PART I

CHAPTER I

INTRODUCTION

Molecular spectroscopy is the study of the

absorption or emission of electromagnetic radiation

by molecules. The experimental data that such studies

provide are the frequencies or wavelengths of the

radiation and the amount of radiation emitted or

absorbed by the molecules. One can often understand

the nature of the molecular changes that are responsible

for the emission or absorption of the radiation. In

such cases, the experimental spectroscopic data can

be used to determine quantitative values for various

molecular properties. Remarkably detailed and exact

measurements of the size, shape, flexibility and

electronic arrangement of a molecule can be obtained.

It will become apparent that spectroscopy offers one

of the most powerful tools for a great variety of

molecular - structure studies. 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

the 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, vibra-

tional 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 be deter-

mined. 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 formu-

lated 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'' .

$$\nu = F' - F''$$

$$= (F'_{el} - F''_{el}) + (F'_v - F''_v) + (F'_r - F''_r)$$

$$= \nu_{el} + \nu_v + \nu_r \tag{1}$$

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.

1.1   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 consti-

tuent 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 :

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

Then the equation (1) can be written as

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

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

$$\mathcal{D} = \mathcal{D}_{oo} + (\omega'_o v' - \omega'_o x'_o v'^2 + \omega'_o y'_o v'^3 - \ldots)$$

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

where $\mathcal{D}_{oo}$ 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

$$\mathcal{D}_{oo} = \mathcal{D}_e + (\tfrac{1}{2}\omega'_e - \tfrac{1}{4}\omega'_e x'_e + 1/8\ \omega'_e y'_e)$$

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

Usually $\omega_e y_e$ is small and it is neglected. From

equation (3), the value of ω_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

$$\Delta^2 G_{v+1} = \Delta G_{v+3/2} - \Delta G_{v+\frac{1}{2}} = -2\omega_e x_e \tag{4}$$

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.

1.2   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 proba-

bilities 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 neighbour-

        hood 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.

1.3   ISOTOPE EFFECT IN A BAND SYSTEM

The shift of vibrational energy levels due to

the two isotopic molecules can be given by,

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

The displacement of the corresponding band is

thus expressed by

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

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

$$- (\rho^2 - 1)\left[\omega_e'x_e'(v' + \tfrac{1}{2})^2 - \omega_e''x_e''(v'' + \tfrac{1}{2})^2\right] \quad (6)$$

In above equations the superscript 'i' refers to the isotopic molecule having more abundance and $\rho = \sqrt{\dfrac{\mu}{\mu^i}}$ where μ is 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. 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.

1.4 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

$$\nu = \nu_o + F'(J') - F''(J'') \quad (7)$$

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 :

$$F_v(J) = B_v J(J+1) - D_v J^2(J+1)^2 + \ldots\ldots \quad (8)$$

Equation (7) can be written as

$$\nu = \nu_0 + B_v' J'(J'+1) - D_v' J'^2(J'+1)^2 + \ldots$$

$$- B_v'' J''(J''+1) + D_v'' J''^2(J''+1)^2 + \ldots \quad (9)$$

Applying selection rules $\Delta J = J' - J'' = 0, \pm 1$, three series of lines in a band are expected. Lines corresponding to $\Delta J = +1, 0, -1$ 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

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

$$\mathcal{V}_Q = \mathcal{V}_0 \qquad + (B'_V - B''_V)J + (B'_V - B''_V)J^2 \qquad\qquad (11)$$

$$\mathcal{V}_P = \mathcal{V}_0 \qquad - (B'_V + B''_V)J + (B'_V - B''_V)J^2 \qquad\qquad (12)$$

where J represents the rotational quantum number of

the lower state.

The P and R branches can be represented

by a single equation

$$\mathcal{V} = \mathcal{V}_0 + (B'_V + B''_V)m + (B'_V - B''_V)m^2 \qquad\qquad (13)$$

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 dĕgraded towards the violet.

The 'm' value corresponding to the band head

can be obtained by putting $d\mathcal{V}/dm = 0$ 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

$$\mathcal{V}_{head} - \mathcal{V}_{origin} = - \frac{(B'_V + B''_V)^2}{4(B'_V - B''_V)} \qquad (15)$$

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. $\Delta_2 F''(J)$. Thus

$$R(J-1) - P(J+1) = F''_V(J+1) - F''_V(J-1) = \Delta_2 F''(J) \qquad (16)$$

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. $\Delta_2 F'(J)$.

$$R(J)-P(J) = F'_v(J+1) - F'_v(J-1) = \Delta_2 F'(J) \qquad (17)$$

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

$$R(J)-Q(J) = F'_v(J+1) - F'_v(J) = \Delta_1 F'(J)$$

$$Q(J+1)-P(J+1) = F'_v(J+1) - F'_v(J) = \Delta_1 F'(J)$$

$$(18)$$

$$R(J) -Q(J+1) = F''_v(J+1) - F''_v(J) = \Delta_1 F''(J)$$

$$Q(J) -P(J+1) = F''_v(J+1) - F''_v(J) = \Delta_1 F''(J)$$

Here $\Delta_1 F(J)$ refere 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,

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

$$= 4B_v(J+\tfrac{1}{2}) \qquad (19)$$

and

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

$$= 2B_v(J+1) \tag{20}$$

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, $\Delta_2 F'(J)$, 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 $\Delta_2 F(J)$ is given by

$$\Delta_2 F(J) = (4B_v - 6D_v)(J+\tfrac{1}{2}) - 8D_v(J+\tfrac{1}{2})^3 \qquad (21)$$

The plot of $\Delta_2 F(J)/(J+\tfrac{1}{2})$ versus $(J+\tfrac{1}{2})^2$ gives a

straight line with slope $8D_v$. The plot $\Delta_2 F(J)/(J+\tfrac{1}{2})$

versus $(J+\tfrac{1}{2})^2$ 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 constants 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.

$$B_v = B_e - \alpha_e (v + \tfrac{1}{2}) \qquad (22)$$

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

$$D_v = D_e + \beta_e(v+\tfrac{1}{2}) + \ldots \ldots \tag{23}$$

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

$$D_e = \frac{4B_e^3}{\omega_e^2} \tag{24}$$