where K, L, M, ... represent the closed shells. In the Calcium atom only s and p sub-groups are filled in M shell.

Following the notations of Mulliken (1932) the lowest electronic configuration for CaI molecule may be written as

$$(K\ K\ L\ L\ M_{sp}\ M\ N)\ (z\sigma)^2\ (y\sigma)^2\ (w\pi)^4\ (x\sigma)$$

Where ($z\sigma$) and ($y\sigma$) represent the bonding and anti-bonding orbitals of the type ($4s\sigma_{Ca} + 5s\sigma_{I}, \sigma$) and ($4s\sigma_{Ca} - 5s\sigma_{I}, \sigma$). ($w\pi$) represents the bonding orbital

($5p\pi_I$, π) and ($x\sigma$) represents the bonding orbital of the type ($5p\sigma_I$, σ). This configuration gives the electronic state ${}^2\Sigma^+$ which must be the ground state for CaI molecule.

The molecules CaF, CaCl, CaBr and CaI are formed from the normal calcium atom (${}^1S_0$) and respective halide atoms in their ground state (${}^2P_{3/2}$). Thus one of the possible electronic states of these molecules is ${}^2\Sigma^+$ (Herzberg 1950) i. e.

$$\left.\begin{array}{l} 4s^2 \; {}^1S_g \; (\mathrm{Ca}) + 2s^2 \; 2p^5 \; (\mathrm{F}) \\ 4s^2 \; {}^1S_g \; (\mathrm{Ca}) + 3s^2 \; 3p^5 \; (\mathrm{Cl}) \\ 4s^2 \; {}^1S_g \; (\mathrm{Ca}) + 4s^2 \; 4p^5 \; (\mathrm{Br}) \\ 4s^2 \; {}^1S_g \; (\mathrm{Ca}) + 5s^2 \; 5p^5 \; (\mathrm{I}) \end{array}\right\} \cdots\cdots\cdots {}^2\Sigma^+$$

Probable electronic levels of CaI molecule can also be derived considering the separate atoms of Calcium and Iodine. The ground states of Ca and I atoms are (${}^1S_0$) and (${}^2P_{3/2}$) respectively. Hence the ground state of CaI molecule is expected to dissociate into Ca ($^1S_0$) and I($^2P_{3/2}$) atoms. The electronic terms that can be derived from Ca (^1S) + I (^2P) are $^2\Sigma^+$ and $^2\Pi$. An approach of the united atom will help to find out which out of the two states is a low lying state. Calcium has twenty electrons with the configuration,

$$1s^2 \quad 2s^2\ 2p^6 \quad 3s^2\ 3p^6 \quad 4s^2$$

and Iodine has fifty three electrons with the configuration,

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2 4p^6\ 4d^{10}\ 5s^2\ 5p^5.$$

The molecule CaI can be supposed to have been formed by splitting the united atom Tantalum (Ta) which has seventy three electrons with contiguration,

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^3\ 6s^2.$$

The normal electronic state of Ta is ^2S state. Hence the electronic term of CaI that results by splitting Ta atom is $^2\Sigma$. Therefore the ground state of CaI molecule can be fixed as $^2\Sigma^+$.

The correlation between various states of CaI molecule in separate atoms model to united atom Ta will give the nature of stability of molecular states. States formed by separate atoms model which can not correlate with the low lying states ^2S, ^2P, ^2D of the united atom Ta are unstable. Consider now Calcium atom in its first excited state and Iodine in the normal state. This will give rise to Ca (^3P_u) + $5s^2\ 5p^5\ 2P_g(I) \longrightarrow {}^2\Sigma^+$, $^2\Pi_{3/2}$, $^2\Pi_{1/2}$. These are the possible excited states for CaI molecule allowed by the selection rules and transition probability.

The electron configuration of the first excited A $^2\Pi$ state for CaI may be given as

$$(z\sigma)^2\ (y\sigma)^2\ (w\pi)^4\ (x\pi)\ \ldots\ldots\ldots\ {}^2\Pi_{3/2}$$

or $$(z\sigma)^2\ (y\sigma)^2\ (w\pi)^3\ (x\pi)^2\ldots\ldots\ldots\ {}^2\Pi_{1/2}$$

The next excited state B $^2\Sigma$ arises from

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

in which an electron from ($y\sigma$) orbital goes to ($x\sigma$) orbital.

The configuration

$$(z\sigma)^2\,(y\sigma)^2\,(w\pi)^4\,(x\sigma)^0\,(v\pi)\ldots\ldots\ {}^2\Pi$$

gives the C ${}^2\Pi$ state. The C - X systems for alkaline earth halides are red degraded. The relative lowering of vibrational frequency of C - state with respect to ground state can be explained as due to the transition of an electron from a bonding orbital ($x\sigma$) to an antibonding orbital ($v\pi$). The D ${}^2\Sigma$ state may be attributed to $(z\sigma)^2\,(y\sigma)^2\,(w\pi)^4\,(x\sigma)^0\,(v\pi)^0\,(u\sigma)\ldots\ldots{}^2\Sigma$. Similarly the electronic states for CaF, CaCl and CaBr can be derived. Since the electron configuraties of alcaline earth elements Be, Mg, Ca, Sr and Ba are very much alike, the schemes of electronic states of their corresponding monohalides show considerable similarities.

The most probable scheme of electronic states for halides of alkaline earth elements may be suggested as follows :

Ground state : $X\ {}^2\Sigma^+$
First excited state : $A\ {}^2\Pi$
Second excited state : $B\ {}^2\Sigma^+$

Third excited state : $C^2\Pi$

Fourth excited state : $D\ ^2\Sigma$

7.2 ELECTRON CONFIGURATION FOR HALIDES OF ZINC

The two atoms that form the diatomic halide molecule of Zinc belong to different periods of periodic table and thus have very different nuclear charges. As described earlier the lowest electronic configurations for the atoms in the present case are as follows :

Zn : K L M $4s^2$

Cl : K L $3s^2$ $3p^5$

Br : K L M $4s^2$ $4p^5$

I : K L M N $5s^2$ $5p^5$

If the molecules ZnCl, ZnBr and ZnI are formed from normal Zinc atom (^1S_o) and the atoms Cl, Br and I respectively in their normal states ($^2P_{3/2}$) then the possible electronic states of the molecule are $^2\Sigma^+$ and $^2\Pi$ (Herzberg 1950) that is,

$4s^2\ {}^1S_g$ (Zn) + $3s^2 3p^5\ {}^2P_u$ (Cl)

$4s^2\ {}^1S_g$ (Zn) + $4s^2 4p^5\ {}^2P_u$ (Br) .... ${}^2\Sigma^+$ and ${}^2\Pi$

$4s^2\ {}^1S_g$ (Zn) + $5s^2 5p^5\ {}^2P_u$ (I)

By considering the problem from the approach of the united atom model it was shown that ${}^2\Sigma$ and ${}^2\Pi$ are the low lying electronic states. Further the lowest electronic states of the molecules will usually dissociate into normal atoms. It is therefore likely that ${}^2\Sigma^+$ and ${}^2\Pi$ are the low lying ~~the~~ states of the halides of Zinc.

Following Mulliken's (1932) notation, the lowest electronic configurations for the three molecules ZnCl, ZnBr and ZnI may be written respectively as :

K K L L M $(z\sigma)^2\ (y\sigma)^2\ (w\pi)^4\ (x\sigma)$, ${}^2\Sigma^+$

K K L L M M $(z\sigma)^2\ (y\sigma)^2\ (w\pi)^4\ (x\sigma)$, ${}^2\Sigma^+$

K K L L M M N $(z\sigma)^2\ (y\sigma)^2\ (w\pi)^4\ (x\sigma)$, ${}^2\Sigma^+$

Thus the ${}^2\Sigma^+$ state may in all probability be the same ${}^2\Sigma^+$ state derived by combining a normal zinc atom with a normal halogen atom. As in the case of BeF, if it is considered that most of the molecular binding is due to $(w\pi)^4$ group the electron configuration of the first excited low - lying state of halides of Zinc may be written as

$$(z\sigma)^2\ (y\sigma)^2\ (w\pi)^3\ (x\sigma)^2\ \ldots\ldots\ldots\ {}^2\pi\text{state}$$

This ${}^2\pi$ state will also be one of the low lying states and it may be expected to be nearer to the lowest ${}^2\Sigma^+$ state. It is to be expected that the ${}^2\pi$ state will also dissociate into normal Zinc atom and the respective halogen atom. This state results from the removal of an electron from a strongly bonding π orbital from $(z\sigma)^2\ (y\sigma)^2\ (w\pi)^4\ (x\sigma)$, ${}^2\Sigma^+$ to antibonding σ orbital. It is to be expected that the vibrational frequency of the ${}^2\pi$ state should be less than that of the ${}^2\Sigma^+$ state. Thus the first band system of ZnI may be expected due to transition :

$$(z\sigma)^2\ (y\sigma)^2\ (w\pi)^3\ (x\sigma)^2\ \ldots\ {}^2\pi \rightarrow (z\sigma)^2\ (y\sigma)^2\ (w\pi)^4\ (x\sigma)\ldots\ {}^2\Sigma^+$$

No such system seems to have been observed as yet in this molecule or any other similar halide molecules. It is likely that the energy of the transition is low and the corresponding bands appear in the infra-red, for, successive electron orbits of a molecule, as in the case of an atom become closer together as the molecule gets heavier and in ZnI the two states may be very near to each other. Or, our failure to detect the bands of the above transition (${}^2\Pi - {}^2\Sigma^+$) may be due to the fact that ${}^2\Pi$- state is a repulsive one. The latter is more probable as it is in agreement with the general observation that the potential energy curves of about half or more than half of the molecular states derived from the two atoms in specified states are either repulsive or form shallow minima at very large inter nuclear distance. (Mulliken 1932). Further if most of the binding strength is attributed to the π^4 group of electrons, the change of electron configuration from $\pi^4\sigma$ to $\pi^3\sigma^2$ may have made the molecule unstable. i.e. potential energy curve repulsive. Hence the electronic state $\sigma^2\sigma^2\pi^3\sigma^2 \ldots {}^2\Pi$

may be a repulsive one, lying close to and having the same dissociation products as the state $\sigma^2\ \sigma^2\ \pi^4\ \ldots\ {}^2\Sigma^+$, the lowest state of ZnI molecule. On this view it is expected that every transition into the lowest state might be accompanied also by the transition into the repulsive $^2\Pi$ - state, whereas the former gives rise to discrete bands, the latter (if selection rules permit) gives a continuum at or in proximity of the long wavelength end of discrete bands.

The next excited state - B of low energy may be represented by $(z\sigma)^2\ (y\sigma)\ (w\pi)^4\ (x\sigma)^2\ \ldots\ {}^2\Sigma$ in which the change of an electron from inner $(y\sigma)$ orbital to an outer $(x\sigma)$ orbital should result in the reduction of vibrational frequency.

The excited states of the molecules can be derived by assuming that they result from the combination of the first excited state of Zinc atom ($^3P_0$) and the halogen atom in its normal state ($^2P_{3/2}$) .

The electron configuration and the molecular states C, D, D_1 and E corresponding to band systems in the ultraviolet region have been described by Ramasastry (1949). The upper levels C and D are interpreted as the components of a $^2\Pi$ state and the system occur in the vicinity of the resonance line ^1S —— ^3P of Zinc. The electronic configuration of these levels can be represented as : $\sigma^2 \sigma^2 \pi^4 \sigma^0 \pi$ .... $^2\Pi_r$. The products of dissociation being ^3P (Zn) and ^2P (I),

The electronic configuration of the upper levels B, C, D, D_1 and E of the different systems of ZnI may be given as below :

$\sigma^2 \sigma \pi^4 (x\sigma)^2$ .... $^2\Sigma$ ...... Level B

$\sigma^2 \sigma^2 \pi^4 (x\sigma)^0 (v\pi)^1$ .... $^2\Pi_r$ ...... Level C and D

$\sigma^2 \sigma^2 \pi^4 (x\sigma)^0 (v\pi)^0 (u\sigma)^1$..... $^2\Sigma$ Level D_1

$\sigma^2 \sigma^2 \pi^4 (x\sigma)^0 (v\pi)^0 (u\sigma)^0 (t\pi)^1$... $^2\Pi_r$ level E

Such an assignment is consistent with the changes in the vibrational frequency of the upper states relative to the ground state of the molecule. Unlike the $(v\pi)$ orbital which is slightly bonding in ZnI and slightly antibonding in ZnCl and ZnF, the ($t\pi$) orbit is highly antibonding and ($u\sigma$) still more antibonding than ($x\sigma$).

7.3 ELECTRON CONFIGURATION FOR INDIUM MONOIODIDE

It is sufficient for practical purpose to consider only those electrons which are in the outermost orbits. The electron configurations for atoms in Indium Iodide molecule can be given as :

In : $K\ L\ M\ N_{spd}\ 5s^2\ 5p$

I : $K\ L\ M\ N\ 5s^2\ 5p^5$

Where K, L, M .... represent closed shells. In the Indium atom, only s, p, d subshells of N orbit are filled.

Following the notation of Mulliken (1932) the lowest electronic configuration for InI molecule may be written as

$$K\ K\ L\ L\ M\ M\ N_{spd}\ N\ (z\sigma)^2\ (y\sigma)^2\ (w\pi)^4\ (x\sigma)^2$$

Where ($z\sigma$) and ($y\sigma$) represent the bonding and antibonding orbitals of the type ($5s\sigma_{In} + 5s\sigma_I ; \sigma$) and

$(5s\sigma_{In} - 5s\sigma_{I}\,;\,\sigma)$. The orbital $(w\pi)$ is of bonding nature $(5p\pi_{In} + 5p\pi_{I}\,;\,\pi)$ and $(x\sigma)$ represents the bonding orbital $(5p\sigma_{I}\,;\,\sigma)$. This configuration gives the electronic state $^1\Sigma^+$, which must be the ground state for Indium iodide molecule.

Probable electronic levels of Indium Iodide can also be derived by considering the separate atoms of Indium and Iodine. The ground states of Indium and Iodine atoms are $^2P_{1/2}$ and $^2P_{3/2}$ states respectively. Hence the ground states of Indium Iodide is expected to dissociate into In $(^2P_{1/2})$ and I $(^2P_{3/2})$. Electronic terms that can be derived from In(^2P) + I(^2P) are $^3\Sigma$, $^1\Sigma$, $^1\Pi$, $^3\Pi$, $^3\Delta$ and $^1\Delta$. An approach of the united atom will help to find out, which out of these states is the low lying state. In has 49 electrons with the configuration K L M N_{spd} $5s^2$ 5p and Iodine has 53 electrons with configuration K L M N $5s^2$ $5p^5$. The molecule InI can be supposed to have been formed by splitting the corresponding united atom Nobelium (No) with 102 electrons. The normal electronic state of No is ^1S state.

Hence the electronic term of InI that results by hypothetical splitting of No must be ${}^{1}\Sigma^{+}$. Therefore the ground state of InI must be ${}^{1}\Sigma^{+}$ state. Thus electron configuration for Indium Iodide for the ground state can be written as

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

Excitation of an $(x\sigma)$ electron to $(v\pi)$ orbital will give rise to two states viz ${}^{1}\pi$ and ${}^{3}\pi$ from the resulting configuration

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

By Hund's rule of multiplicity, ${}^{3}\pi$ state will lie deeper than ${}^{1}\pi$ state. Observed A - X and B - X systems of Indium Iodide have typical features of ${}^{1}\Sigma - {}^{1}\Sigma$ and ${}^{1}\pi - {}^{1}\Sigma$ transition. Molecular constants for A and B states suggest that these states must arise from the configuration of electrons alike.

${}^{1}\pi - {}^{1}\Sigma^{+}$ transition is attributed to C - X system of InI which is analogous to those of similar molecules (InCl, InBr). However $^1\Pi$ - state is repulsive in the case of InI molecule which gives a continuum at 3180 A°. The $^3\Pi$ - state belongs to Hund's case (a) due to its large coupling constant (648.9 cm^{-1}). Hence $^3\Pi_0$, $^3\Pi_1$ and $^3\Pi_2$ states are analogous to $^1\Sigma$, $^1\Pi$ and $^1\Delta$states respectively. $^3\Pi_2$ —— X $^1\Sigma^+$ transition is a forbidden one whereas $^3\Pi_1$ —— X $^1\Sigma^+$ has been ascribed to B - X system of InI. The transition $^3\Pi_0$ —— X $^1\Sigma^+$ is attributed to A - X system.

7.4 CONCLUSIONS

This section of the chapter describes the conclusions drawn from the present study.

(a) CALCIUM IODIDE

In the present investigation the A - X and B - X systems in red region ($\lambda\lambda$ 6175 A°-6600 A°) of CaI molecule have been studied in detail. It has been observed from the vibrational analysis of the bands that B state shows a spin splitting of about 3.4 cm^{-1}. This spin splitting may be interpreted as an interaction between B state and the states nearer to it. It is mainly due to first excited state (A $^{2}\Pi$), since it is lying close to the B state. Such a spin splitting is established for the B state of CaCl molecule by comparing the value of spin splitting constant from rotational analysis of 0,0 band of B - X system CaCl molecule along with the value obtained from Van Vleck's theoretical result for pure precession. The agreement between experimental and theoretical values of spin splitting constant supports the fact that it is due to the interaction between the states B and A. Spin splitting of B state of CaI molecule may be explained on similar basis.

The electron configuration of CaI molecule shows that for the B state an electron from the antibonding $(y\sigma)$ orbital goes to the bonding $(x\sigma)$

dispersion, vibrational isotopic effect due to Zn^{64}, Zn^{66} and Zn^{68} is established. This effect was not observed for bands of 0,0 sequences as the isotopic shift for the bands of this sequence is too small to resolve at the dispersion employed here. However spectrogram shows the isotopic separation for other sequences. The aim of the isotopic analysis was to check the vibrational assignments reported by earlier workers leading to the correctness of analysis.

(c) INDIUM IODIDE

In an attempt to record A - X and B - X systems at higher dispersion, a group of bands in the region λλ3490 A°-3600 A° was obtained and later analyzed. The vibrational analysis reveals the lower state frequency as 148.0 cm^{-1} which is in close agreement with the vibrational frequency of B - state of InI molecule. Further the upper state (D) frequency 191.9 cm^{-1} obtained from present analysis does not agree with any of the experimentally known frequencies of InI molecule. Therefore the system may be ascribed to an electronic transition between two excited states, the lower state of which may be B$^3\Pi_1$. The system D ⟶ B $^3\Pi_1$ being not observed in absorption also indicates that the ground state is not involved in the transition. The ν_e value indicates that the upper state must lie in the region of 53062.23 cm^{-1} above the ground state. The nature of the upper state (D) can be studied by rotational analysis only. The upper state - D showing relatively higher vibrational frequency than that of the B - state which may be due to excitation of the (xσ) electron of nonbonding nature to the bonding orbital of D - state. Hence the violet degradation of D ⟶ B $^3\Pi_1$ band system can be explained in terms of increase in bonding that leads to decrease in internuclear distance for the upper state - D. Bonding property of any electronic.. Orbital depends on the number of electrons present. As we go from lighter to heavier molecules, the effect of inter electronic repulsion will become more and there will be a change in the nature of bonding. This phenomenon is clearly exhibited by Indium halide molecules. It was stated that the excited states A , B and C are due to excitation of an ($x\sigma$) electron to a $v\pi$ orbital. In ordinary cases $x\sigma$ is a bonding and $v\pi$ is an antibonding orbital. Hence excitation of $x\sigma$ electron to $v\pi$ orbital will couse a lowering of vibrational frequency (w_e) with respect to the ground state. This will give rise to a system of bands degraded to longer wavelengths. In case of InI molecule, the systems A $^3\Pi_0 - X\,^1\Sigma^+$, B $^3\Pi_1 - X\,^1\Sigma^+$ and D $\longrightarrow$ B $^3\Pi_1$ show~~s~~ violet degradation indicating the predominance of inter electronic repulsion in heavier molecules which

is

is quite contarary in case of lighter molecules.

Rotational analysis of the $A\,^3\Pi_0 — X\,^1\Sigma^+$ system in the region λλ3948 - 4293 A° of three bands 0,0; 1,0 and 0,1 is reported for the first time and accurate rotational constants for these bands are obtained graphically. The appearance of single P and R branches in case of 0,0; 1,0 and 0,1 bands confirms the transition $A\,^3\Pi_0 — X\,^1\Sigma^+$. The 0,0 band of $B\,^3\Pi_1 — X\,^1\Sigma^+$ system was selected for rotational analysis. Since the structure of the band could not be adequately resolved even at the highest available dispersion (0.4 A°/mm), the rotational constants were evaluated from average value of the second differences of wavenumbers ($\Delta^2\nu$) of poorly resolved lines of 0,0 band. The rotational constants thus obtained agree with theoretically computed values within range of experimental erors.