CHAPTER 6

ELECTRON CONFIGURATION AND MOLECULAR STATES OF HALIDES OF CADMIUM

The nature of the electron states involved in the emission of the band spectra of diatomic halides of cadmium will now be discussed in this chapter. The theory of molecular formation is well discussed in number of standard textbooks and will not be given here in detail.

It is well known that the nature of electron states arising in a molecule with a given number of electrons can be predicted either from the 'united atom' or 'the component atoms,' but a criterion for the stability of these molecular states is still lacking. However, mathematical methods have been developed by Heitler and London (1927) by means of which it is possible to infer the nature of variation of U(r) as the atoms approach each other making r smaller and from it to determine whether a state will be repulsive or stable.

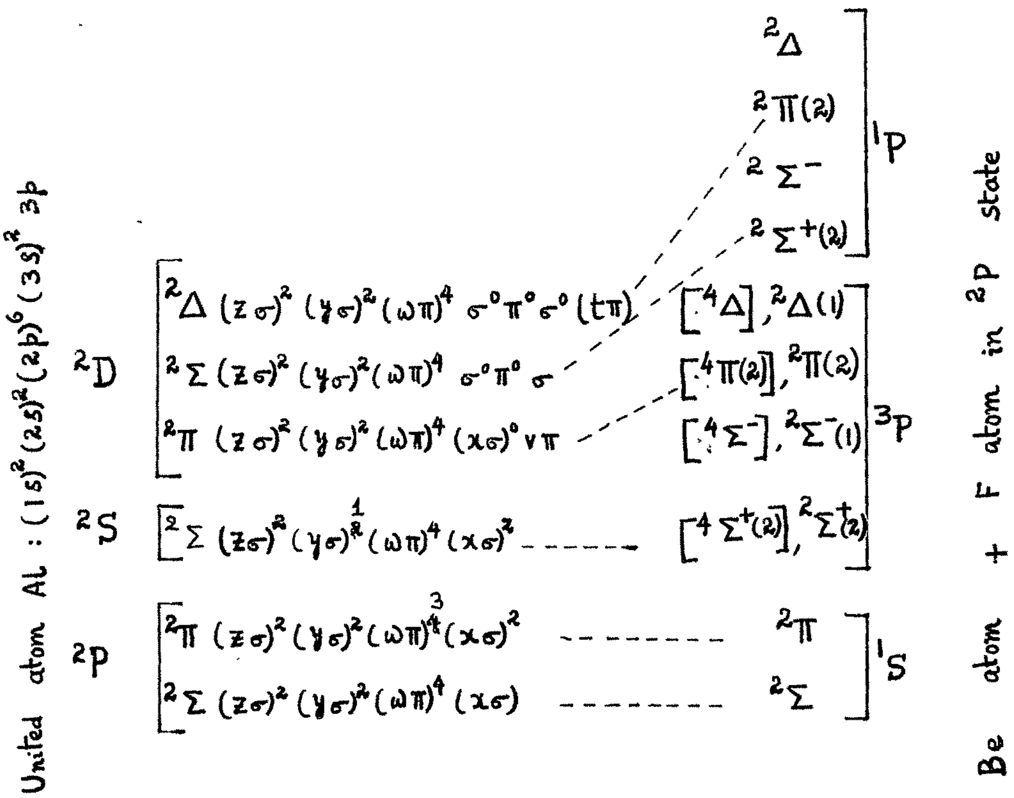
The other primary need is the knowledge not only of stability of various molecular states which may arise from a molecule with a known number of electrons, but also some idea about how their energy value depends on Λ and S. We also need detailed information on the order of the strength of binding of individual electron orbits. Hund, Herzberg, Mulliken and others have contributed a greater part of the work in this field. They have attempted to correlate electron orbits in the separate atoms with those in the actual molecules and also with those which occur in the limiting case of the united atom.

In what follows the standard methods of approach for finding the possible electron states are used. Since the molecules under investigation resemble BeF, the discussion will be oriented with respect to this molecule in the beginning.

The BeF molecule has Aluminium as the 'united atom'. Since the detailed derivations are always available in standard works, the various states and the correlations between them in the tabular form only are given below.

TABLE 25

CORRELATION OF Be + F ATOMS WITH UNITED ATOM Al.



The method suggested above holds true more precisely for hydride molecules in comparison to those which have comparable nuclei. In the latter case the change from separate atoms to molecular conditions requires approximately half the electrons to be promoted to satisfy Pauli's principle. In practice molecular conditions will be intermediate between these limiting cases and it is possible by examining experimental data to see how these extremes may be correlated.

If one compares the ground state frequencies of BeO (12 electrons) and BeF (13 electrons) and their electron configuration viz

BeO	KK	$\sigma^2\sigma^2\pi^4$, $^1\Sigma$	$\omega_e'' = 1487$ cm^{-1}
BeF	KK	$\sigma^2\sigma^2\pi^4\sigma$, $^2\Sigma$	$\omega_e'' = 1266$ cm^{-1}

it is observed that the addition of one more electron to BeO to form BeF results in the reduction of ω_e value i.e. the added electron has a definite anti-bonding tendency. One can make a similar comparison for halides of Ag, Cd and In in which the metal atom has one electron more than the preceeding one. The frequencies given in the following table correspond to ground state.

TABLE 26

GROUND STATE FREQUENCIES OF HALIDES OF Ag, Cd AND In

Metal	Suggested electron configuration of halides.	Fluoride.	Chloride.	Bromide	Iodide.
Ag	$\sigma^2\sigma^2\pi^4$, $^1\Sigma$	-	343.6	247.7	206.2
Cd	$\sigma^2\sigma^2\pi^4\sigma$, $^2\Sigma$	540	330.5	230.0	178.5
In	$\sigma^2\sigma^2\pi^4\sigma^2$, $^1\Sigma$	534	317.4	221.0	177.1

The ω_e values in each column show a decrease from Ag to In. In the light of suggested electron configurations it may therefore be suggested that outer electrons have a slight anti-bonding effect. However, in comparison to the reduction of frequency of BeF with respect to BeO, the magnitude in the above case is quite small which indicates that for the heavier molecules the ground state frequency is determined by the heaviness of the molecule and the relative change due to the changes in electron configuration is small.

It has been pointed out by Howell (1943) that most of the molecular binding is due to the π^4 group and the removal of an electron from this group reduces the vibrational frequency considerably. This can be seen clearly from the observed vibrational frequncies of the normal and excied state of BeO molecule. One gets

$$\begin{array}{ll} \sigma^2\sigma^2\pi^4 \quad {}^1\Sigma & \omega_e = 1487 \\ \sigma^2\sigma^2\pi^3\sigma \quad {}^1\Pi & \omega_e = 1128 \end{array} \Big> 359$$

$$\begin{array}{ll} \sigma^2\sigma\,\pi^4\,\sigma \quad {}^1\Sigma & \omega_e = 1371 \\ \sigma^2\sigma\,\pi^3\,\sigma^2 \quad {}^1\Pi & \omega_e = 1006 \end{array} \Big> 365$$

The observed ground states of halides of cadmium may now be attributed to the ${}^2\Sigma$ term of the configuration given as

$$KK\ (z\sigma)^2(y\sigma)^2(\omega\pi)^4(x\sigma)\ \ldots\ldots\ldots\ {}^2\Sigma$$

The first excited state A is observed to be an inverted ${}^2\Pi$ state in all the isoelectronic molecules BO, CN, CO^+ and N_2^+ and may be attributed to the configuration

$$KK\ (z\sigma)^2(y\sigma)^2(\omega\pi)^3(x\sigma)^2\ \ldots\ldots\ldots\ {}^2\Pi_i$$

in which an electron is transferred from the strongly bonding $(\omega\pi)$ orbital to the $(x\sigma)$ orbital which should result in decrease in the vibrational frequency of the A ${}^2\Pi_i$ state. The bands observed in the extreme red region for all the molecules are clearly degraded to the red and appear to form different systems and could not be the extensions of B-systems. Thus in all probabilities they may belong to the transition. ${}^2\Pi_i - {}^2\Sigma$

The next excited state of low energy may be represented by

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

in which the change of an electron from inner ($y\sigma$) orbital to an outer ($x\sigma$) orbital must result in the reduction of the vibrational frequency. In the study of the spectra of HgCl, HgBr and HgI by Wieland in the visible region (1946, 1960) it has been observed that $\omega_e' < \omega_e''$ as per expectation. The B-systems of all the molecules in the present study support this view point and the transition may in all probability be ${}^2\Sigma^+ - {}^2\Sigma^+$ This ${}^2\Sigma^+$ state and the other excited states of higher energy should naturally be derived from Cd and halogen atoms with one or the other or both of them in their excited states. The possible states when Cd atom is in its first excited state and halogen atom in its normal state are given in table (25). One of the two levels may therefore correspond to the upper state of the visible bands and may belong to the above mentioned configuration.

The upper levels of the systems C and D have been interpreted as components of ${}^2\Pi$ state and the systems occur in the vicinity of the resonance line ${}^1S - {}^3P$. This state may therefore be one of the expected $^2\Pi$ state mentioned in table (25) above and can be represented by the following configuration.

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

with possible products of dissociation ^3P(Cd) and ^2P (halogen). The remaining two states viz. $^2\Sigma^+$ and $^2\Pi$ may probably be repulsive states.

The other excited states may correspond to ^1P(Cd) and ^2P (halogen atom) as shown in table (25). This combination gives six molecular states of which only four levels should be taken because of the selection rules. We may represent these states by the following electronic configurations.

$$KK\,(z\sigma)^2\,(y\sigma)^2\,(w\pi)^4\,(x\sigma)^0\,(v\pi)\,(u\sigma)^1\ \ldots\ldots\ {}^2\Sigma$$

and $KK\,(z\sigma)^2\,(y\sigma)^2\,(w\pi)^4\,(x\sigma)^0\,(u\sigma)^0\,(t\pi)^1\ \ldots\ldots\ {}^2\Pi_r$

or alternatively we may write as

$$\pi^4 p\sigma\,(^1P)\ \ldots\ldots\ {}^2\Sigma \quad \text{and} \quad \pi^4 p\pi\,(^1P)\ \ldots\ldots\ {}^2\Pi_r$$

to distinguish them from those arising from ^3P(Cd).

In view of the observations in the present investigation on the new system of CdBr and a fragmentary system in case of CdI near to the system reported earlier by Wieland (1946), it is possible to account for the above two states.

An exact correspondance will be established if we assume that the states derived from ^3P state of Cd and ^2P state of halogen atom give rise to the upper states of A, B, C and D systems and those arising from ^1P state of Cd and ^2P state of halogen atom give rise to the upper states of lower ultra-violet region systems. From the observed values of ν_e for these band systems it appears appropriate if the levels $^2\Sigma^+$ and $^2\Pi$ arising due to above mentioned combination be assigned to the upper states of D' and E systems respectively of both CdBr and CdI molecules. The proximity of the E system to $^1P-{}^1S$ line of Cd, and the occurrence of D' system to the longer wavelength side are consistent with this idea. If this assumption is correct the E systems should have their second components also. Further the evidence for considering the Wieland system for CdI as due to $^2\Pi \rightarrow {}^2\Sigma$ transition based on the appearance of Q and R heads should not be neglected.

Further work on the structure of the heads with better dispersion could throw more light in solving this problem. This therefore creats a doubt for assigning Cornell's system a transition $^2\Sigma \rightarrow {}^2\Sigma$

for which there is some justification as the conclusion is arrived at by the measurement of a few bands only. The appearance of a continuum to the longer wavelength side of Cornell's system for CdCl should also be taken into account.