PART I

CHAPTER I

INTRODUCTION

During the course of last four to five decades considerable progress has been made in the investigation of molecular spectra. Among the various means for investigating the structure and intrinsic properties of molecules, spectroscopic study occupies a unique position. Since 1930 the study and interpretation of molecular spectra has undergone a rapid progress and has proved to be a very important tool. From the spectra various discrete energy levels of a molecule can be derived directly, from which one can obtain detailed information about the motion of the electrons and the vibration and rotation of the nuclei in the molecules. In the case of atomic spectra, the total energy of an atom in a given state is almost entirely electronic. While in a molecule it is regarded as sum of electronic, vibrational and rotational 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 which give rise to molecular spectrum. Transitions between an upper and a low-lying electronic state of a molecule give rise to the band spectra. The study of electronic motions has led to a theoretical understanding of chemical valence. Heat of dissociation of molecules can be calculated with great accuracy from the vibrational frequencies. The forces between the atoms in the molecules can also be determined. From the rotational frequencies one can obtain accurate information about the geometrical arrangement of the nuclei in the molecule and in particular, extremely accurate values of the internuclear distances. Hence the study of band spectra is of great importance to get valuable information regarding the molecules.

Since 1925, with the application of quantum mechanics, the theory of band spectra of diatomic molecules, has undergone very rapid development. It has helped much in understanding the problem of the electronic structure of molecules and the products of dissociation.

The most probable electron configurations for lighter diatomic molecules and order of their electron binding have been determined by Mulliken (1932). However no such systematic scheme has yet been formulated for heavier diatomic molecules as they involve greater number of electrons and molecular orbitals having 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. A successful utilization of this method of approach depends entirely on the existence of accurate molecular data derived mainly from spectroscopic studies involving the vibrational and rotational analyses of the spectra of molecules and also on the studies on ionization potential. Comparatively few band systems have been studied in detail for heavy molecules and the molecular constants of many of them are not known accurately. Therefore 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.

A systematic investigation on the molecular constants for a group of related molecules such as the 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 compare various molecular constants derived and their dependance on the energy levels of the constituent atoms can be investigated. This will also help in the search for missing analogous band systems.

A detailed investigation of the rotational structure of the band system is of great significance in understanding some of the properties of the nuclei of the constituent atoms of the molecule.

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 (1953), Herzberg (1950), Barrow (1962), Walker and Straw (1962), King (1964) and

Kovac's (1969). In order to make the thesis self-contained a brief theoretical account related to the present study of band system will be given.

The possible energy values of a diatomic molecule can be expressed as functions of certain quantum numbers associated with motions of the electrons and nuclei. These quantum numbers can be divided into three groups:

(a) A group which defines the energy depending on the electronic motions, which the molecule would have if the nuclei could be held stationary.

(b) A single quantum number 'v' which defines the vibration of the nuclei.

(c) A group of quantum numbers associated with the rotation of the nuclei and with the finer details of the electronic motions. In the scheme of quantum numbers belonging to this group the interactions between electron motions and nuclear rotations must be taken into account.

The wave number ν of any line in the spectrum can be obtained by taking the difference of two terms, one of higher energy F' and other of lower energy F".

$$\begin{aligned}\nu &= F' - F'' \\ &= (F'_{el} - F''_{el}) + (F'_v - F''_v) + (F'_r - F''_r) \\ &= \nu_{el} + \nu_v + \nu_r \qquad (1)\end{aligned}$$

The bands of a band system with $\nu_{el} \neq 0$ are electronic bands.

Usually, $\nu_{el} \gg \nu_v \gg \nu_r$, corresponding to the relative energy level spacing of F_{el}, F_v and F_r. All the spectrum lines associated with a definite pair of electronic states are collectively called a band system. These lines of a band system are again divided into limited groups of lines called bands, each band being associated with a definite pair of vibrational states belonging to the two different electronic states involved in the transition.

VIBRATIONAL STRUCTURE OF A BAND SYSTEM

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 as

$$E = E_e + E_v + E_r$$

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

$$\nu = \nu_e + \nu_v + \nu_r$$

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 defines 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 by the following equation:

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

Then the equation (1) can be written as

$$\nu = \nu_e + \left[\omega'_e(v'+\tfrac{1}{2}) - \omega'_e X'_e(v'+\tfrac{1}{2})^2 + \omega'_e Y'_e(v'+\tfrac{1}{2})^3 - \cdots\right]$$
$$- \left[\omega''_e(v''+\tfrac{1}{2}) - \omega''_e X''_e(v''+\tfrac{1}{2})^2 + \omega''_e Y''_e(v''+\tfrac{1}{2})^3 - \cdots\right] \quad (2)$$

where the single-primed letters refer to the upper state and double-primed letters refer to the lower state. In equation (2) 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 upper electronic state can take place with any vibrational level of the lower electronic state. Equation (2) may also be written as

$$\nu = \nu_{00} + (\omega'_0 v' - \omega'_0 x'_0 v'^2 + \omega_0 y'_0 v'^3 - \ldots\ldots)$$

$$- (\omega''_0 v'' - \omega''_0 x''_0 v''^2 + \omega''_0 y''_0 v''^3 - \ldots\ldots)$$

where ν_{00} is a term independent of v' and v'' and is usually known as (0,0) band as it corresponds to the transition $v' = 0$ to $v'' = 0$. By substituting the values of $v' = 0$ and $v'' = 0$ in the equation (2), it will be

$$\nu_{00} = \nu_e + (\tfrac{1}{2}\omega'_e - \tfrac{1}{4}\omega_e x'_e + 1/8\,\omega'_e y'_e)$$

$$- (\tfrac{1}{2}\omega''_e - \tfrac{1}{4}\omega''_e x''_e + 1/8\,\omega''_e y''_e) \quad \ldots\ldots\ldots (3)$$

Usually $\omega_e y_e$ is small and it is neglected. From equation (3), the value of ν_e can be calculated and substituted in equation (2). In fact equation (2) 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 usually 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 of 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 wave numbers of various bands in a table called the "Deslandres table" in such a way that the difference of frequencies in adjacent columns or rows is approximately constant and varies uniformly and regularly. Thus the differences between the wave numbers in the columns in the table gives the spacing between vibrational levels in the lower electronic state and the differences between wave numbers 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'' 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.

$$\Delta G_{v+\frac{1}{2}} = G(v+1) - G(v)$$

$$= \omega_e - 2\omega_e X_e - 2\omega_e X_e v$$

where $G(v) = E_v/hc$ is called the term value. In the above equation the cubic terms have been neglected, $\omega_e Y_e$ being very small.

The second difference has constant value

$$\Delta^2 G_{v+1} = \Delta G_{v+3/2} - \Delta G_{v+\frac{1}{2}} = -2\omega_e X_e \qquad (4)$$

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.

INTENSITY DISTRIBUTION IN A BAND SYSTEM

A theoretical interpretation of the observed intensity distribution is given by Franck (1925) and by Condon (1926, 1928). The relative intensities of bands depend upon the initial distribution of the molecules as well as on the relative transition probabilities as a function of vibrational quantum numbers. The intensity distribution in a band system can be interpreted with the help of potential curves of electronic states involved. According to Franck-Condon principle the electronic transition in a molecule takes place so rapidly compared with the vibrational motion of the nuclei that the internuclear distance can be regarded as fixed during the transition. The following types of distributions are generally observed:

(a) When $r'_e \simeq r''_e$ (and $\omega'_e \simeq \omega''_e$), the most probable transitions are those where $v' = v''$ and the Condon parabola consists of two almost coincident branches along the diagonal of the v' and v'' array.

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

(c) If $r'_e \ll r''_e$ (and $\omega'_e \gg \omega''_e$), the (0,0) band may not be observable and the bands in its neighbourhood will be generally weak in intensity. The two branches of the Condon parabola will be quite open and the intensity in this case tends to follow the progressions rather than the sequences.

(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 used. General practice is to make visual estimates of the relative intensities of the bands on a scale of ten. This data is only of the importance 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.

ISOTOPE EFFECT IN A BAND SYSTEM

The shift of vibrational energy levels due to the two isotopic molecules can be given by,

$$G^{i}(v) - G(v) = (\rho-1)\,\omega_e(v+\tfrac{1}{2}) - (\rho^2-i)\,\omega_e x_e(v+\tfrac{1}{2})^2 + \ldots\ldots \qquad (5)$$

The displacement of the corresponding band is thus expressed by

$$\Delta\nu = \nu^{i} - \nu$$

$$= (\rho-1)\left[\omega'_e(v'+\tfrac{1}{2}) - \omega''_e(v''+\tfrac{1}{2})\right]$$

$$- (\rho^2-1)\left[\omega'_e x'_e(v'+\tfrac{1}{2})^2 - \omega''_e x''_e(v''+\tfrac{1}{2})^2\right] \qquad (6)$$

In above equations the superscript 'i' refers to the isotopic molecule having more abundance and $\rho = \sqrt{\frac{\mu}{\mu^i}}$ where μ is the reduced mass. From this expression it is evident that the separations 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. The study of isotopic effect in a band system provides an important check on the correctness of the vibrational analysis and helps to decide the career of a band system.

STRUCTURE OF INDIVIDUAL ELECTRONIC BAND

In a single band ν_{el} and ν_v are fixed while ν_r varies. Equation (1) can be written as

$$\nu = \nu_0 + F'(J') - F''(J'') \qquad (7)$$

where $F'(J')$ and $F''(J'')$ are the rotational terms of the upper and lower states respectively. ν_0 is called the band origin or the zero line.

Among a non-rigid vibrating symmetric top model for a diatomic molecule the equation for rotational term values can be written in the following form:

$$F_v(J) = B_vJ(J+1) - D_vJ^2(J+1)^2 + \ldots\ldots \qquad (8)$$

Equation (7) can be written as

$$\nu = \nu_0 + B'_vJ'(J'+1) - D'_vJ'^2(J'+1)^2 + \ldots\ldots$$

$$- \; B''_vJ''(J''+1) + D''_vJ''^2(J''+1)^2 + \ldots\ldots \qquad (9)$$

Applying selection rules ΔJ = J'-J" = 0, ±1, three series of lines in a band are expected. Lines corresponding to ΔJ = +1,0,-1 are said to belong to R, Q and P branches respectively.

If one neglects the small term D_v in equation (9) the following formulae give the wave numbers of R, Q and P branches

$$\nu_R = \nu_0 + 2B'_v + (3B'-B''_v)J + (B'_v-B''_v)J^2 \qquad (10)$$

$$\nu_Q = \nu_0 \qquad + (B'_v-B''_v)J + (B'_v-B''_v)J^2 \qquad (11)$$

$$\nu_P = \nu_0 \qquad - (B'_v+B''_v)J + (B'_v-B''_v)J^2 \qquad (12)$$

where J represents the rotational quantum number of the lower state.

The P and R branches can be represented by a single equation

$$\nu = \nu_0 + (B'_v+B''_v)m + (B'_v-B''_v)m^2 \qquad (13)$$

where m = -J for the P branch and m = J+1 for the R branch. Owing to the quadratic term in equation (13) one of the two branches turns back forming a band head. A head is formed in the R branch if $B'_v-B''_v$ is negative and lies on the short wavelength side of the zero line and the band is shaded towards the red. If $B'_v-B''_v$ is positive, head is formed by P branch and the band is degraded towards the violet.

The 'm' value corresponding to the band head can be obtained by putting $d\nu/dm = 0$ in the equation of head forming branch and is given by

$$m_{head} = \frac{B'_v + B''_v}{2(B'_v - B''_v)} \qquad (14)$$

The equation for separation of head to origin can also be derived and is

$$\nu_{head} - \nu_{origin} = -\frac{(B'_v+B''_v)^2}{4(B'_v-B''_v)} \qquad (15)$$

In Q branch the head is formed at the beginning of the Q branch and lies very near to the origin.

The rotational constants B'_v, D'_v and B''_v, D''_v for the upper and lower states are usually evaluated from combination differences. In a simple band where P and R branches are present there is to every line in the P branch a corresponding line in the R branch with the same upper state. The wave number difference of these two lines is equal to the separation of one of the lower-state rotational levels from the next but one viz. $\Delta_2F''(J)$. Thus

$$R(J-1) - P(J+1) = F''_v(J+1) - F''_v(J-1) = \Delta_2F''(J) \qquad (16)$$

Similarly, the difference between the wave numbers of the two lines with a common lower state is equal to the separation of one of the upper state rotational levels from the next but one viz. $\Delta_2F'(J)$.

$$R(J) - P(J) = F'_v(J+1) - F'_v(J-1) = \Delta_2F'(J) \qquad (17)$$

Combination relations between R, Q and P branch lines can be derived in similar way and are

$$\begin{aligned} R(J) - Q(J) &= F'_v(J+1) - F'_v(J) &= \Delta_1 F'(J) \\ Q(J+1)-P(J+1) &= F'_v(J+1) - F'_v(J) &= \Delta_1 F'(J) \\ R(J) - Q(J+1) &= F''_v(J+1) - F''_v(J) &= \Delta_1 F''(J) \\ Q(J) - P(J+1) &= F''_v(J+1) - F''_v(J) &= \Delta_1 F''(J) \end{aligned} \qquad (18)$$

Here $\Delta_1 F(J)$ refers to the separation of successive rotational levels. If the expression (8) for $F_v(J)$ neglecting the term D_v, is substituted for $\Delta_2 F(J)$ then,

$$\Delta_2 F(J) = F_v(J+1) - F_v(J-1) = B_v(J+1)(J+2) - B_v(J-1)J$$

$$= 4B_v(J+\tfrac{1}{2})$$

and

$$\Delta_1 F(J) = F_v(J+1)-F_v(J) = B_v(J+1)(J+2) - B_v(J+1)J$$

$$= 2B_v(J+1)$$

It is seen that combination differences to a first approximation are a linear function of the rotational quantum number J.

By plotting the combination difference versus J a straight line is obtained. From the slope of the graph, the value of rotational constant B_v can be obtained.

If two or more bands with the same v' are studied the combination differences, $\Delta_2F'(J)$, for the upper state of the two bands must agree exactly irrespective of perturbations. The agreement between corresponding combination differences for bands with the same lower or the same upper vibrational states provides an important sensitive check on the correctness of a rotational analysis.

If the term D_v in equation (8) is not neglected then $\Delta_2F(J)$ is given by

$$\Delta_2F(J) = (4B_v-6D_v)(J+\tfrac{1}{2}) - 8D_v(J+\tfrac{1}{2})^3$$

The plot of $\Delta_2F(J)/(J+\frac{1}{2})$ versus $(J+\frac{1}{2})^2$ gives a straight line with slope $8D_v$. The plot $\Delta_2F(J)/(J+\frac{1}{2})$ versus $(J+\frac{1}{2})^2$ serves as a criterion for the correctness of numbering to the branches. If there is misnumbering the straight line will deviate for lower values of J (Youngner and Winans, 1960).

Standard methods to assign correct numbering to the different branch lines in bands have been described by Herzberg (1950).

The value of rotational constant B_v and D_v will be different for different vibrational states of an electronic state. B_v value decreases almost linearly with the increasing v and is represented by the following equation

$$B_v = B_e - \alpha_e(v+\tfrac{1}{2})$$

The constant B_e can be said to be belonging to completely vibrationless state.

In the similar way the variation in D_v is represented by the expression

$$D_v = D_e + \beta_e(v+\tfrac{1}{2}) + \ldots.$$

The constants D_e, B_e and ω_e are related by the following relation

$$D_e = \frac{4B_e^{\,3}}{\omega_e^{\,2}}$$

SPIN SPLITTING

The effect of electron spin can be clearly observed in transitions like $^2\Sigma - {}^2\Sigma$. $^2\Sigma$ states always belong strictly to Hund's case (b) and selection rule $\Delta K = \pm 1$ holds. The separation of two sub-levels with $J = K+\frac{1}{2}$ and $J = K-\frac{1}{2}$ for a given K is, in general very small. However, with larger resolution each line of P and R branches splits into three components according to the selection rule $\Delta J = 0, \pm 1$. $J = 0$ holds if ΔJ is unequal to ΔK; and intensity of these components falls off rapidly. Therefore, in practice, there is a doublet P and a doublet R branch.

If we distinguish the term components having $J = K+\frac{1}{2}$ with the subscript 1 and those having $J = K-\frac{1}{2}$ with subscript 2, we obtain for the four main branches

$$R_1(K) = \nu_0 + F_1'(K+1) - F_1''(K)$$
$$R_2(K) = \nu_0 + F_2'(K+1) - F_2''(K)$$
$$P_1(K) = \nu_0 + F_1'(K-1) - F_1''(K)$$
$$P_2(K) = \nu_0 + F_2'(K-1) - F_2''(K)$$

In the case of $^2\Sigma$ states rotational term values are given by

$$F_1'(K) = B_v K(K+1) + \tfrac{1}{2}\gamma K$$

and $$F_2(K) = B_v K(K+1) - \tfrac{1}{2}\gamma(K+1)$$

where γ is spin splitting constant.

The line splitting in P and R branches is

$$\Delta\nu_{12}(P) = P_1-P_2 = (\gamma'-\gamma'') - \tfrac{1}{2}(\gamma'+\gamma'')$$

and $$\Delta\nu_{12}(R) = R_1-R_2 = (\gamma'-\gamma'')K + \tfrac{1}{2}(3\gamma'-\gamma'')$$

Thus splitting increases linearly with K. The combination difference must be formed either between R_1 and P_1 or R_2 and P_2

$$\Delta_2F_1(K) = 4B_v(K + \tfrac{1}{2}) + \gamma$$

$$\Delta_2F_2(K) = 4B_v(K + \tfrac{1}{2}) - \gamma$$