PART - I

CHAPTER - I

INTRODUCTION

The study of molecular spectra has become one of the most important means for investigating molecular structure and therefore in the last few decades considerable progress has been made in the investigations and theoretical interpretations of molecular spectra of various substances. From the study of spectra, various discrete energy levels of molecules can be derived directly and from the study of energy levels of molecules, one can get the complete information regarding motion of electrons (Electronic Structure), vibration and rotation of the nuclei in the molecules. The detailed study of electronic motion gives theoretical understanding of chemical valence and vibrational frequencies provide the knowledge of forces between the atoms, heat of dissociation and vibrational temperature of a molecule can be calculated. The rotational frequencies give information about the geometrical arrangement of nuclei in the molecule.

In an atom, the total energy in a particular state is almost entirely electronic, but in a molecule, the total energy is the sum of the electronic, vibrational and rotational energy of which the electronic energy is much more greater than the other two. It means that the vibrational and rotational transitions are superposed on the electronic transition giving rise to the molecular spectrum, what is called the band spectrum. Hence the study of band spectra gives perfect and detailed information regarding the electronic structure of molecules and geometrical arrangement of the atoms in them.

Since 1925, with the application of

quantum mechanics, the theory of the spectra of diatomic molecules has undergone very rapid development and has helped much especially in understanding the nature of electronic states of molecules and the products of dissociation.

The most probable electron configuration for the lighter diatomic molecules and the order of their electron binding have been determined by Mulliken (1932). However no such scheme has yet been formulated for heavier molecules as they involve greater number of electrons and molecular orbitals having approximately equal energy. The structure of lightest molecules, such as H_2 and He_2 has been interpreted by Heitler and London (1927). This enables us to determine the electron configuration of other lighter molecules by successive addition of electrons to the H_2 and He_2 molecules. A successful utilization of this method depends entirely on the accuracy of the molecular constants derived from the vibrational and rotational analyses of the spectra of these molecules and also on the studies of their ionization potentials. Band systems have been studied in detail for heavy molecules but 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 valence electrons provide much useful information about the electronic states involved and allows us to interpret them in terms of their electron configurations. This procedure can be used to compare various molecular constants derived and their dependence on the energy levels of the constituent atoms. This will also help in the search for missing analogous band systems. Moreover, a detailed investigation of the rotational structure enables us to understand some of the properties of nuclei of the constituent atoms of the molecule e.g. binding energies, internuclear distances, dipole moments, quardrupole moments and nuclear statistics etc.

The theory and methods of analysing the

electronic spectra have been well established and are discussed in detail by Mulliken (1930, 1931, 1932), Jevons (1932), Johnson (1949), Herzberg (1950), Gaydon (1953), Barrow (1962), Walker and Straw (1962), King (1964) and Kovacs (1969). In order to make the thesis self - contained, a brief theoretical account related to the present study of band spectra will be described now.

The theoretical work on spectroscopy based on quantum concepts started with Niels Bohr. According to him, an atom or a molecule can not exist in the state having arbitrary energy but only in discrete energy states, which are known as stationary states. According to Bohr, electromagnetic radiation (Energy) is not emitted while an electron moves in its orbit but only when it jumps from one state of higher energy E_1 to another state of lower energy E_2. The liberated energy $(E_1 - E_2)$ is emitted as a quantum of electromagnetic radiation (Photon), i.e.

$$E_1 - E_2 = h\nu' = hc\nu$$

where ν' = frequency of radiation emitted

ν = wave number of radiation emitted

c = velocity of light in vacuum.

This equation is also known as Bohr's frequency condition. According to the selection rule, only those transitions are possible in which the quantum number l (the number designating a particular atomic state) changes by $\Delta l = \pm 1$ where l is the orbital quantum number. The transitions other than $\Delta l = \pm 1$ are said to be forbidden transitions. The wave number of a spectral line is usually represented as the difference between two quantities called "Terms". The word "Term" is used synonymously with energy state or quantum state, the word "Term value" is used synonymously with energy value.

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 :

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

(2) A single quantum number "v" which defines the state of vibration of the nuclei.

(3) A group of quantum numbers associated with the rotation of the nuclei and with the finer details of the electronic motions. In this scheme of these quantum numbers, interactions between electronic motion and nuclear rotation must be considered.

VIBRATIONAL STRUCTURE OF ELECTRONIC SPECTRUM

In a molecule the total quantizable energy consists of three components viz.

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

where E_e = sum of electronic energy E_{el} and potential V_n.

E_v = energy due to vibration of nuclei.

E_r = energy due to rotation of nuclei.

Now the electronic energy E_{el} depends on the internuclear distance r. This dependence will be different for different electronic states. The sum of electronic energy E_{el} and coulomb potential V_n acts as the potential energy under whose influence the nuclei carry out their vibrations. The electronic state in question will be stable only if the potential energy in its dependence on the internuclear distance is a minimum. If there is no minimum the electronic state is unstable i.e. the two atoms repel each other for any value of internuclear distance.

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 another of lower energy (F")

$$\begin{aligned}\nu &= F' - F'' \\ &= (F'_e - F''_e) + (F'_v - F''_v) + (F'_r - F''_r) \\ &= \nu_e + \nu_v + \nu_r \qquad \text{..........(2)}\end{aligned}$$

For a given band ν_r varies for each of its rotational lines, while ($\nu_e + \nu_v$) is constant and defines the band origin ν_o. For a given band system, ν_v varies from band to band, ν_e being constant and defining the system origin.

All the spectrum lines associated with a definite pair of electronic states are collectively called "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 transitions.

The equation for energy in terms of term values is given as

$$T = T_e + G(v) + F(J) \qquad \text{..........(3)}$$

To study the vibration and rotation of a molecule in different electronic states we can use the model of the vibrating rotator, where

$$G(v) = \omega_e(v+1/2) - \omega_e x_e(v+1/2)^2 + \omega_e y_e(v+1/2)^3 \qquad \text{.....(4)}$$

and

$$F(J) = B_v J(J+1) - D_v J^2(J+1)^2 \qquad \text{.....(5)}$$

In order to study the arrangement of bands, the term ν_r in equation (2) can be safely disregarded. For a given electronic transistion, $F'_e - F''_e$ remains constant and $\nu_r = 0$ for band origin, we express the vibrational structure of the electronic transition by

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

$$= \nu_e + \omega'_e(v'+1/2) - \omega'_e x'_e(v'+1/2)^2 + \omega'_e y'_e(v'+1/2)^3$$

$$-\omega''_e(v''+1/2) + \omega''_e x''_e(v''+1/2)^2 - \omega''_e y''_e(v''+1/2)^3 \quad .....(6)$$

where ν is the wave number of a band head, v' and v" are the vibrational quantum numbers, ω'_e and ω''_e are the vibrational frequencies of the molecule in these states and $\omega'_e x'_e$, $\omega''_e x''_e$, $\omega'_e y'_e$ and $\omega''_e y''_e$ are the anharmonicities of the upper and lower state respectively. In principle, any vibrational level of the upper electronic state can combine with any other vibrational level of the lower electronic state.

Due to lack of resolution the band origins are not usually observed and hence for vibrational analysis band heads are measured instead of band origins and therefore discrepancy arises in the vibrational constants but it is very small. In the equation, the single primed letters refer to the upper state and the double primed letters refer to the lower state. By putting the value v' = 0 and v" = 0 in equation (6) the following expression can be readily obtained

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

$$-(1/2\,\omega''_e - 1/4\,\omega''_e x''_e + 1/8\,\omega''_e y''_e) \quad .....(7)$$

Here ν_{oo} is a term independent of v' and v" and is called (0,0) band as it corresponds to the transition v' = 0 ——— v" = 0. The equation (6) can also be written in terms of ν_{oo} as

$$\nu = \nu_{oo} + (\,\omega'_o v' - \omega'_o x'_o v'^2 + \omega'_o y'_o v'^3 - ......)$$

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

$$.....(8)$$

In fact equation (7) referes to the band origins but in 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. Since the separation between νorigin and νhead is small, the error in the vibrational constants derived from the band head measurements is often negligible.

The vibrational analysis of a band system is usually made by arranging the wave numbers of various bands in a scheme called "Deslandres table" (Herzberg, 1950). In this scheme the bands having the same upper state will come in the same column and those having the same lower state will come in the same row. The differences of the wavenumbers between the columns in the table give the spacing between the vibrational levels in the lower electronic state and the differences between wavenumbers in the rows give the spacing between the vibrational levels in the upper electronic state. The separation of successive vibrational levels of an electronic state is given by the first difference

$$\Delta G(v+1/2) = G(v+1) - G(v)$$

$$= \omega_e - 2\omega_e x_e - 2\omega_e x_e v \qquad \text{.....(9)}$$

The second difference gives

$$\Delta^2 G(v+1/2) = \Delta G(v+3/2) - \Delta G(v+1/2)$$

$$= -2\omega_e x_e \qquad \text{.....(10)}$$

Thus vibrational constants ω_e and $\omega_e x_e$ for both the states and the system origin ν_e can be determined from the observed wavenumbers of the band heads. By neglecting cubic terms, following equation represents the bands of a sequence (Δv = const)

$$\nu = \nu_{00} + \omega'_0 \Delta v - \omega'_0 x'_0 (\Delta v)^2 - (\omega''_0 - \omega'_0 + 2\omega'_0 x'_0 \Delta v)\, v'' - (\omega'_0 x'_0 - \omega''_0 x''_0)\, v''^2 \qquad \ldots\ldots(11)$$

If v'' is small and has the opposite sign to that of the quadratic term, a reversal can take place in the succession of bands in a sequence. It can be observed that with increasing v'', bands draw together and eventually turn back. The turning point may be called head of heads. At the turning point v'' will be obtained by taking

$$\frac{d\nu}{dv''} = 0$$

$\therefore$ From equation (11)

$$\nu_t = \frac{\omega'_0 - 2\omega'_0 x'_0 \Delta v - \omega''_0}{2(\omega'_0 x'_0 - \omega''_0 x''_0)} \qquad \ldots\ldots(12)$$

Formation of head of heads has been observed for molecules like InBr, CN etc.

INTENSITY DISTRIBUTION IN A BAND SYSTEM

A simple theoretical interpretation of the observed intensity distribution is given by Franck (1925) and by Condon (1926, 1928). According to Franck - Condon 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". "Only those transitions will be more favourable in which the change in velocity and relative position will be minimum". 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 numbers. The intensity distribution in a band system can be interpreted with the help of potential curves of electronic states involved. The following types of intensity distribution are generally observed :

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

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

(3) If $r'_e << r''_e$ (and $\omega'_e >> \omega''_e$), 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.

(4) If $r'_e >> r''_e$ (and $\omega'_e << \omega''_e$), the intensity distribution will be similar to that of (3).

VIBRATIONAL AND ROTATIONAL ISOTOPIC EFFECTS IN A BAND SYSTEM

Isotopic effect has been found to be very important in the analysis of band spectra. The potential energy functions of two isotopic molecules are observed to be identical. This is because the potential energy function depends on the motion of the electrons (which varies very slightly due to the mass difference of the isotopes), and on the coulomb repulsion (which remains the same in isotopic molecules).

Neglecting the cubic and higher powers, the vibrational isotopic separation between bands, in a transition designed by fixed value of v' and v", can be written as

$$\Delta\nu_v = \nu_i - \nu$$

$$= (\rho - 1)[\omega'_e(v'+1/2) - \omega''_e(v''+1/2)] - (\rho^2 - 1)$$

$$[\omega'_e\, x'_e\, (v'+1/2)^2 - \omega''_e\, x''_e\, (v''+1/2)^2] \qquad .....(13)$$

The rotational isotopic shift in a band can be written as

$$\Delta\nu_r = \nu_r - \nu_r^i$$

$$= (\rho^2-1)[B'J'\,(J'+1) - B''J''\,(J''+1)]$$

$$= (\rho^2-1)\,\nu_r \qquad .....(14)$$

In equations (13) and (14) $\varrho = \sqrt{\mu/\mu_i}$, μ and μ_i being the reduced masses of the lighter and heavier molecules respectively.

The study of the vibrational isotopic shifts in a band system provides a good check for the correctness of the vibrational assignments and the study of rotational isotopic shifts in a band system provides a good check for the correctness of J numbering. The bands corresponding to the lighter isotopic molecule will be more separated from the system origin than those of the heavier molecule. The intensity of the isotopic bands depends on the relative abundance of the isotopic masses of the constituent atoms.

Many new isotopes have been discovered with the knowledge of isotopic shifts in band spectra. The intensity of the emitter of the bands can be varified by means of isotope effect.

CLASSIFICATION OF ELECTRONIC STATES AND ELECTRONIC TRANSITIONS

The electrons move in an electric field

which is symmetric about the internuclear axis in a diatomic molecule. Therefore the component of angular momentum of electrons about the internuclear axis will be a constant of motion. If L is the total electronic angular momentum, the component M_L can have the values

$$M_L = L, L - 1, L - 2, \ldots\ldots - L .$$

In an electric field, states having the same (M_L) will have the same energy and are said to be degenerate.

If $\Lambda = | M_L |$, Λ can have the values 0, 1, 2,.....L. According to the values of $\Lambda = 0, 1, 2, \ldots\ldots L$, the corresponding molecular states are designated as Σ, Π, Δ,_____.

In the molecule, the vector sum of spin of individual electrons gives total spin S. Due to the orbital motion of the electrons, there will be an internal magnetic field in the direction of the internuclear axis which interacts with the magnetic field produced due to the spin of the electrons to affect a splitting in the electronic levels. The component of total spin S along the internuclear axis can have values

$$\Sigma = S, S-1, S-2, \ldots\ldots\ldots, -S .$$

Therefore the number of splitted levels will be 2S + 1.

HUND'S COUPLING CASES

The vector sum of (1) electronic spin angular momentum Σ (2) electronic orbital angular momentum Λ and (3) angular momentum due to nuclear rotation N will give resultant angular momentum symbolised by J. The method of distinguishing different modes of coupling of angular momenta was first suggested by Hund (1930). Here the most commonly occuring cases (a), (b) and (c) are briefly discussed.

Hund's Case (a)

In this case it is assumed that the interaction of nuclear rotation with electronic motion is very weak but the electronic motion itself is coupled very strongly with the internuclear axis. The total angular momentum along the internuclear axis is $\Omega = \Lambda + \Sigma$ will be constant of motion, which, with N (angular momentum due to nuclear rotation) forms the total angular momentum J. In this case, the different multiple levels will be fairly well separated and the rotational energy levels having J less than Ω will be absent. Usually Π and Δ states belong to case (a).

Hund's Case (b)

In this case, the spin vector S will be very weakly coupled to the internuclear axis. The component of orbital angular momentum Λ and the angular momentum due to nuclear rotation N form a resultant K having values $K = \Lambda, \Lambda + 1, \Lambda + 2, \ldots\ldots$. Now, this angular momentum K and the spin angular momentum S form the total angular momentum J, which can have the values

$J = (K + S), (K + S - 1) \ldots\ldots\ldots (K - S)$.

The case (b) is generally observed in Σ States.

Hund's Case (c)

Apart from cases (a) and (b) there are

cases (c), (d), (e) and intermediate between these cases also. In case (c), Λ and Σ are not defined but L and S first form resultant J_a, which is then coupled to internuclear axis with a component Ω. The angular momentum N of the nuclear rotation and Ω then form resultant J, just as in case (a). Sometimes due to increase in rotational energy, transition from one case to another may occur (Herzberg, 1950).

ROTATIONAL STRUCTURE OF INDIVIDUAL ELECTRONIC BAND

In a single band, ν_e and ν_v are fixed while ν_r varies. The wave number of a rotational line is given by

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

where $\nu_o = \nu_e + \nu_v$ is constant and is called band origin or zero line. $F'(J)$ and $F''(J)$ are rotational terms of the upper and lower states respectively.

The rotational term is represented by

$$F_v(J) = B_v J(J+1) - D_v J^2 (J+1)^2 \qquad .....(15)$$

where $B_v = h/8\pi^2\mu r^2c$.

Using equation (13), we write

$$\nu = \nu_o + B'_v J' (J'+1) - D'_v J'^2 (J'+1)^2 - B''_v J''(J''+1) + D''_v J''^2 (J''+1)^2 \quad .....(16)$$

In the case of a symmetric top molecule, selection rules are $\Delta J = 0, \pm 1$. According to these selection rules, series of lines are expected in a band. Lines corresponding to $\Delta J = -1, 0, +1$ are said to form P, Q and R branches respectively. The wave numbers of rotational lines in these branches are given by

$$\nu_P = \nu_o - (B'_v + B''_v) J + (B'_v - B''_v) J^2 \quad .....(17)$$

$$\nu_Q = \nu_o + (B'_v - B''_v) J + (B'_v - B''_v) J^2 \quad .....(18)$$

$$\nu_R = \nu_o + 2B'_v + (3B'_v - B''_v) J + (B'_v - B''_v) J^2 \quad .....(19)$$

where J stands for rotational quantum number of the lower state. In the above three equations the terms containing D_v being small at low J values have been neglected.

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

$$\nu = \nu_o + (B'_v + B''_v)\ m + (B'_v - B''_v)\ m^2 \qquad .....(20)$$

where m = -J for P branch and

m = J + 1 for R branch.

In most cases, owing to the quadratic term in equation (20), 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 red. If $(B'_v - B''_v)$ is +ve, head is formed by P branch and the band is degraded towards the violet. The 'm' number corresponding to the band head is given by

$$m_H = \frac{(B'_v + B''_v)}{2(B'_v - B''_v)} = \frac{d}{2e} \qquad .....(21)$$

The head to origin distance can be calculated by using the equation

$$\nu_h - \nu_{origin} = -\frac{d^2}{4e} \qquad .....(22)$$

It is important to notice that in Q branch the head is formed at the beginning of the branch and lies very near to the origin.

The rotational constants B'_v, D'_v and B''_v and D''_v for upper and lower states are usually evaluated from combination differences. In a simple band, where only P and R branches are present, for every line in the P branch there is a corresponding line in the R branch with the same upper or lower state. The wavenumber difference of these two lines is equal to the separation of either the lower or the upper rotational levels from the next but one viz $\Delta_2 F''(J)$ or $\Delta_2 F'(J)$ which will be given as

$$R(J-1) - P(J+1) = F''_v(J-1) - F''_v(J+1)$$

$$= \Delta_2 F''(J) \qquad \text{.....(23)}$$

and

$$R(J) - P(J) = F'_v(J+1) - F'_v(J-1)$$

$$= \Delta_2 F'(J) \qquad \text{.....(24)}$$

In the case of a band having P, Q and R branches, following combination relations are used

$$R\,(J) - Q\,(J) = F'_v\,(J + 1) - F'_v(J) = \Delta_1\,F'(J) \qquad \ldots..(25)$$

$$Q(J + 1) - P(J + 1) = F'_v(J + 1) - F'_v(J) = \Delta_1\,F'(J) \qquad \ldots..(26)$$

$$R\,(J) - Q(J + 1) = F''_v(J + 1) - F''_v(J) = \Delta_1 F''(J) \qquad \ldots..(27)$$

$$Q\,(J) - P(J + 1) = F''_v(J + 1) - F''_v(J) = \Delta_1\,F''(J) \qquad \ldots..(28)$$

where $\Delta_1\,F(J)$ refers to the seperation of the successive rotational levels. Substituting from equations (17, 19) we get

$$\frac{\Delta_2 F(J)}{(J + 1/2)} = 4B_v - 8D_v\,(J + 1/2)^2 \qquad \ldots..(29)$$

A plot of $\dfrac{\Delta_2 F(J)}{(J + 1/2)} \longrightarrow (J + 1/2)^2$

will be a straight line whose slope gives $8D_v$ and intercept gives $4B_v$. This plot serves as a criterion for the correctness of J numbering of the branch lines. If there is a misnumbering the graph will deviate from the straight line for lower values of J (Youngner and Winans, 1960). Standard methods to assign correct numbering to the different branch lines have been described by Herzberg (1950). Rotational constants can also be determined by the same graphical procedure from $\Delta_1F(J)$ values.

$$\Delta_1F(J) = 2B_v (J + 1) - 4D_v (J + 1)^3 \qquad .....(30)$$

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. The agreement between corresponding combination differences for bands with the same lower or upper vibrational states provides an important sensitive check on the correctness of the rotational analysis.

If we want to determine the vibrational constants of a molecule very accurately, we must use the band origins and not the band heads. A convenient method that makes use of most measured lines for determining the band origin is as follows :

From observed wavenumbers of all J values, sum R(J - 1) + P(J) is formed and from equations (17, 19) we get

$$R(J - 1) + P(J) = 2\nu_o + 2(B'_v - B''_v) J^2 \qquad .....(31)$$

When R(J - 1) + P(J) is plotted against J^2, a straight line is obtained whose intercept with the ordinate axis gives 2 ν_o and its slope is $2(B'_v - B''_v)$. If an intense Q branch is present, the most convenient way of determining ν_o is to use Q branch.

$$Q(J) = \nu_o + (B'_v - B''_v) J(J + 1) \qquad .....(32)$$

The value of rotational constants B_v and D_v will change for different vibrational levels according to the following equation

$$B_v = B_e - \alpha_e (v + 1/2) + ... \qquad .....(33)$$

where α_e is Rotation - vibration interaction constant and B_e Corresponds to completely vibrationless state. Variation of D_v is given by

$$D_v = D_e + B_e (v + 1/2) + \ldots\ldots \qquad \ldots\ldots(34)$$

where the constants D_e, B_e and ω_e are related by the equation

$$D_e = 4B_e^{\,3}/\omega_e^2 \qquad \ldots\ldots(35)$$

The vibrational quanta ΔG and constant α_e can be determined as follows (Jenkins and Mckellar, 1932).

The combination differences between corresponding lines of two bands having the same upper state,

$$R_{v,v''_1}(J) - R_{v',v''_2}(J) = G''(v''_2) - G''(v''_1)$$
$$-(B_{v''_1} - B_{v''_2})J(J + 1) \ \ldots\ldots(36)$$

and between corresponding lines of two bands having same lower state

$$R_{v'_2,v''}(J) - R_{v'_1,v''}(J - 1) = G'(v'_2) - G'(v'_1)$$
$$-(B_{v'_1} - B_{v'_2})\ J(J + 1)$$
$$\ldots\ldots(37)$$

are formed. The graph of these combination differences against $J(J + 1)$ is straight line, whose intercept gives $G(v_2) - G(v_1)$ and slope gives $(B_{v_1} - B_{v_2})$ from which ΔG and α_e can be calculated.

In the above discussion, we have not considered the influence of the rotational constant D at low J values.

Now, by introducing D term, equation (18) becomes

$$\nu = \nu_o + (B'_v + B''_v)\, m + (B'_v - B''_v - D'_v + D''_v)\, m^2$$

$$-2(D'_v + D''_v)\, m^3 - (D'_v - D''_v)\, m^4 \qquad .....(38)$$

for P and R branches, $m = -J$ for P branch and $m = J + 1$ for R branch.

And

$$\nu = \nu_o\, (B'_v - B''_v)\, J(J + 1) - (D'_v - D''_v)\, J^2\, (J + 1)^2$$

$$.....(39)$$

for Q branch.

From the above equations, it is clear that P and R branches may have as many as three heads, while Q branch may have two heads. For sufficiently higher value of J, additional heads P^*, Q^*, and R^* will appear with shading opposite to that of normal P, Q and R heads. Such a reversal of shading occurs only if $(D'_v - D''_v)$ has the same sign as $(B'_v - B''_v)$ even if this is the case, the extra heads usually lie at such a high J value that they are not observed due to very low intensity.

Λ - TYPE DOUBLING :

In Hund's cases (a) and (b) the interaction between the rotation of the nuclei and angular momentum L has been neglected. But it is found to produce a splitting into two components for each value of J in the state with $\Lambda \neq 0$. This splitting is found to increase with increasing rotation. This is known as Λ -type doubling.

In Λ -type doubling two component levels with somewhat different energies have the same value of J, thus it differs from spin splitting. For multiplet states, the rotational levels of each component of the multiplet including those with

$\Omega = 0$, split into two Λ - type components. In general it will amount to only a fraction of a cm^{-1}. In some cases for large values of J, it will reach a value of few cm^{-1}, the splitting is relatively greater for terms with the smallest Ω. The nature of Λ - type doubling for different electronic levels has been discussed in detail by Hill and Van Vleck (1928), Mulliken (1930, 1931, 1932), Herzberg (1950) and Kovacs (1969). Due to the Λ - type doubling equations 25, 26, 27 and 28 no longer hold exactly and the so called combination defect occurs.

$$R(J) - Q(J) = Q(J + 1) - P(J + 1) + \varepsilon$$

$$\approx \Delta_1 F'(J) \qquad .....(40)$$

$$R(J) - Q(J + 1) = Q(J) - P(J + 1) + \varepsilon$$

$$\approx \Delta_1 F''(J) \qquad .....(41)$$

It is observed that the $\Delta_1 F''(J)$ values for different bands with the same lower state need not agree exactly, because the Λ - type doubling in different upper states may have different magnitude.

But Δ_2F'' values of bands with the same lower state should agree exactly even if perturbations are present. In equations (40) and (41), ε is the sum of Λ - type doubling of the successive levels. The splitting on one level is very nearly one half of this.

$$\tfrac{1}{2}\,\varepsilon = (B_v^c - B_v^d)\,J(J+1)$$

$$= q\,J\,(J+1) \qquad .....(42)$$

where B_v^c and B_v^d are the B_v values for doubling components c and d respectively. In practice the mean value of B_v^c and B_v^d is usually used as true B_v value. The combination defect ε will be the same for like symmetry and it would have opposite sign for unlike symmetry.

The knowledge of this combination defect help us in understanding the exact nature of electronic levels involved in a transition.

SPIN SPLITTING

The effect of electron spin can be clearly observed in transitions like $^2\Sigma$ —— $^2\Sigma$.

$^2\Sigma$ state always belongs strictly to Hund's case (b) and selection rule $\Delta K = \pm 1$ holds. The separation of two sublevels with $J = K + \frac{1}{2}$ and $J = K - \frac{1}{2}$ for a given K is in general very small. However, with large resolution each line of P and R branches splits into three components according to the selection rule $\Delta J = 0, \pm 1$. $\Delta J = 0$ holds if $\Delta J \neq \Delta K$ 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 the four main branches

$$R_1(K) = \nu_0 + F'_1(K + 1) - F''_1(K) \quad \text{.....(43)}$$

$$R_2(K) = \nu_0 + F'_2(K + 1) - F''_2(K) \quad \text{.....(44)}$$

$$P_1(K) = \nu_0 + F'_1(K - 1) - F''_1(K) \quad \text{.....(45)}$$

$$P_2(K) = \nu_0 + F'_2(K - 1) - F''_2(K) \quad \text{.....(46)}$$

Rotational term values for $^2\Sigma$ State are given by

$$F_1\ (K) = B_v\ (K + 1) + \tfrac{1}{2}\gamma K \qquad .....(47)$$

and

$$F_2\ (K) = B_v\ K(K + 1) - \tfrac{1}{2}\gamma(K + 1) \qquad .....(48)$$

where γ is known as spin splitting constant.

In P and R branch, the line splitting is given by

$$\Delta\nu_{12}\ (P) = P_1 - P_2 = (\gamma' - \gamma'')\ K - \tfrac{1}{2}(\gamma' + \gamma'') \qquad .....(49)$$

and

$$\Delta\nu_{12}\ (R) = R_1 - R_2 = (\gamma' - \gamma'')\ K + \tfrac{1}{2}(3\gamma' - \gamma'') \qquad .....(50)$$

This shows that splitting increases linearly with K. The combination difference must be formed either between R_1 and P_1 or R_2 and P_2. From equations (47) and (48) we get the values of $\Delta_2 F$ as

$$\Delta_2\ F_1\ (K) = 4\ B_v\ (K + \tfrac{1}{2}) + \gamma \qquad .....(51)$$

and

$$\Delta_2\ F_2\ (K) = 4\ B_v\ (K + \tfrac{1}{2}) - \gamma \qquad .....(52)$$

This exhibits that the Δ_2 F curves for the two components of a $^2\Sigma$ state form parallel straight lines and their vertical separation is 2γ.

PERTURBATION

In the case of some bands one line or several successive lines deviate more or less strongly from the formula

$$\nu = c + dm + em^2 \qquad .....(53)$$

Sometimes even a splitting into two lines appears or for a multiplet band, the multiplet splitting may be abnormally great at some places in the band or the intensity is abnormally small for one or more lines in the band.

Displacement from the regular position and weakening of intensity may also appear simultaneously. These abnormalities are due to perturbation. When perturbations appear for a number of successive J values, they usually have a resonance - like behaviour i.e. The deviations from the normal position and intensity increases rapidly to a maximum with increasing J and then decreases rapidly to zero.

The perturbations in the fine structure of a band are due to perturbations in the rotational term series, either of the upper or of the lower state. Therefore, if a perturbation appears at a certain place in a P branch of a band, it will also be observed for the same J' or J" values in the corresponding R branch of the band and is of the same type and magnitude. Further more, the perturbation will also appear in all other bands that involve the same perturbed vibrational state as upper or lower state. But it is observed that in most of the cases the combination relations must hold exactly even if strong perturbations are present and therefore analysis is possible.

The levels that result from the approximate wave equation without the interaction term produces a shift. The shift of a given level depends inversely on its separation from the perturbing energy levels. These shifts are always in the sense of a repulsion. In addition, each of the two states assumes properties of the other. The mutual repulsion of two states of approximately equal energy gives an explanation for the occurence of perturbation in band spectra, since it can easily happen that a level belonging to a different electronic state has the same energy as a level of a given series.

SELECTION RULE FOR PERTURBATION

The magnitude of perturbation depends not only on the smallness of the energy difference of the unperturbed levels but also on the magnitude of the matrix element

$$W_{12} = \int \Psi_1^* W \Psi_2 \, d\tau \qquad .....(54)$$

of the perturbation function W i.e. it depends on the eigen functions of the two states involved. The perturbation occurs only when W_{12} is non-vanishing. The conditions for non-vanishing W_{12} i.e. the selection rules for perturbation have been derived by Kroning (1928). They are determined by the quantum numbers and symmetry properties of the two states considered.

These selections rules are

$\Delta J = 0$ ....(a)

$\Delta S = 0$ ....(b)

$\Delta \Lambda = 0, \pm 1$ ....(c)

$+ \not\leftrightarrow -$ ....(d)

$s \not\leftrightarrow a$ ....(e)

(a), (d) and (e) are rigorous.

(b) holds only approximately.

(c) holds only when Λ is defined.
i.e. Hund's case (a) and (b).

In Hund's case (c) it must be replaced by $\Delta \Omega = 0, \pm 1$.

Perturbations with $\Delta \Lambda = 0$ are the perturbations between states of the same type, so Mulliken (1937) called them homogeneous perturbations and those with $\Delta \Lambda = \pm 1$ are called heterogeneous perturbations. Dieke (1941) called them as vibrational and rotational perturbations respectively.

ROTATIONAL TEMPERATURE

The intensity distribution in a band can be used for calculating the temperature of the source of emission. The variation of the intensity of the line in rotation-vibration band as a function of J is given essentially by the thermal distribution of the rotational levels. The intensity depends on the value of (2J + 1) for the upper and lower states. It should be noted that the J values of the initial state must be used in the exponential term.

The intensity of a line of the rotation or rotational-vibration band in emission is given by

$$I_{em} = \frac{C_{em}\,\nu^4}{Q_r}\,(J' + J'' + 1)\,e^{-B'J'(J'+1)hc/KT} \qquad \ldots\ldots(55)$$

where C_{em} is the constant depending on the change of dipole moment and the total number of molecules in the initial vibrational level. For a given rotation-vibration band at a given temperature, the factor $\frac{C_{em}}{Q_r}$ is very nearly constant. Therefore the intensity distribution resembles closely with the distribution of the rotational levels, a maximum of intensity occurring in each branch at about the same J value.

It is observed that with increasing temperature the band extends farther and the intensity maxima of the two branches move outward and at the same time become flatter. The decrease of the height of the maximum with increasing temperature is due to the increase of the state sum Q_r in the denominator of the above expression. It is also observed that the total intensity of the band remains constant as long as the temperature is not so high that the number of molecules in the lower vibrational level (v = 0) is appreciably reduced.

From equation (55) we have

$$\log \frac{I_{em}}{J'+J''+1} = A - \frac{B'_v \, J'(J'+1)\, hc}{kT}$$

where $A = \log C_{em} \nu^4/Q_r$ is considered as constant. By plotting $\log I_{em}/(J' + J'' + 1) \longrightarrow J'(J' + 1)$ a stright line is obtained. The slope of the line gives the value of $B'_v\, hc/kT$. i.e. If the line intensities have been measured and the rotational constants are known, the temperature of the source can be calculated. In the present work this method is used to determine rotational temperature of the source of emission.

Experimentally it is found that the intensity distribution in emission bands occurring in electric discharge is the same as in purely thermal excitation. If a molecule is excited by electron collision, no great change in the angular momentum of the system can be produced and therefore, the distribution of the molecules over the different rotational levels in the upper electronic state is practically the same as in the ground state. But the distribution corresponds to thermal equilibrium at a certain effective temperature and hence this will also be at least approximate case in upper state. However, we must be quite clear that this normal intensity distribution in electric discharge results from the circumstances that the angular momentum is not strongly altered in excitation by electron collisions.

Even if the fine structure of the bands is not resolved, the shape of the band profiles varies as a function of temperature and used for determining the rotational temperature of the source of emission. It must be emphasized that the temperature thus obtained is **"Effective Temperature"**. It represents true temperature only if either the excitation is strictly thermal or is of such a type that it does not affect the thermal distribution. A good indication that this condition is fulfilled in a given case is the agreement of the temperature obtained independently from rotational and vibrational intensity distributions.

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