PART I

CHAPTER I

INTRODUCTION

Various methods for investigating the structure of molecules and their intrinsic properties are known since long. Amongst them, spectral study of the molecules occupies a unique position. Molecular spectra can be conveniently classified according to the type of molecular energy that is being changed in a transition. In an atom the total energy in a particular state is almost entirely electronic whereas that of a molecule is regarded as the sum of electronic, vibrational and rotational energy of which the electronic energy is much more greater than the other two. It is the vibrational and rotational transitions superposed on the electronic transition that gives rise to the molecular spectrum or what is called a band spectrum. Whereas the Raman and infra-red spectra are produced by transitions involving only ground state, the band spectra result due to electronic transitions between an upper and a low-lying electronic state. Hence the study of band spectra is of greatest value for a knowledge of the electronic structure of molecules and the geometrical arrangement of the atoms in them and also for the theoretical understanding of chemical valence and dissociation energy of molecules.

The application of quantum mechanics to the theory of band spectra of diatomic molecules has played an important role in solving the problems of electronic structure. This has been found true especially in the case of our knowledge regarding the electronic states and the products of dissociation of molecules.

The most probable electron configurations for the lighter diatomic molecules and the order of their electron binding have been determined by Mulliken (1932). But such a systematic scheme for the heavier diatomic molecules has not been formulated so far, as they possess greater number of electrons and have molecular orbitals of approximately equal energy. The molecules whose structure can best be interpreted are H_2 and He_2 (Heitler and London, 1927). This interpretation has provided a secure foundation with which the successive addition of an electron to the configuration of H_2 and He_2 has enabled to determine the electron configurations of the lighter molecules. However, a successful utilization of this method of approach depends entirely upon the available accurate molecular data derived mainly from the spectroscopic studies involving the vibrational and rotational analyses of the band spectra and also from the studies on ionization potential. Comparatively few band systems have been studied in detail for heavy diatomic molecules and the molecular constants of many of them are not known accurately. Consequently any additional experimental data on the spectra of heavy diatomic molecules will be helpful in the construction of an improved electronic scheme for these molecules.

The variation of spectroscopic properties of a group of related molecules, such as hydrides, oxides or halides of the elements of a column of the periodic table or a group of molecules with the same number of electrons provides much useful information about the electronic states involved and in the interpretation in terms of their electron configurations. This procedure can be used to correlate various molecular constants derived and their dependence on the energy levels of the constituent atoms can be investigated. This will also help in the search for missing analogous band systems.

The oxides, sulphides and halides of zinc, cadmium and mercury have not been studied so extensively as those of the fourth group elements. The present investigation has been taken up mainly to study the ultraviolet spectra of the diatomic molecules, mercury chloride, mercury bromide and mercury iodide in emission. The results obtained and the conclusions drawn therefrom are presented in this thesis. A comparison of the results obtained in the present study has been made with the available spectroscopic data on the halides of zinc and cadmium.

The theory and methods of analysing electronic spectra have been well established over several years ago and are discussed in detail by Mulliken (1930, 1931, 1932), Jevons (1932), Johnson (1949), Gaydon (1947), Herzberg (1950), Barrow (1962), Walker and Straw (1962) and King (1964). In order to make the thesis self-contained, a brief theoretical account related to the study of band spectra will now be given in the following order:

(i) The vibrational structure of band systems.
(ii) The intensity distribution in a band system.
(iii) The isotope effect in a band system.

(i) THE VIBRATIONAL STRUCTURE OF BAND SYSTEMS:

The total quantizable energy of a molecule can be considered as made up of three parts viz. electronic, vibrational and rotational and is usually represented by

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

In other words, the emitted or absorbed frequencies may be given as the sum of three constituent parts:

$$\nu = \nu_e + \nu_v + \nu_r \qquad \ldots \qquad (2)$$

For a given band, ν_r varies for each of its rotational line while $(\nu_e + \nu_v)$ is constant and defines the band origin. For a given band system, ν_v varies from band to band, ν_e being constant and defining the system origin. The energy difference for the electronic states is such that the energy absorbed or emitted in a transition between them will lie within the visible to the ultraviolet region of the spectrum.

For a given electronic transition ν_e is a constant and rotational energy ν_r is so small compared to ν_v that it can be safely disregarded for the instant. If now the vibrational energy E_v is expressed in the following form:

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

then equation (2) can be written as

$$\nu = \nu_e + \left[\omega_e'(v'+\tfrac{1}{2}) - \omega_e'x_e'(v'+\tfrac{1}{2})^2 + \omega_e'y_e'(v'+\tfrac{1}{2})^3 - \ldots\right]$$
$$- \left[\omega_e''(v''+\tfrac{1}{2}) - \omega_e''x_e''(v''+\tfrac{1}{2})^2 + \omega_e''y_e''(v''+\tfrac{1}{2})^3 - \ldots\right] \qquad \ldots. \quad (3)$$

where the single-primed letters refer to the upper state and the double-primed letters refer to the lower state. In expression (3) v' and v'' are the vibrational quantum numbers of the upper and lower states respectively, ω_e' and ω_e'' being the vibrational frequencies of the molecule in these states and $\omega_e'x_e'$ and $\omega_e''x_e''$, the anharmonicity constants. This equation represents all possible transitions between different vibrational levels of the two participating electronic states. There is no strict selection rule for the vibrational quantum number v and hence transition between each vibrational level of the upper electronic state can take place with any vibrational level of the lower electronic state. The formula (3) may also be written as:

$$\nu = \nu_{00} + (\omega_0'v' - \omega_0'x_0'v'^2 + \omega_0'y_0'v'^3 - \ldots.)$$
$$- (\omega_0''v'' - \omega_0''x_0''v''^2 + \omega_0''y_0''v''^3 - \ldots.) \qquad \ldots. \quad (4)$$

where ν_{00} is a term independent of v' and v" and is usually called the (0,0) band as it corresponds to the transition v' = 0 — v" = 0. By putting the value of v' = 0 and v" = 0 in formula (3), the following expression for $\nu_{0,0}$ can be readily obtained.

$$\nu_{0,0} = \nu_e + (\tfrac{1}{2}\omega_e' - \tfrac{1}{4}\omega_e'x_e' + \tfrac{1}{8}\omega_e'y_e') - (\tfrac{1}{2}\omega_e'' - \tfrac{1}{4}\omega_e''x_e'' + \tfrac{1}{8}\omega_e''y_e'') \quad \ldots\ldots (5)$$

Usually $\omega_e y_e$ is very small and hence neglected. From equation (5), the value of ν_e can be calculated and substituted in equation (3). In fact equation (3) refers to the band origins but in the usual practice the positions of the band heads are measured as it is difficult to determine the band origins without detailed analysis of the rotational structure. However, as the separation between ν_{origin} and ν_{head} is small, the error in the vibrational constants derived from the band head measurements is often negligible. The error can be minimised by taking the measurements on Q heads if they are observed as they lie very near to the band origins.

To analyse a band system the usual procedure (Herzberg, 1950) is to arrange the wavenumbers of various bands in a table called the Deslandres table in such a way that the difference of frequencies in adjacent column or row is approximately constant and varies uniformly and regularly. Thus the differences between the wavenumbers in the columns in the table give the spacing between vibrational levels in the lower electronic state and the differences between the wavenumbers in the rows give the spacing between the vibrational levels in the upper electronic state. The group of bands when arranged in such a Deslandres table, having a constant value of $\Delta v = v' - v''$ is called a sequence whereas the different bands in the same horizontal row or in the same vertical column having the same v' or v'' values are said to form v' or v'' progressions respectively. Neglecting the cubic terms the separation of the successive vibrational levels for a group of bands is given by the first difference:

$$\begin{aligned} G_{v+\frac{1}{2}} &= G(v+1) - G(v) \\ &= \omega_e - 2\,\omega_e x_e - 2\,\omega_e y_e v. \end{aligned}$$

The second difference has the constant value

$$\begin{aligned} \Delta^2 G_{v+1} &= G_{v+1\frac{1}{2}} - G_{v+\frac{1}{2}} \\ &= 2\,\omega_e x_e . \end{aligned}$$

The vibrational constants ω_e and $\omega_e x_e$ for the upper and the lower states and the system origin ν_e can thus be determined from the observed position of the band heads.

(ii) INTENSITY DISTRIBUTION IN A BAND SYSTEM:

The relative intensities of the bands depend upon the initial distribution of the molecules as well as on the relative transition probabilities as a function of vibrational quantum number. A simple theoretical interpretation of the observed intensity distribution is given by Franck (1925) and is further developed by Condon (1926, 1928). According to Franck-Condon principle electronic transition in a molecule takes place so rapidly compared to the vibrational motion of the atomic nuclei that the internuclear distance can be regarded as fixed during the transition.

The intensity distribution in a band system can be interpreted with the help of potential curves of the electronic states involved. The following types of distributions are of frequent occurrence:

(a) When $r_e' \doteqdot r_e''$ (and $\omega_e' \doteqdot \omega_e''$) the most probable transitions are where $v' = v''$. Consequently the Condon parabola consists of two almost coincident branches along the diagonal of the v', v'' array.

(b) When the difference in r_e values is not too large, Condon parabola will be observed with moderately separated branches.

(c) If $r_e' \ll r_e''$ (and $\omega_e'' \ll \omega_e'$), the (0,0) band may not be having observable intensity and generally the bands in the vicinity of (0,0) will be weak in intensity.

(d) If $r_e' \gg r_e''$ (and $\omega_e' \ll \omega_e''$), the intensity distribution will be similar to that of (c).

The estimation of the relative intensities of the bands in an extensive system is rather inaccurate on account of the variation of the spectral sensitivity of the photographic plates and the transmittance of the filters employed. It is the usual practice to make visual estimates of the relative intensities of the bands on a scale of ten. Importance of this data is just to provide a guess about the presence or absence of each band under certain conditions of excitation but such estimates nevertheless provide certain general indications which have received simple theoretical interpretations.

(iii) ISOTOPE EFFECT IN A BAND SYSTEM:

Isotope effect has been found to be very important in the analysis of band spectra. The shift of vibrational energy levels due to the two isotopic molecules can be given by

$$G^i(v) - G(v) = (\rho-1)\,\omega_e(v+\tfrac{1}{2}) - (\rho^2-1)\,\omega_e x_e(v+\tfrac{1}{2})^2 + \ldots\ldots \qquad \ldots\ldots (6)$$

The displacement of the corresponding bands is therefore expressed by

$$\begin{aligned}\Delta\nu &= \nu^{i} - \nu \\ &= (\rho-1)\left[\omega_e'(v'+\tfrac{1}{2}) - \omega_e''(v''+\tfrac{1}{2})\right] \\ &\quad - (\rho^{2}-1)\left[\omega_e'x_e'(v'+\tfrac{1}{2})^{2} - \omega_e''x_e''(v''+\tfrac{1}{2})^{2}\right] \qquad \ldots \quad (7)\end{aligned}$$

In equations (6) and (7) the superscript i refers to the isotopic molecule which has more abundance and $\rho = \mu/\mu^{i}$, μ being the reduced mass. From this expression it is evident that the separation of the bands corresponding to the lighter of the two isotopic molecules from the origin is more as compared to that for the corresponding heavier isotopic molecule. The intensity of the isotopic bands depends upon the relative abundance of the isotopic masses of the constituent atoms.

A knowledge of isotope shifts in the band spectra has led to the discoveries of many new isotopes. It has contributed to the determination of the ratio of the masses of isotopes concerned. The observation of [illegible] isotope effect in a band system is an important check on the correctness of the vibrational analysis carried out. The identity of the emitter of the bands can be verified by means of isotope effect, since the magnitude of the isotope shift depends upon the masses of the participating atoms.