PART I

CHAPTER 1

INTRODUCTION

There are several different methods of studying the structure and intrinsic properties of molecules. Among these methods, spectroscopic study of the molecules occupies a unique position. Unlike an atom, the energy of a molecule consists of three parts, electronic, vibrational and rotational, the last two energies being much smaller than the first one. It is the vibrational and rotational transi~~s~~tions superposed on the electronic transition that gives rise to a molecular spectrum or what is usually known as a band spectrum. Thus the distinguishing feature of a band spectrum is that, it is produced due to the transition~~s~~ between excited and ground states, whereas Raman and infrared spectra are produced by the transitions in the ground state only. Hence the study of band spectra is of the greatest value for a knowledge of the electronic structure of molecules, for the theoretical understanding of chemical val~~a~~ence and the heat of dissociation of molecules in addition to the accurate determination of molecular constants.

With the application of new quantum mechanics to the theory of band spectra of diatomic molecules, the problems of electronic structure of molecules have been solved with greater success. This has been especially true in respect of our knowledge of the nature of electronic states of molecules and those of their component atoms on dissociation.

The most probable electron configurations of the lighter diatomic molecules and the order of their electron bindings have been determined by Mulliken (1932), but no such systematic scheme has yet been formulated for the heavier molecules. For heavier molecules the theoretical predictions for the excited states are ambiguous because of the greater number of electrons and more orbitals involved in molecular formation, which have approximately equal energy. This consequently leads to a complicated spectrum even under high dispersions. The molecules whose structure can best be interpreted theoretically (Heitler and London, 1927) are H_2 and He_2 and with these providing a secure foundation, the successive addition of single electrons to them has enabled the configurations of the simpler molecules to be determined. However, a successful untilisation of this method of approach depends entirely on the existence of accurate molecular data which are derived mainly from spectroscopic studies involving the vibrational and rotational analysis of the band spectra of molecules and also from studies on ionisation potentials. At present comparatively few measurements have been made upon the spectra of heavy diatomic molecules and from these mostly vibrational constants have been derived. Consequently any additional experimental data on the spectra of heavy diatomic molecules will be very useful in the construction of an improved electronic scheme for these molecules.

Further the variation in spectroscopic properties of a group of chemically similar compounds offers an interesting study in the spectra of diatomic molecules. The spectra of hydrides, alkali metals, halogens and some groups of halides have been studied in varying degrees of detail; however all these compounds represent a rather special valency type in which one of the constituent atoms can lose or gain only one electron in bond formation.

The sulphides, oxides, halides, selenides and tellurides of zinc, cadmium and mercury group have not been so extensively studied as those of the fourth group. The object of the present investigation was to study the emission spectra of some of the halides of second group in the visible and ultra-violet regions and to determine as accurately as possible their vibrational constants by the equipments available in the laboratory. In this thesis are reported the study of the emission spectra of the halides of cadmium (except cadmium fluoride molecule). In addition to this the vibrational constants of these halides are compared with those of the heavy halide molecules of silver, indium etc. in which one has one more electron than the preceding one. By following the changes in these constants from molecule to molecule, information regarding their electronic configuration was sought.

Further the investigations by Ramasastry (1947) indicate a possibility of bands in the extreme red region for the halides of this group. The major aim of the present investigation was to investigate the B - Systems of the halides of cadmium and to study whether the bands reported to occur in the red, form a system having still a lower energy than that of B - system. The analysis of some of the systems of bands reported in the literature was incomplete, hence these systems were reinvestigated.

Wieland (1929) was the first to investigate the band spectrum of cadmium chloride in the course of his extensive study of the halides of zinc, cadmium and mercury, as excited by a high-frequency oscillatory discharge. This work led him to believe that diffuse bands in the visible region were due to triatomic molecules, but the later work by the same author (1960) and in colloboration with Herczog (1946) indicated that these bands were due to the respective diatomic molecules. Cornell (1938) in his work on ultra-violet spectra of the chlorides of zinc, cadmium and mercury ascribed all these spectra to the diatomic molecules. This had led to so many interesting developments yielding the information about the nature of molecular states involved, that it has been found possible to extend the scope of the investigation so as to include a critical review of all the halides of this group.

A practical application of the analysis of $B^2\Sigma \rightarrow X^2\Sigma$ systems of band is that a very exact calculation of the binding energy of the ground state can be done, whose stability especially in the diatomic cadmium halogens and also in all diatomic combinations of the elements of the second group, is an interesting problem. Such a band system in case of halides of mercury (HgCl, HgBr and HgI) was studied by Wieland (1960, 1941). According to the elementary valancy theory of Heitler and London, these elements and also He in its $^1S_0$ ground state should not have any stable binding at all. The fact that it does possess this, and sometimes in a very specific manner, is explained by Heitler (Maxx's Hand B.der Radiologies VI_2 485 (1934) and Nordheim - Poschl Ann. Physik <u>26</u>, 258 (1936)) with the help of the higher terms of the same class. The band system $B^2\Sigma \rightarrow X^2\Sigma$ of the radicals CdX discussed here lead to exact calculations about the stable upper state B, and also give best proof for the correctness of the theories advanced by Heitler and London and also by Mulliken.

A birds - eye - view of the various factors related to the study of band spectrum is given below :

1. The gross structure of band systems,
2. Intensity distribution in a band system

and 3. Isotopic effect in a band system.

In order to complete the vibrational analysis of band spectrum, the study of electronic states and electronic configuration is also of paramount importance. It is discussed in detail in chapter (6). The above factors will now be briefly described. The details are given in many excellent text books (e.g. Herzberg (1950), Johnson (1949), Gaydon (1947), King (1964), Barrow (1962), Jevons (1932), etc.

1. THE GROSS STRUCTURE OF BAND SYSTEMS

It is quite common to treat the energy of a molecule as made up of three parts viz., electronic, vibrational and rotational. It is vibrational and rotational transitions superposed on the electronic transition that give rise to the molecular or band spectra. As is well known the electronic band spectra are observed in the visible and ultra-violet region and the various bands and their fine structure are being due to the associated changes in the vibrational and rotational energies that accompany the electronic transition.

Thus the total energy (E) of a molecule may be expressed as

$$E = E_e + E_v + E_r \qquad ......(1)$$

The total energy of the electrons (E^{el}) depends on the internuclear distance as also the Coulomb potential of the nuclei (V_n). The minimum of $E^{el} + V_n$ is taken to be the electronic energy of the state. Born and Oppenheimer have shown that to a satisfactory approximation the first and second derivatives of the electronic eigen-function with respect to the internuclear distance is negligible. Using this condition $E^{el} + V_n$ is to a good approximation the potential energy for the vibrational motion of the nuclei and is denoted by Ee. Thus in equation (1) E_e is the electronic energy, E_v is the vibrational energy and E_r is the rotational energy.

If the rotational transition is disregarded provisionally, and if the vibrational energy E_v is expressed in the form

$$E_v = \omega_e(v+\tfrac{1}{2})hc - \omega_e x_e(v+\tfrac{1}{2})^2 hc + \omega_e y_e(v+\tfrac{1}{2})^3 hc + ... \qquad .....(2)$$

then the frequency of the spectrum due to energy change accompanying an electronic transition may be expressed as

$$\nu = E_{v'} - E_{v''}/hc + \frac{E_e' - E_e''}{hc}$$

$$\begin{aligned}\nu &= \nu_e + \Big[\big\{ \omega_e' (v'+\tfrac{1}{2}) - \omega_e' x_e' (v'+\tfrac{1}{2})^2 + \omega_e' y_e' (v'+\tfrac{1}{2})^3 + \cdots\cdots \big\} \\ &\qquad - \big\{ \omega_e'' (v''+\tfrac{1}{2}) - \omega_e'' x_e'' (v''+\tfrac{1}{2})^2 + \omega_e'' y_e'' (v''+\tfrac{1}{2})^3 + \cdots\cdots \big\} \Big]\end{aligned}$$

where $\qquad\qquad\qquad \cdots\cdots\cdots (3)$

$$\nu_e = \frac{E_e' - E_e''}{hc}$$

In these expressions the single primes denote the upper state and double primes denote the lower state constants. Thus the v' and v" are the vibrational quantum numbers in the final and initial states respectively. ω_e' and ω_e'' are the equilibrium vibrational frequencies of the molecule in these states and $\omega_e' x_e'$ and $\omega_e'' x_e''$ are the corresponding anharmonicity constants. As the rotational energy is neglected in the above expression the frequency ν gives the origins of the series of the vibrational bands.

Expression (3) can also be written as

$$\begin{aligned}\nu &= \nu_{00} + (\omega_0' v' - \omega_0' x_0' v'^2 + \cdots\cdots) \\ &\qquad - (\omega_0'' v'' - \omega_0'' x_0'' v''^2 + \cdots\cdots) \qquad \cdots\cdots\cdots (4)\end{aligned}$$

where ν_{00} is a term independent of v' and v" and is usually called the frequency of the (0,0) band~~s~~ as it corresponds to the transition v'=0→v"=0. Substituting v'=0 and v"=0 in the expression (3) it becomes

$$\nu_{00} = \nu_e + \left(\tfrac{1}{2}\,\omega_e' - \tfrac{1}{4}\,\omega_e' x_e' + \cdots\cdots\right) - \left(\tfrac{1}{2}\,\omega_e'' - \tfrac{1}{4}\,\omega_e'' x_e'' + \cdots\cdots\right) \quad \cdots\cdots\cdots\cdots(5)$$

Where ν_e is known as the system - origin.

Upon introducing the value of ν_e from the above expression in equation (3) we get

$$\nu_{head} = \left[\nu_{00} - \tfrac{1}{2}(\omega_e' - \omega_e'') + \tfrac{1}{4}(\omega_e' x_e' - \omega_e'' x_e'')\right] + \left[\omega_e'(v' + \tfrac{1}{2}) - \omega_e' x_e'(v' + \tfrac{1}{2})^2\right] - \left[\omega_e''(v'' + \tfrac{1}{2}) - \omega_e'' x_e''(v' + \tfrac{1}{2})^2\right] \quad \cdots\cdots(6)$$

When a new band system has been found and assigned the (v', v'') value it is a common practice to arrange the bands in the system in a table, called "Deslandres table", in such a way that the difference in the frequencies in adjacent columns is approximately constant and varies uniformly and similarly in the rows. Thus the differences between the columns in the table give the vibrational spacing in the lower electronic state and of the rows will give vibrational spacing of the upper electronic state.

In a band system, a series of band having a constant value of $(v' \sim v'')$ is called a "sequence" and a set of bands having a definite value of either v' or v" is known as "progression". It is evident that this method of analysis should in principle be applied to the band origins. Nevertheless use is made of this method in vibrational analysis of the spectra of diatomic molecules, measuring the band heads only, because as long as $\nu_{head} - \nu_{origin}$ is small the derivation of vibrational constants by making use of band head data introduces only a small error. As the head of Q branch lies near to ν_0, band head data of Q heads give accurate value of vibrational constants.

Neglecting the cubic terms the separation of the successive levels in a set of bands is given by the first difference,

$$\Delta G(v+\tfrac{1}{2}) = G(v+1) - G(v)$$
$$= \omega_e - 2\omega_e x_e - 2\omega_e x_e v$$

The second difference has the constant value

$$\Delta^2 G(v+1) = \Delta G(v+\tfrac{3}{2}) - \Delta G(v+\tfrac{1}{2})$$
$$= 2\omega_e x_e$$

The vibrational constants ω_e and $\omega_e x_e$ can thus be determined from the observed position of the band heads. In the present investigation, the vibrational constants ω_e and $\omega_e x_e$ for the ground state as well as for upper excited states of the halides of cadmium were determined.

(2) INTENSITY DISTRIBUTION IN A BAND SYSTEM.

In extensive band systems which lie within the photographic spectral region, the estimation of the relative intensities of bands from end to end of the system is rather inaccurate due to variation of the plate sensitivity. Quantitative data over such long regions are rare and the usual practice is to estimate the band intensities visually on a scale of ten arbitrarily. The only importance of this data is to provide a guess for the presence or absence of each band under certain conditions of excitation and observation. Nevertheless such estimates do provide certain general indications which have received simple theoretical interpretation.

The intensity of a band connected with a given pair of vibrational energy levels (v', v''), depends upon the number of molecules in the initial vibrational level and the probability of the transition from the initial to the final level. A simple theoretical interpretation of the observed distribution is given by Condon (1926).

According to this principle "the electron jump in a molecule takes place so rapidly in comparison to the vibrational motion that immediately afterwards the nuclei still have very nearly the same relative position and velocity as before the jump". The net effect is thus the instantaneous substitution of one law of force by another.

The intensity distribution in band spectra is interpreted through the $U(r):r$ curves of the electronic states involved. The following are the typical cases of frequent occurrence:

(i) when $r_e' \doteqdot r_e''$ and $\omega_e' \doteqdot \omega_e''$ the Franck-Condon parabola of most favoured transitions consists of two almost coincident branches along the diagonal of v',v" scheme.

(ii) when $r_e' < r_e''$ and $\omega_e' > \omega_e''$ (violet degraded bands) or $r_e' > r_e''$ and $\omega_e' < \omega_e''$ (red degraded bands) parabolas with moderately separated branches are obtained.

(iii) when $r_e' << r_e''$ and $\omega_e' >> \omega_e''$ the parabola of most favoured transitions widens out and its branches follow v',v" progressions, the (0,0) band for such cases is impossible and bands in the neighbourhood of the system origin are very weak.

(iv) when $r_e' >> r_e''$ and $\omega_e' << \omega_e''$ the intensity distribution is similar to that of (iii).

Differences in the intensity distribution within certain limits occur in most of the band systems as the experimental conditions are varied.

(3) ISOTOPIC EFFECT IN A BAND SYSTEM

An accurate measurement of the isotopic effect can be used to obtain a precise value for the ratio of the masses of two kinds of isotopic atoms concerned (from $\rho = \sqrt{(\mu/\mu_i)}$). Under favourable conditions, the accuracy of the ratio of the masses so obtained is comparable with the accuracy of mass spectrographic values. Apart from that, the study of the isotopic effect in electronic band spectra has led to the discovery of new isotopes and to an unambiguous confirmation of the quantum mechanical formula for the energy levels of the oscillator.

Further by the study of the isotopic effect it is possible to decide the carrier of an observed band system. Usually in emission spectra, band systems often appear due to chemically unstable molecules which are formed in the discharge and are not readily identified. Sometimes band systems of impurities appear frequently with much greater intensity irrespective of their concentration. Since the magnitude of the isotopic effect depends on the masses of the two atoms forming a molecule, it can be used to decide the various possibilities for the carrier of the band system. In the present work is reported the study of the isotopic effect in the case of cadmium bromide molecule.