CHAPTER VII

ELECTRON CONFIGURATION AND CONCLUSIONS

In this chapter possible electronic states for diatomic molecules of group II(a)- monohalides will be discussed on theoretical basis and will be compared 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 CaCl 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 determining electronic configurations of the molecule.

It is thus sufficient for practical purpose to consider only those electrons which are in the outermost orbits. 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 CaCl molecule may be written as

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

where $(z\sigma)$ and $(y\sigma)$ represent the bonding and antibonding orbitals of the type $(4s\sigma_{Ca} + 3s\sigma_{Cl}, \sigma)$ and $(4s\sigma_{Ca} - 3s\sigma_{Cl}, \sigma)$. $(w\pi)$ represents the bonding orbital $(3p\pi_{Cl}, \pi)$ and $(x\sigma)$ represents the bonding orbital of the type $(3p\sigma_{Cl}, \sigma)$. This configuration gives the electronic state $^2\Sigma^+$ which must be the ground state for CaCl 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.

$4s^2\ {}^1S_g(Ca) + 2s^2 2p^5(F)$
$4s^2\ {}^1S_g(Ca) + 3s^2 3p^5(Cl)$ ..... ${}^2\Sigma^+$
$4s^2\ {}^1S_g(Ca) + 4s^2 4p^5(Br)$
$4s^2\ {}^1S_g(Ca) + 5s^2 5p^5(I)$

Probable electronic levels of CaCl molecule can also be derived considering the separate atoms of Calcium and Chlorine. The ground states of Ca and Cl atoms are $({}^1S_0)$ and $({}^2P_{3/2})$ respectively. Hence the ground state of CaCl molecule is expected to dissociate into $Ca({}^1S_0)$ and $Cl({}^2P_{3/2})$ atoms. The electronic terms that can be derived from $Ca({}^1S) + Cl({}^2P)$ are ${}^2\Sigma^+$ and ${}^2\Pi$. An approach of the united atom wiil 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 Chlorine has seventeen electrons with the configuration

$$1s^2 \quad 2s^2 2p^6 \quad 3s^2 3p^5.$$

The molecule CaCl can be supposed to have been formed by splitting the united atom Rubidium (Rb) which has thirty seven electrons with configuration

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

The normal electronic state of Rb is ^1S state. Hence the electronic term of CaCl that results by splitting Rb atom is $^2\Sigma$. Therefore the ground state of CaCl molecule can be fixed as $^2\Sigma^+$.

The correlation between various states of CaCl molecule in separate atoms model to united atom Rb will give the nature of stability of molecular states. States formed by separate atoms model which cannot correlate with the low lying states ^2S, ^2P, ^2D of the united atom Rb are unstable. Consider now calcium atom in its first excited state and chlorine in the normal state. This will give rise to $Ca(^3P_u) + Cl(^2P_u)$ — $\Sigma^+(2)$, $\Sigma^-(2)$ and Δ, out of which only those allowed by selection rules and transition probability considerations should be considered. In a similar way the next excited state for CaCl can be derived to be $^2\Pi$ and $^2\Sigma$ respectively.

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

$$(z\sigma)^2\ (y\sigma)^2\ (w\pi)^4\ (x\pi)\ \ldots\ldots\ ^2\Pi_r$$

or

$$(z\sigma)^2\ (y\sigma)^2\ (w\pi)^3\ (x\pi)^2\ \ldots\ldots\ ^2\Pi_i$$

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

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

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 anti bonding 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, CaBr and CaI can be derived. Since the electron configurations of alkaline earth Be, Mg, Ca, Sr and Ba are very much alike, the schemes of electronic states of their corresponding monohalides show considerable similarities. The experimentally observed electronic states for the halides of Be, Mg, Ca, Sr and Ba are depicted in fig. 10 to give a comparative idea.

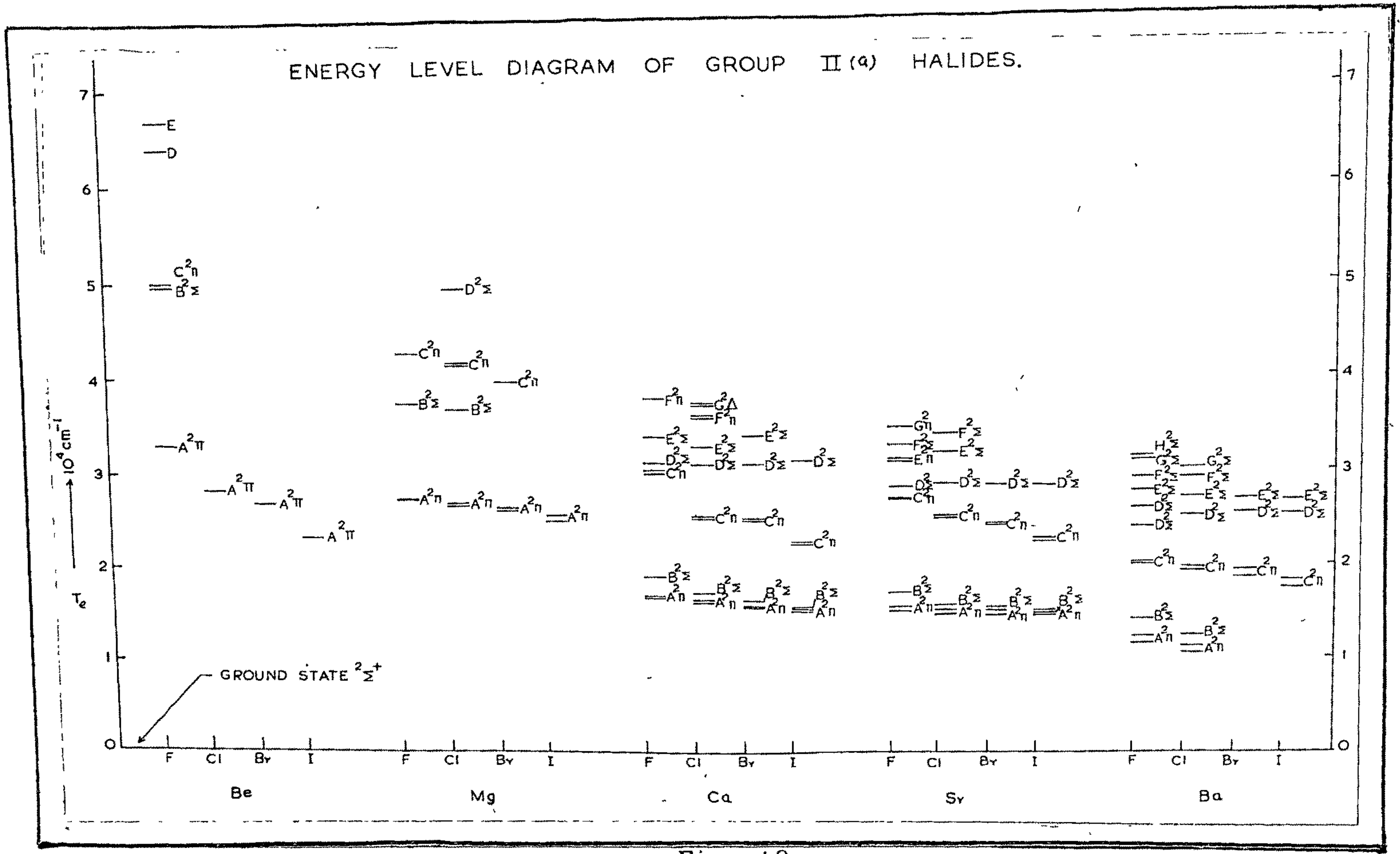

Fig. 10

Energy level diagram of group II(a) halides.

Hence the most probable scheme of electronic states for rare earth halides 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	$D^2\Sigma$.

RESULTS AND CONCLUSION

This section of the chapter deals with the results obtained from the present study and conclusions drawn therefrom.

Calcium Chloride:

In the present investigation the B-system of CaCl molecule has been studied in details. It has been observed from the vibrational analysis of the bands that the B-level has considerable spin splitting. This spin splitting can be interpreted as an interaction between the B-level and levels nearer to it. It is mainly due to the first excited level $A^2\Pi$, since it is lying very close to the B-level. Further this spin splitting can be calculated using Van Vleck's well known formula for pure precession:

$$\gamma = \frac{2A\ B_v\left[\ell(\ell+1)\right]}{\nu(\Pi,\Sigma)}$$

where A - doublet π interval

B_v = rotational constant

l = angular momentum quantum number

$\nu(\pi,\Sigma)$= difference between Σ level and the average of the π sub-levels.

The calculations for the case under consideration shows, $\gamma = 0.06\ cm^{-1}$. The rotational analysis of the (0,0) band of the B-system of CaCl molecule carried out in the present work also gives $\gamma = 0.061\ cm^{-1}$ which is in close agreement with the theoretically calculated value. This supports the assumption that spin splitting in the B level is entirely due to the interaction between the levels B and A.

The electron configuration of CaCl molecule shows that for the B state an electron from the antibonding ($y\sigma$) orbital goes to the bonding ($x\sigma$) orbital. In the usual cases this would mean an increase in bonding between the atoms and hence the vibrational frequency of the B-level is expected to be greater than the vibrational frequency of the ground state. Consequently the sequences in the band system should be degraded to violet. Also as the bonding increases, the internuclear distance for the upper state decreases and hence the degradation of the bands is expected towards violet. However it is observed from the analysis that eventhough the bands are degraded to violet, the sequences are degraded to red. This may mean that both $(y\sigma)$ and $(x\sigma)$ orbitals may not hold the strict conventional bonding in this molecule and perhaps one of these or both may have a non-bonding nature. In a recent paper Barrow and Beale (1967) also suggested that in the case of MgF molecule, the X and the B levels are increasingly non bonding in nature. However a study of the vibrational frequencies of the B-system of heavier molecules in this group (i.e. SrI) shows a clear violet degradation both in the sequence and in the bands.

Barium Iodide:

The C-X system of BaI molecule has a long and intense (0,0) sequence. The reason for this may be that the internuclear distance for the zero vibrational level of C-state and the ground state does not alter much and the potential curves for both the states may be the same. This may be the reason that the bands of the (0,0) sequence do not show sharp heads. However the bands in the (0,1) and (0,2) sequences have sharp heads of low intensity. This may be explained as follows. The transitions $\Delta v \neq 0$ may involve appreciable change in internuclear distance. In this case a sequence having sharp band heads of low intensity is expected according to Frank-Condon principle.

The electron configuration of the BaI molecule shows that for the C-level, an electron from the bonding orbital ($x\sigma$) is excited to an antibonding orbital ($v\pi$). This results in a decrease in the bond strength and consequently a decrease in the vibrational frequency. But from the present analysis it is observed that C-level in this molecule is more strongly bound than the ground state.

The two band systems in the region $\lambda\lambda$ 3970-3800 A° and $\lambda\lambda$ 3800-3565 A° were reanalysed and modified vibrational constants were obtained. These two band systems were designated as D — X and E — X systems analogous to similar molecules. The D state arises due to the excitation of an electron from the ($x\sigma$) orbital to ($t\sigma$) orbital. The bonding of ($t\sigma$) orbital electron may be higher compared to an electron in the ($x\sigma$) orbital. This assumption is supported by the observed fact that the vibrational frequency of the D state (161.1 cm^{-1}) is greater than that of the ground state (152.15 cm^{-1}). When an electron from ($x\sigma$) orbital gets excited to a ($q\sigma$) orbital the resulting state is $^2\Sigma$ and is designated as E. $(q\sigma)$ orbital is also a bonding orbital and hence the violet degradation of E-X band system can be explained as usual.

<u>Strontium Iodide</u>:

In SrI molecule, a new system was observed for the first time. The vibrational analysis suggests that the system is a $^2\Sigma - {}^2\Sigma$ transition. The lower state is fixed as the ground state. The upper state is showing a vibrational frequency greater than the ground state. The upper state can be assigned an electronic transition

$$(z\sigma)^2\ (y\sigma)^2\ (w\pi)^4\ (x\sigma)^0\ (v\pi)^0\ (t\sigma)$$

giving rise to an electronic state $^2\Sigma$. The upper state showing relatively higher vibrational frequency may be due to the excitation of the $(x\sigma)$ electron which may be a non-bonding one to the bonding $(t\sigma)$ orbital. However C.A. Fowler Jr. (1941) suggests that in the group II monohalides, the higher excited states other than B and C may be due to the excitation of the $(x\sigma)$ electron into higher and higher energies having the closed shell $(z\sigma)^2\ (y\sigma)^2\ (w\pi)^4$ undisturbed. The more highly excited the $(x\sigma)$ electron is the more nearly will the resulting state resemble to the normal state of the ionised molecule which becomes its limit. The spectra of ionised molecules in this group are unknown but from the spectra of the molecules which are isoelectronic with the ionised halides in this group, the ground state frequency of the ionised molecules in this group can be calculated. It is seen that they lie very much higher than any of the vibrational frequency observed for the normal molecules.

Calcium Iodide:

In CaI molecule, a new system is observed. The lower state of this system is fixed as the A-state of the molecule. The upper state is lying very much higher than any other observed levels. The vibrational frequency is much higher than the observed values. This may be explained on similar basis.