V P & R P T P SCIENCE COLLEGE

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Atomic and Molecular Spectroscopy
[STUDY MATERIAL]

UNIT- II SPECTRA OF MOLECULE

1.1. SEPARATION OF ELECTRONIC AND NUCLEAR MOTION: THE BORN-OPPENHEIMER APPROXIMATION

Consideration of allowed energy states, *i.e.*, energy level scheme, is the key to the discussion of emission and absorption spectra of molecules which arise from transitions between these energy states. Compared to atoms, energy level scheme of molecules is complicated because:

(i) the nuclear motion in molecules cannot be ignored as we do in atoms. This nuclear motion gives rise to many more energy levels in a molecule than in an atom. For example, in a diatomic molecule, the nuclei vibrate along the internuclear axis giving rise to vibrational energy and also the whole system rotates about the centre of mass giving rise to rotational energy.

(ii) we cannot classify molecular energy states according to the angular momentum, **L**, as we do in atoms because it is not conserved in molecules. However, in diatomic molecules, the component of angular momentum along the internuclear axis is conserved due to symmetrical charge distribution about this axis and is used to classify molecular energy states.

The energy allowed to the molecule may, in principle, be obtained by solving the Schrödinger equation for the system of interacting nuclei and electrons:

$$H\psi = E\psi$$

but this is only possible for the very simplest of molecular examples. The nuclei and electrons in a molecule are subject to comparable forces, but as the electrons are very much lighter than the nuclei their motions are very much rapid. Therefore, to a good approximation, motions of electrons can be considered separately as compared to those of nuclei. This separation of the nuclear and electronic motions is embodied in the *Born-Oppenheimer approximation*. According to this approximation, the molecular Schrödinger equation can be solved in two steps:

(i) We first investigate the electronic problem on the assumption that the nuclei are fixed. Thus the wave equation is solved for electronic motion alone in which positions of nuclei occur only as parameters.

(ii) Then solve the wave equation for the motion of nuclei alone in which the characteristic eigen value of the electronic wave equation occurs as a part of the potential energy function of the nuclear motion.

The complete Hamiltonian operator,

$$\left(-\frac{h^2}{8\pi^2 m}\nabla^2 + V\right)$$

for a molecule consisting of p nuclei and i electrons will include the terms for both nuclei-nuclei interactions, nuclei-electronic interactrons as well as electronic-electronic interactions. Thus

$$H = -\sum_p \frac{h^2}{8\pi^2 M_p}\nabla_p^2 - \sum_i \frac{h^2}{8\pi^2 m}\nabla_i^2 + V_{nn} + V_{ne} + V_{ee} \qquad \ldots (1)$$

where first term represents the kinetic energy operator of all the nuclei with masses $M_1, M_2, \ldots M_p$; the second term represents the kinetic energy operator of all the electrons (mass m). The rest terms, V_{nn} is potential energy function arising from nuclear-nuclear interactions,

V_{ne} is the potential energy function arising from nuclear-electronic interactions and V_{ee} is the potential energy function arising from electronic-electronic interactions.

If we take that nuclei are fixed in position then kinetic energy term $-\sum_p \frac{h^2}{8\pi^2 M_p} \nabla_p^2$ should be zero and V_{nn} should be constant. Then the Hamiltonian for the electrons would be

$$H_e = -\sum_i \frac{h^2}{8\pi^2 m} \nabla_i^2 + V_{ne} + V_{ee} \qquad \ldots (2)$$

Remaining terms in eq. (1), if denoted by H_n, are

$$H_n = -\sum_p \frac{h^2}{8\pi^2 M_p} \nabla_p^2 + V_{nn} \qquad \ldots (3)$$

so that total Hamiltonian is $H = H_n + H_e$.

Following Born and Oppenheimer, the molecular wave function can be written as a product of electronic and nuclear wavefunctions. If ψ is the eigen function for the whole system, ψ_e, a function of the coordinates of both the nuclei and the electrons, and ψ_n a function of the coordinates of the nuclei only, then

$$\psi = \psi_e \psi_n \qquad \ldots (4)$$

The total eigen function ψ and the total eigen value E are given by the wave equation

$$H\psi = E\psi$$

which in this case takes the form

$$H\psi_e\psi_n = E\psi_e\psi_n$$

or
$$-\sum_p \frac{h^2}{8\pi^2 M_p} \nabla_p^2 \psi_e\psi_n - \sum_i \frac{h^2}{8\pi^2 m} \nabla_i^2 \psi_e\psi_n + (V_{nn} + V_{ne} + V_{ee})\psi_e\psi_n = E\psi_e\psi_n \qquad \ldots (5)$$

Further we can write

$$\nabla_p^2 \psi_e\psi_n = \psi_n \nabla_p^2 \psi_e + \psi_e \nabla_p^2 \psi_n + 2\nabla_p \psi_e \nabla_p \psi_n$$

and
$$\nabla_i^2 \psi_e\psi_n = \psi_n \nabla_i^2 \psi_e$$

Following Born-Oppenheimer approximation, electronic eigen functions, ψ_e is the only slowly varying function of the nuclear coordinates that is; $\nabla_p \psi_e \ll \nabla_p \psi_p$. Consequently, we can neglect the terms $\nabla_p^2 \psi_e$ and $\nabla_p \psi_e$, and write

$$\nabla_p^2 \psi_e\psi_n = \psi_e \nabla_p^2 \psi_n$$
$$\nabla_i^2 \psi_i\psi_n = \psi_n \nabla_i^2 \psi_e$$

Putting these values in eq. (5), we get

$$-\psi_e \sum_p \frac{h^2}{8\pi^2 M_p} \nabla_p^2 \psi_n - \psi_n \sum_i \frac{h^2}{8\pi^2 m} \nabla_i^2 \psi_e + (V_{nn} + V_{ne} + V_{ee})\psi_e\psi_n = E\psi_e\psi_n$$

or
$$-\psi_e \sum_p \frac{h^2}{8\pi^2 M_p} \nabla_p^2 \psi_n + \psi_n \left\{ -\sum_i \frac{h^2}{8\pi^2 m} \nabla_i^2 + (V_{ne} + V_{ee}) \right\} \psi_e + V_{nn}\psi_e\psi_n = E\psi_e\psi_n \qquad \ldots (6)$$

In the above equation the term

$$\left\{ -\sum_i \frac{h^2}{8\pi^2 m} \nabla_i^2 + (V_{ne} + V_{ee}) \right\} \psi_e = H_e\psi_e \qquad \text{[see eq. (2)]}$$

If the electronic eigen function ψ_e corresponds to electronic eigen values E_e' then

$$H_e\psi_e = E_e'\psi_e \qquad \ldots (7)$$

so that equation (6) can be written as

$$-\psi_e \sum_p \frac{h^2}{8\pi^2 M_p} \nabla_p^2 \psi_n + E_e{}' \psi_n \psi_e + V_{nn} \psi_n \psi_e = E \psi_e \psi_n$$

or

$$\left[-\sum_p \frac{h^2}{8\pi^2 M_p} \nabla_p^2 + E_e{}' + V_{nn} \right] \psi_n = E \psi_n \qquad \ldots (8)$$

or

$$(H_n + E_e{}')\psi_n = E\psi_n \qquad \text{(see eq. (3))}$$

Now refer to earlier discussion. In wave equation (8) for nuclear motion $E_e{}'$ is the characteristic eigen value of the electronic wave equation as part of the potential energy function for the nuclear motion whereas V_{nn} is the potential energy function that refers to nuclear-nuclear interaction. The effective Hamiltonian for molecular wave equation is

$$\left[-\sum_p \frac{h^2}{8\pi^2 M_p} \nabla_p^2 + E_e{}' + V_{nn} \right] \quad \text{or} \quad (H_n + E_e{}')$$

The equation (8) is solved first for a *given electronic state* of the molecule for a range of values of nuclear coordinates (internuclear separations). This will provide values of ψ_e and $E_e{}'$ as continuous functions of nuclear coordinates. After obtaining $E_e{}'$ we put it in eq. (8) and solve it to get expressions for ψ_n and E. A different set of ψ_n and E is obtained for each electronic state of the molecule. Note that E gives characteristic energies for the *whole molecule in the given electronic state of the molecule*. Finally from $\psi = \psi_n \psi_e$ the complete wave function is obtained.

Types of Molecular Energy States and Associated Spectra

Born-Oppenheimer approximation states that to a good degree of approximation the motions of the electrons in a molecule can be treated separately from those of nuclei and that the electronic motion can be solved by assuming the nuclei to be fixed. The electronic energy and the nuclear-nuclear repulsion energy then act as an effective potential for the motions of the nuclei.

The nuclear motion in a molecule is further divided into those corresponding to vibrations, rotations and translations. In the approximation that the electronic, vibrational, rotational and translational motions are truly independent, we may divide the Hamiltonian into corresponding components.

$$H = H_e + H_\upsilon + H_r + H_t$$

where

$$H_e \psi_e = E_e \psi_e, \quad H_\upsilon \psi_\upsilon = E_\upsilon \psi_\upsilon,$$
$$H_r \psi_r = E_r \psi_r \quad \text{and} \quad H_t \psi_t = E_t \psi_t.$$

The complete wave function is then

$$\psi = \psi_e \psi_\upsilon \psi_r \psi_t$$

and the total energy is simply

$$E = E_e + E_\upsilon + E_r + E_t$$

where subscripts e, υ, r and t stand for electronic, vibrational, rotational and translational respectively.

The origin of various types of spectra can be discussed taking as an example the case of a diatomic molecule. Schrödinger equation for nuclear motion in a diatomic molecule is

$$\left[-\frac{h^2}{8\pi^2 M_1} \nabla_1^2 - \frac{h^2}{8\pi^2 M_2} \nabla_2^2 + V(r) \right] \psi = E\psi$$

where M_1 and M_2 are the masses of the nuclei and $V(r)$ is the potential energy function comprising electrostatic energy of the two nuclei and instantaneous electronic energy. ψ is the nuclear eigen function and E is the eigen value for the whole molecule.

Refer to art 2.1. We transform the above equation in polar coordinates for internal motions (involving r only) and putting $m'\left(=\dfrac{M_1M_2}{M_1+M_2}\right)$ as reduced mass, we can arrive at the radial equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{8\pi^2m'}{h^2}\left[E-V(r)-\frac{J(J+1)h^2}{8\pi^2\mu r^2}\right]R=0$$

where J is a quantum number associated with the angular momentum of the molecule. $J(J+1)\dfrac{h^2}{4\pi^2}$ is the square of the total angular momentum. J assumes the values as 0, 1, 2, ...

The above equation can be put in a standard form if $R(r)=\dfrac{1}{r}S(r)$ is substituted. Then we get

$$\frac{d^2S}{dr^2}+\frac{8\pi^2m'}{h^2}\left[E-V(r)-\frac{J(J+1)h^2}{8\pi^2\mu r^2}\right]S=0$$

which is the Schrödinger equation for the motion of a particle of mass μ, moving along a line under a potential energy function

$$V'(r)=V(r)+\frac{J(J+1)h^2}{8\pi^2\mu r^2} \qquad \ldots(1)$$

$$=(E_e'+V_{nn})+\frac{J(J+1)h^2}{8\pi^2\mu r^2} \qquad \ldots(2)$$

where E_e' is eigen value of electronic wave equation (See art 1.1), V_{nn} is potential energy term corresponding to nuclear-nuclear interaction (repulsion). The third term is the centrifugal potential energy term indicating a rotational motion superimposed on the linear vibratory motion of the particle. It means $V(r)$ includes electronic and vibrational energies while third term as rotational energy. A plot of $V(r)$ and of $V'(r)$ as a function of r are shown in Fig. 1.1. and Fig. 1.2.

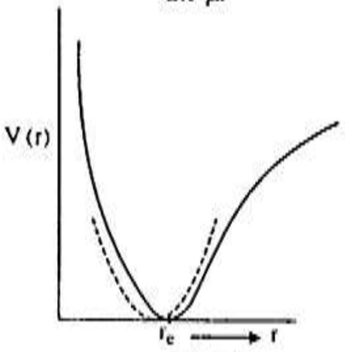

Fig. 1.1

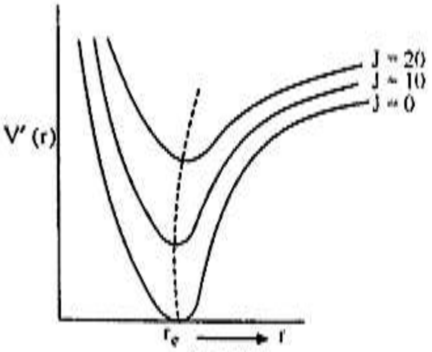

Fig. 1.2

As nuclear vibrations are small oscillations $V(r)$ can be expanded by Taylor series as

$$V(r)=V(r_e)+(r-r_e)\left.\frac{\partial V(r)}{\partial r}\right|_{r=r_e}+\frac{1}{2!}(r-r_e)^2\left.\frac{\partial^2V(r)}{\partial r^2}\right|_{r=r_e}+\ldots$$

If we tatke $V(r_e)=0$ as reference energy and at $r=r_e$ the first derivative $\dfrac{\partial V(r)}{\partial r}=0$ so function

$$V(r)=\frac{1}{2}(r-r_e)^2\left.\frac{\partial^2V(r)}{\partial r^2}\right|_{r=r_e}=\frac{1}{2}k(r-r_e)^2 \quad \text{where} \quad k=\left.\frac{\partial^2V(r)}{\partial r^2}\right|_{r=r_e}$$

represents a parabola (dotted curve of Fig. 1.1). Thus near $r=r_e$, the curve is a parabola and for small displacements $(r-r_e)$, the molecule can be treated as a harmonic oscillator. Note from equation (2), $V(r)|_{\min}=E_e'$ where nuclear-nuclear interaction is ignored. So *energy at the minimum of* $V(r)$ *function is referred to as electronic energy*, E_e.

We know that when two atoms are brought nearer to form a stable molecule, the electronic energy decreases rapidly while energy of repulsion increases. For a certain internuclear separation, the total potential energy becomes a minimum, as we see in Fig. 1.1 and 1.2 that at $r = r_e$, potential energy is minimum. This is the equilibrium internuclear separation. The two nuctei vibrate about their respective equilibrium positions along the internuclear axis and the molecule rotates about the centre of mass. That is why eq. (1) consists of:

(i) energy at the minimum of $V(r)$ function which is referred to as electronic energy E_e; this is the energy which the molecule will possess if the nuclei were fixed and consists of the kinetic and potential energies of extra-nuclear electrons and potential energy of repulsion of the nuclei;

(ii) energy of nuclear vibrations about equilibrium position, r_e, under the potential function, $V(r)$ which is referred to as vibrational energy, E_υ, defined by quantum number, υ;

(iii) energy of rotation of the molecule as a whole which is referred to as rotational energy, E_r, defined by the quantum number J. Thus

$$E = E_e + E_\upsilon + E_r \qquad \ldots (3)$$

or in terms of wave numbers,

$$\frac{E}{hc} = \frac{E_e}{hc} + \frac{E_\upsilon}{hc} + \frac{E_r}{hc}$$

$$\nu = \nu_e + G(\upsilon) + F(\upsilon, J) \qquad \ldots (4)$$

where ν_e is the electronic term, $G(\upsilon)$ is the vibrational term and $F(\upsilon, J)$ is the rotational term.

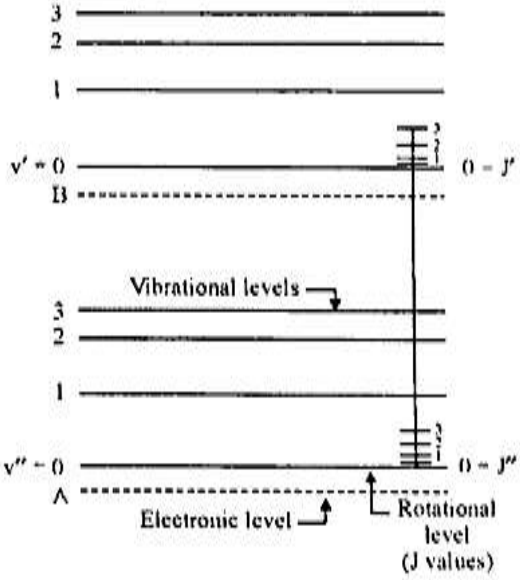

Fig. 1.3. A transition from

$$\left|\begin{array}{l}\text{Electronic level } A\\ \text{vibrational level } \upsilon'' = 0\\ \text{Rotational level } J'' = 1\end{array}\right. \text{ to } \left\{\begin{array}{l}\text{Electronic level } B\\ \text{vibrational level } \upsilon' = 0\\ \text{Rotational level } J' = 3\end{array}\right.$$

is shown in the figure.

Now we conclude that:

(i) a molecule has a number of discrete electronic levels with separations of the same order as in atoms (in Fig 1.3, A and B are electronic levels). *A transition between two electronic levels results in a radiation that falls in the visible or ultra violet region.*

(ii) With each electronic level are associated a number of vibrational energy levels whose spacing decreases with increasing quantum number, υ. *A transition between two vibrational levels results in a radiation that falls in the near infra-red region.*

(iii) With each vibrational level is associated a set of rotational levels whose spacing increases with increasing quantum number, J. *A transition between two rotational energy levels results in a radiation that falls in far infra-red or microwave region.*

In Fig. 1.3, a transition is shown. It is obvious that all the lines that arise from transitions between rotational levels J' and J'' associated with *a given* pair of vibrational levels, υ' and υ'' of a *given* pair of electronic levels (A and B) form a *band*. Therefore each line in each band of the system arises due to a change in all the three energies E_e, E_υ and E_r. Thus

$$\nu = \frac{E' - E''}{hc}$$

$$= \frac{(E_e' - E_e'')}{hc} + \frac{(E_{\upsilon'} - E_{\upsilon''})}{hc} + \frac{(E_{J'} - E_{J''})}{hc}$$

$$= \nu_e + \nu_\upsilon + \nu_r \qquad \ldots (5)$$

with $\nu_e > \nu_\upsilon > \nu_r$. We note that

(i) *For a given band*, ν_e and ν_υ are constants, while ν_r changes from line to line. The position in the band where $\nu_r = 0$ is called band origin; its wave number is $(\nu_e + \nu_\upsilon)$.

(ii) For a given system of bands (band-system), ν_e is constant, where as ν_υ changes from band to band. The position in the system where $\nu_\upsilon = 0$ (and $\nu_r = 0$) is called the system-origin; its wave number is ν_e.

(iii) The electronic band system lies in the visible or ultra-violet region.

Apart from electronic bands, we also have non-electronic bands. They involve transitions in the same electronic level. Such bands are of two types:

(i) **Vibrational-Rotational Bands:** A vibration-rotation *band* arises due to transitions between two vibrational levels of the *same electronic level*. The *lines* of the band result from the transitions between rotational levels of one vibrational level to the rotational levels of other vibrational level. The wavenumber of a line is $\nu_\upsilon + \nu_r$. *Such bands occur in the near infra-red region.*

(ii) **Pure Rotational Bands:** In this case *electronic level is same and vibrational level is also the same.* Transitions between two rotational levels associated with one and the *same* vibrational level of a given electronic state give rise to pure rotation bands or rather lines. The wave number of a line is ν_r. These lines fall in the far infra-red or in the microwave region.

1.2. TYPES OF SPECTRA

We have discussed in detail in SECTION-1 the spectra emitted by *atoms* (when the emitting substance is in atomic state), *i.e.* atomic spectra. The other spectra, outlined in art. 1.1, are emitted by *molecules* (when the emitting substance is in molecular state) containing two or more atoms. Molecular spectra under low dispersion appear as continuous bands and for this reason they are often called 'band spectra'. Usually a band has a sharp intense edge on one side called '*band head*', and gradually decreases in intensity towards the other side.

With high resolving power instruments, band spectra are found to have threefold structure:

(*i*) Each band is seen to be composed of a large number of lines which are crowded together at the long wavelength side, called 'band head' and as they recede from the band head, the lines become more widely separated and also weaker; the lines, however, being so close together as to appear, under low resolution, like a *continuous* spectrum.

(*ii*) There is a regular sequence in which the several bands follow one another, and thus constitute a group of bands.

(*iii*) These different groups of bands are quite close and thus, because of their regular arrangement, form a band system.

Thus, since we find that, like atomic spectra, molecular spectra are also composed of monochromatic lines having approximately the same width, the name 'band spectra' merely signifies the distinction from atomic spectra—the so called line spectra.

Regions of The Spectrum

In Fig. 1.4 we have sketched the regions into which electromagnetic radiations have been divided in an arbitrary manner and boundaries are not precise. The molecular processes associated with each region are quite different and are noted along with the corresponding regions. We brief the description in the following few lines.

(i) **Radio frequency region:** 3×10^6-3×10^{10} c/s; 10 cm–1 cm wavelength, nuclear magnetic resonance (n.m.r.) and electron spin resonance (e.s.r.) spectroscopy. The reversal of spin of a nucleus or electron is the cause of energy change.

(ii) Microwave region (Far infra-red region): 3×10^{10}–3×10^{12} c/s; 1 cm.–100 μ* wavelength. Rotational spectroscopy.

(iii) Infra-red region (Near infra-red region): 3×10^{12}–3×10^{14} c/s; 100 μ – 1 μ wavelength. Vibrational spectroscopy.

(iv) Visible and ultra-violet regions: 3×10^{14}–3×10^{16} c/s; 1 μ–100 Å wavelength. Electron spectroscopy.

(v) X-ray region: 3×10^{16} c/s and above; 100 Å wavelength or less. Energy changes involve the inner electrons of an atom or molecule.

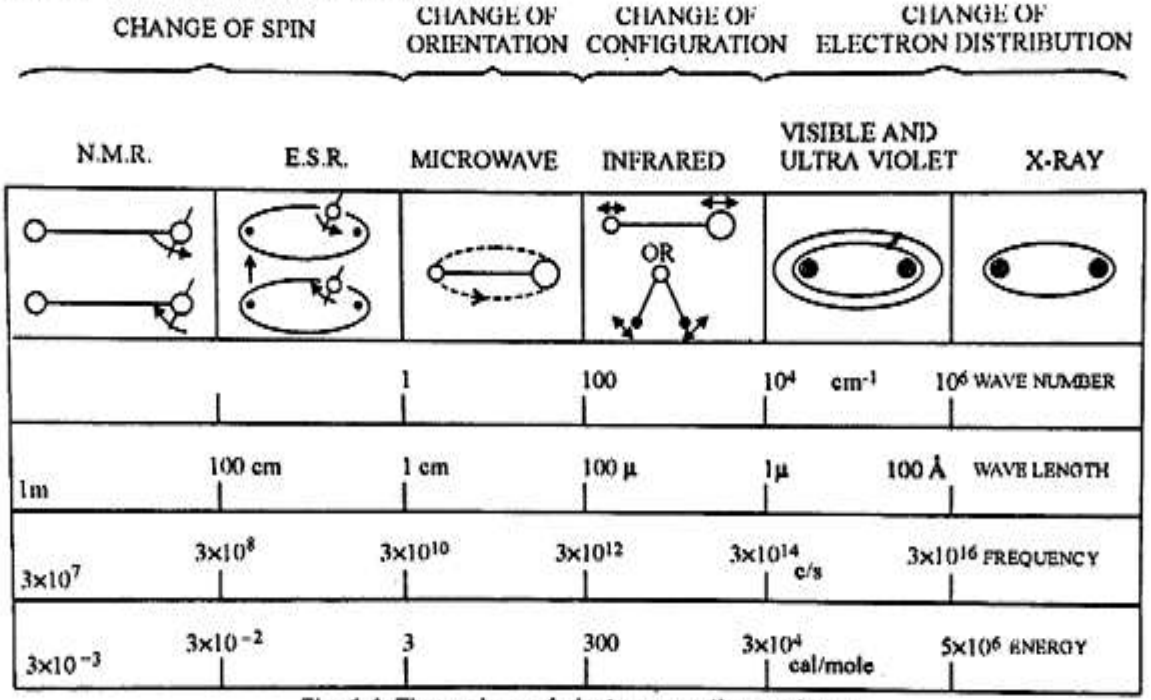

Fig. 1.4. The regions of electromagnetic spectrum.

From the viewpoint of experimental methods and theoretical significance, molecular spectra fall into three groups according as they lie in:

(*a*) the far (long wavelength 20–150μ) infra-red region. This we shall discuss under the head 'Far infra-red spectroscopy'.

(*b*) the near (short wavelength) infrared region. This we shall discuss under the head 'Infra-red spectroscopy'.

(*c*) visible or ultra-violet region. This we shall discuss under the head 'Visible and ultra-violet spectroscopy'.

Thus explanation for three types of band spectra, as discussed in art. 1.1, demands that the internal energy of a molecule, *i.e.*, the energy other than translational, is essentially of three kinds, namely electronic, vibrational, and rotational which are *all quantised* and thus the molecule possesses only certain discrete energy states. The transition between two energy states of a molecule, as a result of absorption or emission of energy, will give rise to a spectral line in the spectrum of that molecule. Suppose energy difference of two states is $(E' - E'')$ then the wave-number (frequency in cm^{-1}) corresponding to this line, arising due to transition between these two states, will be

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*$1\ \mu = 10^{-4}$ cm $= 10^4$ Å.

$$\nu = \frac{E' - E''}{hc} \text{ cm}^{-1},$$

where c is the velocity of light.

The three types of bands, discussed above, are correlated respectively with (*i*) *changes in the rotational energy*, (*ii*) *simultaneous changes of the rotational and vibrational energies, and* (*iii*) *simultaneous changes in the rotational, vibrational and electronic energies.*

We shall here discuss in brief how the changes in these energies produce different types of the bands and make them correspond to different regions.

Electronic Spectra (Ultra-violet or visible region)

We, from various considerations, conclude that a potential of 5 to 10 volts is required to change the energy level of an electron in a molecule or, in other words, two electronic states of an electron have an energy difference of about 5 to 10 electron volts (eV). The frequency* of radiation accompanying an electronic transition of 5 eV (say), which is equivalent to 8×10^{-19} erg/mole, will be

$$\nu = \frac{8 \times 10^{-19}}{6{\cdot}6 \times 10^{-34} \times 3 \times 10^{8}} = 4 \times 10^{6} \text{ m}^{-1}$$

or

$$\lambda = \frac{1}{\nu} = \frac{1}{4 \times 10^{6}} \text{ m} = 25 \times 10^{-6} \text{ cm} = 2500 \text{ Å},$$

which shows that the spectrum accompanying an electronic transition in a molecule, just as with an atom, should appear in the ultra-violet or short wavelength portion of visible spectrum. Since such molecular spectra arise due to transitions from one electronic state to another, they are referred to as electronic spectra.

In each electronic state there are a number of possible vibrational states corresponding to different values of the vibrational energy of the molecule; the two successive vibrational levels of the same electronic state have an energy difference of 0·1 eV. Further the energy corresponding to rotation of the molecule about two (for a linear molecule) or three axes is quantised and thus we conclude that *each* vibrational level has a set of rotational sublevels; the two adjacent rotational levels in one and the same vibrational and electronic state have an energy difference of about 0·005 eV.

Now suppose, in a molecule, electronic transition from initial state to final (excited) state occurs; then it will be accompanied by a change in vibrational energy, the magnitude of change depending upon the vibration levels in the initial and final electronic states. As we have discussed previously, change in electronic state amounts to 5 eV, while in vibrational levels to 0·1 eV and therefore electronic spectrum of the molecule which would fall in the region of 2500 Å will consist of a number of lines with a spacing of about 50 Å. Now for a given electronic and vibrational energy change, there would also be a change in rotational levels giving rise to rotational transitions. Since the rotational quanta are of the order of 0·005 eV, the spacing of these rotational lines will be about 2·5 Å.

Thus for a particular vibrational transition, there will be a set of rotational lines constituting a band and since there will be different vibrational transitions for a given electronic change, the whole system will consist of a system of bands or band groups. Now when different electronic changes are involved, a series of such band groups will constitute the band spectrum of the molecule. We note here that because of the changes in rotational and vibrational energies, the electronic spectrum is a complex one, even if there is only one electronic transition. For a polyatomic non-linear molecule, the different modes of vibration are $(3n - 6)$, where n is the number of atoms in the molecule and each mode will give rise to a band. Further, a non-linear

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*The frequency, wherever mentioned in molecular spectra, is expressed in wave number unit.

molecule will have rotations about three axes. Thus we conclude that inspite of selection rules, the electronic spectra of polyatomic molecules will be very complex. With a diatomic molecule it is not so complex, because firstly such a molecule has only one vibrational mode and secondly it has two identical moments of inertia at right angles while the third is zero. We shall study the case of a diatomic molecule.

Near Infra-red Spectra: In the absence of any electronic transition (no change in electronic state) vibrational transition can occur, *i.e.* there is a possibility of a transition from one vibrational energy level to another with the same electronic (ground) state of the molecules involving an energy change of about 0·1 eV ($1{\cdot}6 \times 10^{-20}$ erg/mole); frequency of radiation will be

$$\nu = \frac{1{\cdot}6 \times 10^{-20}}{6{\cdot}6 \times 10^{-34} \times 3 \times 10^{8}} = 8 \times 10^{4}\ \mathrm{m}^{-1}$$

or

$$\lambda = 125000\ \text{Å} = 12{\cdot}5\ \mu,$$

which shows that these radiations, accompanying vibrational changes within the electronic ground state, should appear in near infra-red portion of the spectrum.

Now such a vibrational transition within a particular electronic state would be associated with various possible rotational changes which lead to the presence of a number of closely spaced spectral lines. Such bands are termed as *vibration rotation* bands. These are generally observed in absorption and in the wavelength region of about 1 to 20 μ. For a diatomic molecule, the mode of vibration is only *one* and hence only one vibration-rotation band for each vibrational transition.

Far Infra-red Spectra: In far infra-red region, transitions occur that are purely rotational in character, unaccompanied by changes in electronic and vibrational energies. Such a transition involves an energy change of 0·005 eV and thus frequency of radiation is

$$\nu = \frac{0{\cdot}005 \times 1{\cdot}6 \times 10^{-19}}{6{\cdot}6 \times 10^{-34} \times 3 \times 10^{8}}$$

$$= \frac{8 \times 10^{-22}}{3 \times 6{\cdot}6 \times 10^{-26}} = \frac{8 \times 10^{4}}{19{\cdot}8}\ \mathrm{m}^{-1}$$

or

$$\lambda = \frac{19{\cdot}8}{800}\ \mathrm{cm} = 2{\cdot}47 \times 10^{-2}\ \mathrm{cm}$$

$$= 2470000\ \text{Å} = 247\ \mu.$$

This shows that these radiations will lie in the far infra-red region. The bands in the far infra-red are therefore called rotational spectra.

END OF PART-I

2.0. SALIENT FEATURES OF ROTATIONAL SPECTRA

(i) The bands which appear in far infra-red region at wavelengths of 200 × 10^4 Å or more are due to transitions involving very small energy changes, about 0·005 eV. With such a small quantum of energy, electronic and vibrational energy states will not be excited or in other words only transitions that are purely rotational in character will appear. Therefore bands that appear in the far infra-red region arise due to the changes in the rotational energy of the molecule unaccompanied by changes in electronic or vibrational energy. Only those molecules which have permanent electric dipole moment can give rise to pure rotational spectra. Thus homonuclear diatomic molecules such as H_2, O_2, N_2 etc. do not exhibit pure rotation spectra* while heteronuclear diatomic such as HF, HCl, HBr etc. do exhibit. The far infra-red spectra are known only in absorption and only for molecules of HCl, HBr, HI, H_2O and NH_3, they have been studied in detail.

(ii) In practice, rotational spectra are observed in absorption. For heteronuclear diatomic molecules such as HF, HCl, HBr, CO etc., the rotational spectra consist of a simple series of absorption maxima which are very nearly equidistant on a wave number scale. A measurement of the frequencies of these maxima help to determine the moment of inertia and the internuclear distance.

(iii) The basic molecular requirement for the emission or absorption of radiation by a transition between rotational energy states is that the molecule must have a permanent dipole moment. This is in line with classical electrodynamics, according to which a rotating molecule can lead to the emission of radiation only if a *changing dipole moment* is associated with it. During the rotation of a heteronuclear diatomic molecule, which have a permanent dipole moment, the component of this dipole moment in a fixed direction changes periodically with the frequency of rotation of the molecule, emitting radiations of the same frequency. However, homonuclear molecules have no dipole moment and hence there is no emission of infra-red radiation.

(iv) Further infra-red radiations can be absorbed by a rotating molecule and thereby increase rotation, only if a permanent dipole moment is present. Such a molecule interacts with the oscillating electric field of the incident radiation to absorb rotational energy and produce absorption spectra.

For experimental arrangement see art. 3.7.

2.1. THE MOLECULE AS A RIGID ROTATOR : EXPLANATION OF ROTATIONAL SPECTRA

If there are only two mass points in a molecule, the line joining the two is an axis of symmetry, and rotation about an axis perpendicular to this line has significane; also, the moment of inertia about all such perpendicular axes will have the same value.

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*Homonuclear molecules, however, show rotational Raman spectra which arise due to the polarisability of the molecules.

As a first approximation, rotating diatomic molecules, whose nuclei are considered as being separated by a definite mean distance, may be treated as a rigid rotator with free axis. Suppose masses m_1 and m_2 are joined by a rigid bar (the bond) whose length is $r_0 = r_1 + r_2$ (Fig. 2.1). The molecule rotates about the centre of gravity C.

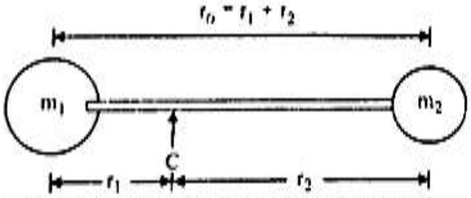

Fig. 2.1. A rigid diatomic molecule treated as two masses m_1 and m_2 joined by a rigid base of length $r_0 = r_1 + r_2$.

We shall calculate rotational energy levels, frequency of spectral lines arising due to transition between two energy levels, and the selection rule for transitions in the case of diatomic molecules. In this analysis we shall assume that the bond between the atoms is stiff and does not change in length (rigid rotator).

Rotational Energy Levels: Let us consider a diatomic molecule with an internuclear distance r_0. The molecule has a natural rotation about the axis through its centre of gravity C as shown in Fig. 2.1.

The moment of inertia of an assembly of i particles, such as the atoms of a molecule, is expressed as

$$I = m_1 r_1^2 + m_2 r_2^2 + m_3 r_3^2 + \dots$$
$$= \sum_i m_i r_i^2,$$

where r_i refers to the distance of particles from the axis of rotation. In the present case,

$$I = m_1 r_1^2 + m_2 r_2^2, \qquad \dots (1)$$

where r_1 and r_2 are the distances of m_1 and m_2 from the axis of rotation through C. As the system is balanced about its centre of gravity, we can have

$$m_1 r_1 = m_2 r_2. \qquad \dots (2)$$

Further $\qquad r_0 = r_1 + r_2. \qquad \dots (3)$

From equations (2) and (3), we find that

$$r_1 = \frac{m_2}{m_1 + m_2} r_0$$

and

$$r_2 = \frac{m_1}{m_1 + m_2} r_0.$$

Putting these values of r_1 and r_2 in equation (1), we arrive at

$$I = \frac{m_1 m_2^2}{(m_1 + m_2)^2} r_0^2 + \frac{m_2 m_1^2}{(m_1 + m_2)^2} r_0^2$$
$$= \frac{m_1 m_2}{m_1 + m_2} r_0^2 = m' r_0^2. \qquad \dots (4)$$

where the reduced mass, m', is defined as

$$m' = \frac{m_1 m_2}{m_1 + m_2}.$$

If the molecule is rotating with angular velcity ω, then classically it would have an energy $\frac{1}{2} I\omega^2$. We have discussed in atomic spectra (Chapter 2) that an electron rotating with angular velocity ω about the nucleus has an angular momentum $I\omega$ which can assume the values that are integral multiples of $\frac{h}{2\pi}$ (Bohr quantum condition); it is easy to write

$$I\omega = J\frac{h}{2\pi}, \quad \text{where} \quad J = 0, 1, 2 \ldots$$

Therefore, allowed rotational energies will be given by

$$E_r = \tfrac{1}{2} I\omega^2 = \frac{1}{2I}(I^2\omega^2)$$

$$= \frac{J^2h^2}{8\pi^2 I}, \qquad \ldots (5)$$

with $J = 0, 1, 2 \ldots$, termed as *rotational quantum number.*

Energy levels of rigid rotator on applying Schrödinger equation: The Schrödinger equation in three dimensions is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0,$$

which when converted into spherical coordinates becomes

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)$$

$$+ \frac{1}{r^2\sin\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0. \qquad \ldots (6)$$

In order to apply the above equation to the problem of rigid rotator, we have to arrive at some conclusions for m, r and V as discussed below:

In cartesian coordinates, the kinetic energy T of a single particle of mass m can be expressed as

$$T = \frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2),$$

which in spherical coordinates is

$$^*T = \frac{1}{2}m(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\dot{\phi}^2\sin^2\theta).$$

If the distance r of the particle from the origin is fixed, the derivative $\dot{r}$ will be zero so that

$$T = \frac{1}{2}mr^2(\dot{\theta}^2 + \dot{\phi}^2\sin^2\theta) \qquad \ldots (7)$$

Since two particles form a rigid rotator, the total kinetic energy will be

$$T = T_1 + T_2$$

$$= \frac{1}{2}m_1r_1^2(\dot{\theta}^2 + \dot{\phi}^2\sin^2\theta) + \frac{1}{2}m_2r_2^2(\dot{\theta}^2 + \dot{\phi}^2\sin^2\theta).$$

As in the case of rigid rotator, the interparticle distance is fixed, potential energy will come out to be zero. Therefore, V is zero and T represents the total energy of the rigid rotator. Consequently,

$$E = T = \frac{1}{2}(m_1r_1^2 + m_2r_2^2)(\dot{\theta}^2 + \dot{\phi}^2\sin^2\theta)$$

From equation (1), we find that the first bracketted term on right hand side represents the moment of intertia I of the rigid rotator. Therefore

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*On putting

$x = r\sin\theta\cos\phi,$

$y = r\sin\theta\sin\phi$

and $z = r\cos\theta.$

$$E = \frac{1}{2} I(\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta).$$

Comparing above equation with equation (7), we can conclude that the rigid rotator behaves like a single particle of mass I placed at a fixed distance, equal to unity (since $r = 1$) from the origin (centre of mass). Consequently, for rigid rotator, we must put.

$V = 0$

$r = 1$

and I in place of m

in equation (6).

For rigid rotator, equation (6) is then

$$\frac{1}{\sin\theta} \cdot \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2 IE}{h^2}\psi = 0. \qquad \ldots(8)$$

From above equation, it is obvious that ψ is a function of θ and ϕ, *i.e.*,

$$\psi = \psi(\theta, \phi).$$

We shall apply the method of separation of variables for the solution of equation (8). For this let us express ψ as the product of two functions, namely, $\Theta(\theta)$ and $\Phi(\phi)$, each involving one variable only, *i.e.*

$$\psi(\theta, \phi) = \Theta(\theta)\,\Phi(\phi)$$

so that
$$\frac{\partial\psi}{\partial\theta} = \Phi\frac{\partial\Theta}{\partial\theta}$$

and
$$\frac{\partial^2\psi}{\partial\phi^2} = \Theta\frac{\partial^2\Phi}{\partial\phi^2}.$$

Putting the values of above differentials and ψ in equation (8), and then multiplying the whole equation by $\frac{\sin^2\theta}{\Theta\Phi}$, we get

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} + \frac{8\pi^2 IE}{h^2}\sin^2\theta = 0.$$

On separating the variables,

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \beta\sin^2\theta = -\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2},$$

where $\beta = \frac{8\pi^2 IE}{h^2}$.

In the above equation, left hand side involves the variable θ only, whereas right hand side involves the variable ϕ only. As the two variables θ and ϕ are independent, the two terms can be equated only when each is equal to a constant, say m^2, so that

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \beta\sin^2\theta = m^2 \qquad \ldots(9)$$

and
$$-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = m^2. \qquad \ldots(10)$$

The solution of equation (10) is

$$\Phi = Ce^{\pm im\phi}$$

For Φ to be a single valued function, it should have same value for $\phi = 0$ and 2π, *i.e.*,

$$\Phi = Ce^{\pm im \cdot 0} = C$$

$$\Phi = Ce^{\pm i2\pi m}$$

should be same. Therefore

$$C = Ce^{\pm i2\pi m}$$

or $$\cos 2\pi m \pm i \sin 2\pi m = 1,$$

which can be true only if m is *zero* or an *integer*.

Now we take up the solution of equation (9); we can write equation (9) on multiplying by $\frac{\Theta}{\sin^2\theta}$ as

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\left(\beta-\frac{m^2}{\sin^2\theta}\right)\Theta=0.$$

Putting $$x = \cos\theta$$

so that $$\frac{\partial\Theta}{\partial\theta}=\frac{\partial\Theta}{\partial x}\frac{\partial x}{\partial\Theta}=-\sin\theta\frac{\partial\Theta}{\partial x}$$

or $$\frac{\partial}{\partial\theta}=-\sin\theta\frac{\partial}{\partial x}$$

in the above equation, we get

$$\frac{1}{\sin\theta}\times-\sin\theta\frac{\partial}{\partial x}\left(-\sin^2\theta\frac{\partial\Theta}{\partial x}\right)+\left(\beta-\frac{m^2}{\sin^2\theta}\right)\Theta=0$$

or $$\frac{\partial}{\partial x}\left\{(1-x^2)\frac{\partial\Theta}{\partial x}\right\}+\left\{\beta-\frac{m^2}{(1-x^2)}\right\}\Theta=0. \qquad \ldots(11)$$

It is Legendre's differential equation; x can assume values from cos 0 or (+1) to cos π or (–1). To solve the above equation, let us write

$$\Theta=(1-x^2)^{m/2}\cdot G$$

so that

$$\frac{\partial\Theta}{\partial x}=-mx(1-x^2)^{(m/2)-1}G+(1-x^2)^{m/2}\frac{\partial G}{\partial x}$$

$\therefore$ $$(1-x^2)\frac{\partial\Theta}{\partial x}=-mx(1-x^2)^{(m/2)}G+(1-x^2)^{m/2+1}\frac{\partial G}{\partial x}$$

Hence the first term of equation (11) is

$$\frac{\partial}{\partial x}\left\{(1-x^2)\frac{\partial\Theta}{\partial x}\right\}=\{-m(1-x^2)^{m/2}+m^2x^2(1-x^2)^{(m/2)-1}\}G$$
$$-\{2x(m+1)(1-x^2)^{m/2}\}G'+(1-x^2)^{(m/2)+1}G'',$$

where $$G'=\frac{\partial G}{\partial x} \quad \text{and} \quad G''=\frac{\partial^2 G}{\partial x^2}.$$

Putting this value of first term in equation (11) and dividing through by $(1-x^2)^{m/2}$, we get

$$(1-x^2)G''-2(m+1)xG'+\{\beta-m(m+1)\}G=0$$

or $$(1-x^2)G''-2axG'+bG=0. \qquad \ldots(12)$$

where $a = m + 1$

and $b = \beta - m(m+1)$.

Let us express $G(x)$ as power series, *i.e.*

$$G(x)=\alpha_0+\alpha_1x+\alpha_2x^2+\alpha_3x^3+\ldots$$

so that $$G'(x)=\alpha_1+2\alpha_2x+3\alpha_3x^2+4\alpha_4x^3+\ldots$$

and $$G''(x)=2\alpha_2+6\alpha_3x+12\alpha_4x^2+\ldots$$

Putting these values in equation (12), we get on arranging the terms in ascending powers of x, that

$$(2\alpha_2 + b\alpha_0)x^0 + [6\alpha_3 + (b - 2a)\alpha_1]x + [12\alpha_4 + (b - 4a - 2)\alpha_2]x^2 + \ldots = 0.$$

Equating the coefficients of every power of x, we get

$$2\alpha_2 + b\alpha_0 = 0$$

$$6\alpha_3 + (b - 2a)\alpha_1 = 0$$

$$12\alpha_4 + (b - 4a - 2)\alpha_2 = 0$$

or in general,

$$(n + 1)(n + 2)\alpha_{n+2} + [b - 2na - n(n - 1)]\alpha_n = 0,$$

where n is zero or an integer. Putting the values of a and b in the above relation, we get the recursion formula

$$\frac{\alpha_{n+2}}{\alpha_n} = \frac{(n + m)(n + m + 1) - \beta}{(n + 1)(n + 2)},$$

for the coefficients in the power series for $G(x)$.

For $G(x)$ to be a polynomial, the series of $G(x)$ must terminate after a finite number of terms which is possible only if

$$(n + m)(n + m + 1) - \beta = 0$$

or

$$\beta = (n + m)(n + m + 1)$$

$$= l(l + 1)$$

We have seen that m must be zero or integer and since the same condition applies to n, the sum $(n + m)$ *i.e.* l should be zero or integer *i.e.*

$$l = 0, 1, 2, 3, \ldots \text{ etc.}$$

We know that

$$\beta = \frac{8\pi^2 IE}{h^2}$$

then

$$\frac{8\pi^2 IE}{h^2} = l(l + 1)$$

so that

$$E = l(l + 1)\frac{h^2}{8\pi^2 I}.$$

Replacing l by J we get

$$\boxed{E_r = \frac{h^2}{8\pi^2 I} J(J + 1), \text{ where } J = 0, 1, 2.} \quad \ldots (13)$$

The above equation obviously relates the allowed rotational energies to a molecular property I and a quantum number **J**. If this energy, E_r, is converted to the units of rotational term values, it becomes

$$\boxed{F(J) = \frac{E_r}{hc} = \frac{h}{8\pi^2 Ic} J(J + 1),} \quad \ldots (14)$$

where $F(J)$ is called *rotational term* (unit m^{-1}). The equation can further be put as

$$F(J) = BJ(J + 1)\ \mathrm{m}^{-1},\ J = 0, 1, 2, \ldots$$

where B, called *rotational constant*, is given by

$$\boxed{B = \frac{h}{8\pi^2 Ic}\ \mathrm{m}^{-1}.} \quad \ldots (15)$$

If we account for the multiplicity of rotational energy levels, the so called *degeneracy*, then the population of the various rotational energy levels can be calculated from Boltzmann's distribution

$$N_J = N_0\, e^{-E_J/kT},$$

in which for the sake of representation an Avogadro's number of molecules has been considered. This equation states that out of molecules N_0, the Avogadro's number, N_J molecules occupy J^{th} state of energy equal to E_J at absolute temperature T K. k is Boltzmann constant. The degeneracy (which implies the existence of more than one energy *state* with the *same energy*) of a rotational level is found to be $(2J + 1)$. Therefore Boltzmann distribution can be written as

$$N_J = (2J + 1)N_0 e^{-E_J/kT},$$

and shows population maximum at a value other than $J = 0$.

Frequency of Spectral line: If a rotational transition occurs from an upper level with quantum number J' to lower level of quantum number J'' then frequency of spectral line, expressed in wave numbers, is given by

$$\begin{aligned} \nu_r &= \frac{E_r' - E_r''}{hc} \\ &= \frac{h}{8\pi^2 Ic}\,[J'(J' + 1) - J''(J'' + 1)] \text{ using eq. (13)} \\ &= B[J'(J' + 1) - J''(J'' + 1)] \end{aligned}$$

If a rotating molecule possesses a dipole moment then it can interect with oscillating electromagnetic radiation. That is, the molecule can withdraw from or give up energy to the radiation and consequently transference of energy from radiation to the molecule or *vice vĕrsa* takes place. In other words, a *molecule must have a dipole moment in order to give rise to rotational spectra.*

Spectral Transition Probabilities and Selection Rules: By the methods of quantum mechanics, the probability of transition between two energy states can be determined. Let us designate the two energy states by the letters m and n; then the probability of a transition between these two states accompanied by the absorption or emission of (dipole) radiation, is determined by the matrix element P_{mn}; the component of P_{mn} in x direction is defined as

$$P_{mn}(x) = \int \psi_m^* \left(\sum_j \varepsilon_j x_j\right) \psi_n \, d\tau, \qquad \ldots (16)$$

where ψ_m and ψ_n are the eigen functions of the two states, ε_j is the electric charge and x_j the x-coordinate of the J^{th} atom in the molecule, $\sum_j \varepsilon_j x_j$ (the summation of $\varepsilon_j x_j$ over all the atoms in the molecule) gives the component of the electric dipole moment in the direction of x-axis, *i.e.* μ_x, so that

$$P_{mn}(x) = \int \psi_m^* \mu_x \psi_n \, d\tau. \qquad \ldots (17)$$

If all the three components in x, y and z directions are zero, no transition can occur and, therefore, for a particular transition to occur, one of the components of P_{mn} must differ from zero. One particular condition, apart from others, under which the integral $P_{mn}(x)$ vanishes is that the component μ_x of dipole moment be zero in the equilibrium state of the molecule or remains so throughout the various moments of electrons and nuclei. This condition leads to the conclusion that a *molecule, which is symmetrical in ground state and consequently does not possess resultant dipole moment, will not interact with the radiation. As a result, the molecule will not yield a spectrum unless an electric moment is produced by disturbing the symmetry of the electrons or of the nuclei.*

For a rigid rotator if we insert the appropriate eigen functions for upper and lower states in equation (17), assuming that μ_x is not zero, it is found that $P_{mn}(x)$ will be zero unless

$J' - J'' = \pm 1$. This means that only those rotational transitions which involve an increase or decrease of unity in the rotational quantum number are permitted. This is termed as the *selection rule* for rotational transitions, *i.e.* the selection rule is

$$\Delta J = J' - J'' = \pm 1. \qquad \ldots (18)$$

For the rotator $J' > J''$ (since J' refers to the upper state), and therefore considering only $\Delta J = +1$, we have for the emitted or absorbed lines of the rigid rotator

$$\begin{aligned} \nu_r &= F(J''+1) - F(J'') \\ &= B(J''+1)(J''+2) - BJ''(J''+1) \\ &= 2B(J''+1), \quad J'' = 0, 1, 2, \ldots \end{aligned}$$

Writing J instead of J'' for lower state, we find

$$\nu_r = 2B(J+1)\,; \; J = 0, 1, 2 \ldots \qquad \ldots (19)$$

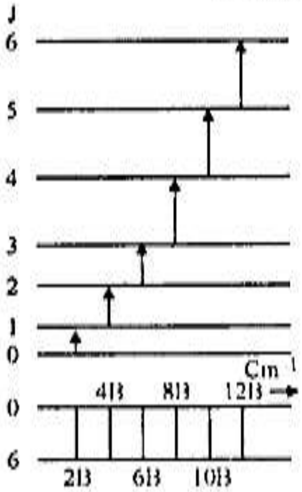

Fig. 2.2. Allowed transitions between the energy levels of a rigid diatomic molecule and the spectrum which arises from them (absorption spectra).

Spectrum

Putting these values for J, we find that the frequencies for consecutive lines in the pure rotation spectrum of a diatomic molecule are $2B$, $4B$, $6B$ etc. Therefore on the frequency (wave number) scale, the lines are equidistant (Fig. 2.2).

The rotational frequency is given by

$$\begin{aligned} &= c \cdot 2B\sqrt{\{J(J+1)\}} \\ &= c \cdot 2BJ, \end{aligned}$$

i.e. the rotation frequency in any given state of the rotator is approximately equal to the frequency of the spectral line that has this state as upper state.

2.2. Diatomic Molecule as a Non-rigid Rotator

Experimental investigations have shown that the successive lines in the far infra-red spectrum are not evenly spaced, but that the frequency separation decreases slightly with increasing J values. The cause of this decrease becomes atonce obvious if we calculate internuclear distance from the rotational constant, B, values. It shows that bond length increases with J and that assumption under which a diatomic molecule is treated as rigid rotator is false and, in fact, all bonds are elastic to some extent. We infer from the increase in length with J that more quickly a diatomic molecule rotates, the greater is the centrifugal force tending to move the atoms apart.

Now we discuss the consequences of the change in bond length with J. Firstly, when a bond is elastic, it will stretch and compress periodically with a certain functional frequency dependent upon the masses of the atoms and the elasticity (or force constant) of the bond, *i.e.*, this means, in other words, that the molecule may have vibrational energy, and if the motion is simple harmonic, force constant is given by

$$k = 4\pi^2\omega^2c^2m',$$

where ω is the vibration frequency (in m^{-1}). The weaker the bond more readily will it distort under centrifugal forces.

The other consequence of elasticity is that the quantities r and B *vary during a vibration.*

We thus see that the three different sets of values must be assigned to B and r, *i.e.*, B_e and r_e (separation between nuclei) at equilibrium, B_0 and r_0 (average inter-nuclear separation) in the vibrational ground state or B_n and r_n in case molecule possesses excess vibrational energy, where n is the vibrational quantum number.

Energy Levels

For non-rigid rotator, Schrodinger wave equation (Refer to Molecular Binding) yields to give the rotational energy levels as

$$E = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 k} J^2(J+1)^2$$

or

$$F(J) = \frac{E}{hc}$$

$$= BJ(J+1) - DJ^2(J+1)^2 \text{ cm}^{-1} \qquad \ldots (1)$$

where D is called centrifugal distortion constant, and is given by

$$D = \frac{h^4}{32\pi^4 I^2 r^2 kc} \text{ cm}^{-1}.$$

and is a positive quantity.

Equation (1) is true when force is simple harmonic. If force field is anharmonic, the expression becomes

$$F(J) = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + KJ^4(J+1)^4 + \ldots \text{ cm}^{-1} \qquad \ldots (2)$$

where H, K, etc. are small constants dependent upon the geometry of the molecule.

From the relations for B and D, we find that

$$D = \frac{16B^3\pi^2 m'c^2}{k}$$

$$= \frac{4B^3}{\omega^2}, \qquad \ldots (3)$$

where ω is the vibration frequency of the bond in normal state. Since B is generally about 10 cm^{-1}, whereas ω is of the order of 1000 cm^{-1}, it is evident that D will be small, namely 10^{-3} cm^{-1} or so.

Spectrum

Fig. 2.3 shows the lowering (not exact in extent) of rotational levels when passing from the rigid to the non-rigid diatomic molecule. The spectra are also compared. Selection rule is still $\Delta J = \pm 1$.

The analytical expression for transition can be written as

$$F(J+1) - F(J) = \nu_r = B[(J+1)(J+2) - J(J+1)]$$
$$- D[(J+1)^2(J+2)^2 - J^2(J+1)^2]$$
$$= 2B(J+1) - 4D(J+1)^2 \text{ cm}^{-1}, \qquad \ldots (4)$$

where ν_r represents both upward transition from J to $(J+1)$ or downward from $(J+1)$ to J. We note from equation (3) that the lines are no longer exactly equidistant but their separation decreases slightly with increasing J. The effect, however, is small owing to the smallness of D as compared to B.

Knowledge of D provides two informations: First, the determination of J value of lines in an observed spectrum and, second, the determination of the vibrational frequency of a diatomic molecule (though not precisely). For hydrogen fluoride, equation (3) has the value

$$\omega^2 = \frac{4B^3}{D} \approx 16{\cdot}33 \times 10^{-6} (\text{cm.}^{-1})^2$$

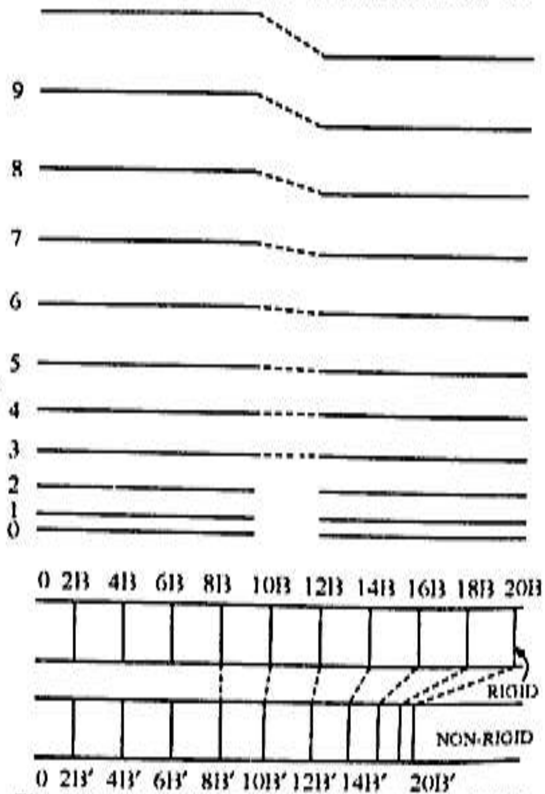

Fig. 2.3. The change in rotational energy levels and rotational spectrum when passing from a rigid to a non-rigid diatomic molecule.

i.e. $\omega \cong 4050 \text{ cm.}^{-1}$

The force constant then follows directly:

$$k = 4\pi^2 c^2 \omega^2 m' = 9{\cdot}6 \times 10^5 \text{ dynes /cm.},$$

which indicates, as expected, that H-F is a relatively strong bond.

2.3. VALIDITY OF THE THEORY : DETERMINATION OF THE INTER-NUCLEAR DISTANCE (BOND LENGTH) AND MOMENT OF INERTIA

We shall apply equation (11) of art. 2.1 to an observed spectrum in order to determine the moment of inertia and hence bond length of a particle, *e.g.*, CO, HCl and HI etc. which exhibit rotational spectra.

(a) **CO molecule:** The first line ($J = 0$) in that rotation spectra of carbon monoxide appears at

$$\nu_r = 3{\cdot}84235 \text{ cm}^{-1}$$

so that from $\nu_r = 2B(J+1) = 2B,$

we get $B = \dfrac{\nu_r}{2} = 1{\cdot}92118 \text{ cm}^{-1}$

Further the *moment of inertia* is calculated from equation

$$I_{CO} = \frac{h}{8\pi^2 Bc}$$

$$= \frac{6{\cdot}62 \times 10^{-27}}{8 \times (3{\cdot}14)^2 \times 1{\cdot}92118 \times 3 \times 10^{10}}$$

$$= 1{\cdot}45673 \times 10^{-39} \text{ gm-cm}^2.$$

To calculate bond length, we shall first find out the value of reduced mass of CO-molecule given by

$$m' = \frac{m_1 m_2}{m_1 + m_2} \cdot \frac{1}{N_0},$$

where N_0 is Avogadro's number.

Taking $m_1 = 12$ gm (for carbon)

$m_2 = 15{\cdot}9949$ gm; (for oxygen)

the *reduced mass of CO-molecule* will be

$$m'_{CO} = \frac{12 \times 15{\cdot}9949}{(12 + 15{\cdot}9949)} \cdot \frac{1}{6{\cdot}244 \times 10^{23}} \text{ gm},$$

so that *bond length* of CO-molecule will be

$$r^2_{CO} = \frac{I_{CO}}{m'_{CO}} = 1{\cdot}2800 \times 10^{-16} \text{ cm}^2.$$

On putting values of I_{CO} and m'_{CO},

$$r_{CO} = 1{\cdot}131 \text{ Å}.$$

The value of bond length of CO molecule has been found in good agreement with the experimental results.

This separation between two energy levels specified by J' and J'' is given by equation (9), *i.e.*

$$(\Delta E)_{J', J''} = E' - E'' = \frac{h^2}{8\pi^2 I} [J'(J'+1) - J''(J''+1)].$$

Energy level separation between $J'' = 1$ (upper level) and $J'' = 0$ (lower level) is

$$(\Delta E)_{1,0} = \frac{h^2}{8\pi^2 I}[2-0] = 2\cdot\frac{h^2}{8\pi^2 I}$$

$$= 2\cdot\frac{(6{\cdot}62\times10^{-27})^2}{8\times(3{\cdot}14)^2\times1{\cdot}456\times10^{-39}}$$

$$= 2\cdot0{\cdot}3832\times10^{-14}\text{ erg}$$

$$= 0{\cdot}07664\times10^{-15}\text{ erg.}$$

which is quite small compared with the value of kT—being $4{\cdot}14\times10^{-4}$ ergs at room temperature. Rotational energy levels usually have energy separations of less than kT.

The factor $\frac{h^2}{8\pi^2 I}$ is termed as the energy level spacing factor.

(b) HCl molecule: From the frequencies of rotational absorption lines for HCl, it is obtained that

$$2\frac{h}{8\pi^2 Ic} = 20{\cdot}7\text{ cm}^{-1}.$$

or

$$2B = 20{\cdot}7\text{ cm}^{-1}.$$

or

$$B = 10{\cdot}35\text{ cm}^{-1}.$$

so that the moment of inertia is

$$I_{\text{HCl}} = \frac{h}{8\pi^2 Bc}$$

$$= \frac{6{\cdot}62\times10^{-27}}{8\times(3{\cdot}14)^2\times10{\cdot}35\times3\times10^{10}}$$

$$= 2{\cdot}70\times10^{-40}\text{ gm-cm}^2.$$

Reduced mass of the HCl molecule is

$$m' = \frac{m_1 m_2}{(m_1+m_2)}\frac{1}{N_0}$$

$$= \frac{(1{\cdot}008)(35{\cdot}46)}{(1{\cdot}008+35{\cdot}46)}\cdot\frac{1}{6{\cdot}024\times10^{23}}$$

$$= 1{\cdot}627\times10^{-24}\text{ gm.}$$

Bond length of HCl molecule is

$$r^2_{\text{HCl}} = \frac{I_{\text{HCl}}}{m'} = \frac{2{\cdot}70\times10^{-40}}{1{\cdot}627\times10^{-24}}$$

or

$$r_{\text{HCl}} = 1{\cdot}29\times10^{-8}\text{ cm}$$

$$= 1{\cdot}29\text{ Å.}$$

The *separation between energy level* $J = 0$ and $J = 1$ will be

$$(\Delta E_r)_{0,1} = 2\cdot\frac{h^2}{8\pi^2 I} = 2Bhc$$

$$= 20{\cdot}7\times6{\cdot}62\times10^{-27}\times3\times10^{10}$$

$$= 0{\cdot}405\times10^{-14}\text{ erg.}$$

(c) HI Molecule: The rotational spectrum in the far infrared of hydrogen iodide consists of a series of equidistant lines with a spacing of $12{\cdot}8\text{ cm}^{-1}$ or

$$2B = 2 \cdot \frac{h}{8\pi^2 Ic} = 12{\cdot}8 \text{ cm}^{-1}$$

Therefore *moment of inertia*:

$$I_{\text{HI}} = \frac{h}{8\pi^2 Bc}$$

$$= \frac{6{\cdot}62 \times 10^{-27}}{8 \times (3{\cdot}14)^2 \times (6{\cdot}4) \times 3 \times 10^{10}}$$

$$= 4{\cdot}372 \times 10^{-10} \text{ gm cm}^2.$$

Reduced mass will be

$$m' = \frac{(1 \times 127)}{(1 + 127)} \frac{1}{6{\cdot}024 \times 10^{23}}$$

$$= 1{\cdot}65 \times 10^{-24} \text{ gm.}$$

Bond length:

$$r^2_{\text{H-I}} = \frac{I_{\text{HI}}}{m'} = \frac{4{\cdot}372 \times 10^{-40}}{1{\cdot}65 \times 10^{-24}}$$

so that $r_{\text{H-I}} = 1{\cdot}63$ Å.

TABLE-1

Internuclear distances from Rotational Spectra

Molecule	I gm cm^2	Bond length (r) Å
Hydrogen fluoride	$1{\cdot}34 \times 10^{-40}$	0·92
Hydrogen chloride	$2{\cdot}66 \times 10^{-40}$	1·29
Hydrogen bromide	$3{\cdot}31 \times 10^{-40}$	1·42
Hydrogen iodide	$4{\cdot}37 \times 10^{-40}$	1·63

Examination of rotational spectra is thus a valuable and accurate means of calculating internuclear distances, at least for simple molecules. For a polyatomic linear molecule, there will be several internuclear distances, which cannot be calculated from a single value of moment of inertia. For a linear triatomic molecule, such as HCN, the rotational spectrum remains simple, but the single measured moment of inertia depends upon *two* internuclear distances. As the internuclear distance can be assumed to remain unaltered by isotopic substitution, the *two* internuclear distances can be computed by examining the spectra of isotopic molecules, such as DCN and HCN in the present example. This examination will provide the further moment of inertia values, and then by solving simultaneous equations (H—C, 1·06 Å : C—N, 1·16 Å), internuclear distances can be calculated.

In gaseous state, especially at very low pressure (10^{-4} mm of Hg), collisions among the molecules are small, and consequently, they can rotate freely. Therefore samples whose rotational spectra are to be studied are usually gaseous.

One disadvantage of this method of structural investigation, even for simple molecules, is that in order to exhibit a *rotational spectra, the molecule should possess a permanent dipole moment.* Molecules like N_2, O_2 and CO_2 do not, therefore, show rotational spectra in far infra-red region.

2.4. ISOTOPE EFFECT IN ROTATIONAL SPECTRA

Any isotopic exchange would bring a change in mass and hence in moment of inertia but not in the internuclear distance in a diatomic molecule. It means that, for different isotopic forms of the same molecule, the rotational energy values and the frequency separation of successive lines in the rotational spectrum will be different. Let us designate the two isotopic forms of the same molecule by subscripts 1 and 2. Then the frequency of rotational lines, neglecting effect of centrifugal force, can be written as

$${}_1\nu_r = \frac{h}{4\pi^2 I_1 c} J \qquad \left(\because \quad \nu_r = 2BJ = 2 \cdot \frac{h}{8\pi^2 Ic} \cdot J\right)$$

$${}_2\nu_r = \frac{h}{4\pi^2 I_2 c} J.$$

Then the shift in frequency due to isotopic change will be

$$\begin{aligned}\Delta\nu_i &= {}_1\nu_r - {}_2\nu_r \\ &= \frac{h}{4\pi^2 c} J \left(\frac{1}{I_1} - \frac{1}{I_2}\right) \\ &= \frac{h}{4\pi^2 c I_1} J \left(1 - \frac{I_1}{I_2}\right) \\ &= \nu_r \left(1 - \frac{I_1}{I_2}\right), \qquad \ldots (1)\end{aligned}$$

where ${}_1\nu_r$ has been taken as ν_r. Since internuclear distances do not change, the ratio of the moments of inertia will be equal to the ratio of the reduced masses, *i.e.*,

$$\frac{I_1}{I_2} = \frac{m_1'}{m_2'} = \rho^2. \qquad \ldots (2)$$

where ρ^2 is to denote the constant value of the ratio.

Putting equation (2) in equation (1), we get

$$\Delta\nu_i = \nu_r(1 - \rho^2).$$

Within the limit of small error ν_r can be replaced by $2BJ$ and, therefore, it follows that

$$\Delta\nu_i = 2BJ(1 - \rho^2).$$

It is thus obvious that isotopic shift increases with the value of J. For most diatomic molecules, exhibiting pure rotation spectra, the isotopic masses are such that ρ^2 differs only slightly from unity due to which resulting isotopic shift is small. Shift of the lines in rotational spectrum accompanying an isotopic change has not been observed because of experimental difficulties. Such an isotopic effect in rotation is inferred from the study of electronic and vibration-rotation bands.

Problem 1. *In the rotational transition for* $J = 0$ *to* $J = 1$ *the absorption lines occur at* $1{\cdot}153 \times 10^{11}$ *c/s in* $C^{12}O^{16}$ *and at* $1{\cdot}102 \times 10^{11}$ *c/s in* C^nO^{16}. *Find the mass number n of the carbon isotope. Given*

$$\textit{Mass of } C^{12} = 12M_{\mathrm{H}}$$

$$\textit{Mass of } O^{16} = 16M_{\mathrm{H}}$$

Solution. Since force constant of the bond involved in CO molecule will not be affected by isotopic substitution, we can write

$$k = 4\pi^2\nu_1^2 m_2' = 4\pi^2\nu_2^2 m_2' \qquad \ldots (1)$$

where ν_1 = frequency of absorption line in case of $C^{12}O^{16}$

m_1' = reduced mass of $C^{12}O^{16}$

$$= \frac{12 \times 16}{12 + 16} = \frac{192}{28} \text{ a.m.u.}$$

$$\nu_2 = \text{frequency of absorption line in case of } C^nO^{16}$$

$$m_2' = \text{reduced mass of } C^nO^{16}$$

$$= \frac{16n}{n+16} \text{ a.m.u.}$$

Therefore from (1),

$$m_2' = \left(\frac{\nu_1}{\nu_2}\right)^2 m_1'$$

or

$$\frac{16n}{n+16} = \left(\frac{1{\cdot}153 \times 10^{11}}{1{\cdot}102 \times 10^{11}}\right) \times \frac{192}{28}$$

$$= 7{\cdot}1745$$

or

$$n = 13 \text{ a.m.u.}$$

Problem 2. *The $J = 1 \leftarrow 0$ transition in HCl occurs at 10.68 cm^{-1}. Regarding the molecule to be rigid rotator, calculate the wavelength of the transition $J = 15 \leftarrow 14$.*

Solution : The Frequency of rotational line is given by

$$\nu_r = BJ'(J'+1) - BJ''(J''+1)$$

Here $J' = 1, \quad J'' = 0$

so that $10.68 = 2B$

Now $\nu_r' = B[15(15+1) - 14(14+1)]$ for $J = 15 \leftarrow 14$ transition

$$= 2B \times 15$$

$$= 10.68 \times 15$$

$$\lambda' = \frac{1}{10.68 \times 15 \text{ cm}} = 64\mu.$$

2.5. ROTATION SPECTRA OF POLYATOMIC MOLECULES

To understand the analysis of the spectra of polyatomic molecules, the readers should be well acquainted with kinematics and dynamics of rigid bodies and also with symmetry elements. A brief description of the terms involved in further articles will be presented here for the convenience of the readers.

Principal Moment of Inertia

Out of $3N$ degrees of freedom of an assembly of N particles, three belong to the rotation of whole assembly about three mutually perpendicular axes. We shall take here that there is no interaction between rotation and vibration *i.e.* molecule is rigid.

We know that moments of inertia of assembly of N particles about any axis of rotation is given by

$$I = m_1 r_1^2 + m_2 r_2^2 + \ \ldots,$$

where m_i is the mass of the particle whose perpendicular distance from the axis is r_i.

We can show that there is one orientation of three mutually perpendicular axes for which corresponding moments of inertia are maxima or minima, and that the origin of these axes is the centre of mass*. The maximum and minimum values are called the principal moments of inertia and their axes are called principal axes. These three principal moments of inertia are conventionally denoted by I_a, I_b and I_c with $I_a \leq I_b \leq I_c$.

Angular Momentum, p, in terms of Principal Moments of Inertia

The general expression, for angular momentum, if the principal axes transformation is not considered, is given by

$$\begin{bmatrix} p_x \\ p_y \\ p_z \end{bmatrix} = \begin{bmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{bmatrix} \begin{bmatrix} \omega_x \\ \omega_y \\ \omega_z \end{bmatrix}$$

where p, ω and I refer to angular momentum, angular velocity, and moment of inertia of the assembly of N particles.

With principal axes transformation, nine components of I are reduced to three only, I_{xx}, I_{yy} and I_{zz}, designated as I_a, I_b and I_c. Let the corresponding angular velocities along the three principal axes be ω_a, ω_b and ω_c, then

$$\begin{bmatrix} p_a \\ p_b \\ p_c \end{bmatrix} = \begin{bmatrix} I_a & 0 & 0 \\ 0 & I_b & 0 \\ 0 & 0 & I_c \end{bmatrix} \begin{bmatrix} \omega_a \\ \omega_b \\ \omega_c \end{bmatrix}$$

or

$$p = I_a\omega_a + I_b\omega_b + I_c\omega_c$$

Kinetic Energy in terms of Principal Moments of Inertia

$$\begin{aligned} T &= \frac{1}{2}(\omega \bullet \mathbf{p}) \\ &= \frac{1}{2} \cdot (p_a\omega_a + p_b\omega_b + p_c\omega_c) \\ &= \frac{1}{2}(I_a\omega_a^2 + I_b\omega_b^2 + I_c\omega_c^2) \\ &= \frac{p_a^2}{2I_a} + \frac{p_b^2}{2I_b} + \frac{p_c^2}{2I_c}. \end{aligned}$$

Analysis of Spectra

In the discussion of rotational energies and rotational spectra of polyatomic molecules, we have to specify the relative values of the three principal moments of inertia of the molecule. On this basis, description will involve three structures, namely, linear, symmetric top and asymmetric top molecules. We can distinguish these cases as follows:

(*i*) *asymmetric tops*: three distinct moments of inertia

$$I_a \neq I_b \neq I_c$$

(*ii*) *symmetric tops:* two moments of inertia are equal

if $I_a = I_b < I_c$ called oblate symmetric top (disc)

if $I_a < I_b = I_c$ called prolate symmetric top (rugby football)

(*iii*) *spherical tops*: all moments of inertia are equal

$$I_a = I_b = I_c = I.$$

(*iv*) *linear and diatomic molecules*: two equal moments of inertia and one zero,

$$I_a = 0 \quad \text{and} \quad I_b = I_c.$$

(A) LINEAR AND DIATOMIC MOLECULES

Linear molecules, in their equilibrium configuration, have

$$I_a = 0$$
$$I_b = I_c = I$$

and this case then refers to art. 2.1 already dealt.

(B) SPHERICAL TOP MOLECULES

The moment of inertia of spherical top molecule is independent of the orientation of the rotational axis in the molecule

$$I_a = I_b = I_c = I$$

and thus there is again only one value of the moment of inertia in spherical top molecules and energy levels are, therefore, given by the equation (14), art. 2.1.

$$F(J) = BJ(J+1), \qquad J = 0,\ 1, 2 \ldots$$

Thus the energy level pattern is identical with that of a linear molecule. Since a spherical top molecule is, by symmetry, nonpolar, its rotation produces no change in moment and no dipole transitions occur. Rotational states can, however, be observed in combination with vibration.

(C) SYMMETRIC TOP MOLECULES

Two moments of inertia are equal in symmetric top molecules and are labelled as I_b. The other is not zero, differs from I_b. It is labelled as I_a. By symmetry considerations* one can show that any molecule with a threefold rotation axis must be a symmetric top and the I_a axis (the top axis) coincides with the symmetry axis. The I_b axes would lie in a plane perpendicular to the top axis. The examples are CH_3Cl and NH_3.

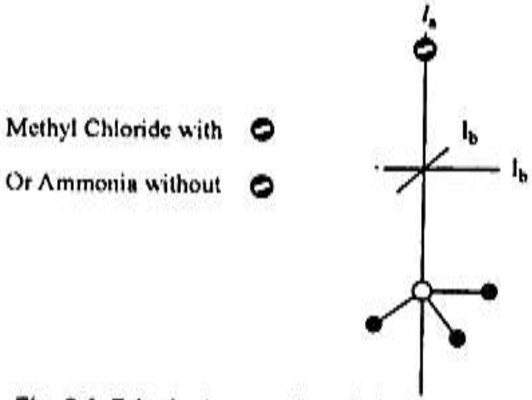

Fig. 2.4. Principal axes of methyl chloride or ammonia

Energy levels and Selection Rules

The rotational energy, in general, is written as

$$E_r = \frac{p_a^2}{2I_a} + \frac{p_b^2}{2I_b} + \frac{p_c^2}{2I_c}$$

(i) Prolate type: If we consider a prolate **symmetric top, $I_a = I_c$, then**

$$E_r = \frac{p_a^2}{2I_a} + \frac{p_b^2}{2I_b} + \frac{p_c^2}{2I_a}. \qquad \ldots (1)$$

As for linear molecules, it is assumed that the total angular momentum is quantised and, in terms of quantum number J, is given by

$$p = \sqrt{\{J(J+1)\}}\left(\frac{h}{2\pi}\right), \quad J = 0, \quad 1, 2, \qquad \ldots (2)$$

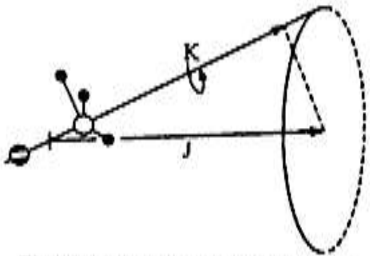

Fig. 2.5. Classical motion of a symmetric top, comprising roation about the top axis and precession of that axis about the total angular momentum.

The rotational energy in such type of molecules depends upon two quantum numbers J and K owing to the fact that here **J**, the classical total angular momentum vector, is not necessarily directed perpendicular to the top axis. The magnitude and direction of **J** is preserved, in classical motion, by the rotation of the molecule about I_a axis and a *precession* or *rotation* of that axis about the direction of **J** (Fig. 2.5). Therefore component K of angular momentum vector **J**, in the direction of top axis (I_a axis or called unique principal inertial axis) is also quantised.

This condition of equation is represented as

$$p_a = K\left(\frac{h}{2\pi}\right), \quad K = 0, \quad \pm 1, \quad \pm 2, \ldots \qquad \ldots (3)$$

Therefore, $$p^2 = p_a^2 + p_b^2 + p_c^2$$
or
$$p_b^2 + p_c^2 = p^2 - p_a^2$$
$$= J(J+1)\left(\frac{h}{2\pi}\right)^2 - K^2\left(\frac{h}{2\pi}\right)^2,$$
on applying eqs. (2) and (3).

Therefore equation (1) becomes
$$(E_r)_{Jk} = K^2\frac{h^2}{8\pi^2 I_a} + J(J+1)\frac{h^2}{8\pi^2 I_b} - K^2\frac{h^2}{8\pi^2 I_b}$$
$$= J(J+1)\frac{h^2}{8\pi^2 I_b} + \left(\frac{h^2}{8\pi^2 I_a} - \frac{h^2}{8\pi^2 I_b}\right)K^2 \text{ erg} \quad \ldots (3a)$$
or the term value is
$$F(JK) = \frac{(E_r)_{Jk}}{hc}$$
$$= \frac{h}{8\pi^2 I_b c}\cdot J(J+1) + \left(\frac{h}{8\pi^2 I_a c} - \frac{h}{8\pi^2 I_b c}\right)K^2 \text{ cm}^{-1}$$
$$= BJ(J+1) + (A-B)K^2 \text{ cm}^{-1} \quad \ldots (4)$$
in which
$$B = \frac{h}{8\pi^2 I_b c} \text{ cm}^{-1}$$
and
$$A = \frac{h}{8\pi^2 I_a c} \text{ cm}^{-1}.$$

The quantum numbers may take values
$$\left.\begin{array}{l} J = 0, 1, 2, \ldots \\ K = 0, \pm1, \pm2, \ldots \pm J, \end{array}\right\} \quad \ldots (5)$$
and thus all states with $K > 0$ are doubly degenerete.

The selection rules are:

Dipole transition : $\Delta J = 0, \pm1; \quad \Delta K = 0.$

For an absorption experiment, pertinent rule is
$$\Delta J = +1; \quad \Delta K = 0. \quad \ldots (6)$$

(ii) Oblate type: For this type of molecule $I_a = I_b < I_c$ and unique axis or top axis or figure axis will be I_c and not I_a.

For an oblate symmetric top, there is a constant angular momentum component equal to $\pm K\left(\frac{h}{2\pi}\right)$ along the top axis (I_c axis). Proceeding exactly in a similar way as adopted for prolate type with $I_a = I_b$, and I_c different, we can arrive at
$$F(J, K) = BJ(J+1) - (B-C)K^2 \text{ cm}^{-1} \quad \ldots (7)$$
where
$$C = \frac{h}{8\pi^2 I_c c} \text{ cm}^{-1}$$
and $(B - C)$ is positive since $I_b < I_c$.

Spectra: Symmetric top molecules with a centre of symmetry (C_2H_6, C_6H_6, BF_3) do not have a dipole moment, and therefore, no pure rotation spectrum is observed in their case. But most of the symmetric molecules have a dipole moment that is directed along top axis. Since their dipole moment lies in the direction of the top axis, no rotation of the molecule about that axis can change any component of dipole moment. Consequently, in such cases, selection rules for a symmetric top are
$$\Delta J = \pm1$$
$$\Delta K = 0$$

As these molecules give rise to pure rotation absorption spectrum, the frequencies of spectral lines will be given by

$$\begin{aligned}\nu &= F(J+1, K) - F(J, K)\\ &= B(J+1)(J+2) + (A-B)K^2 - [BJ(J+1) + (A-B)K^2]\\ &= 2B(J+1)\ \text{cm}^{-1} \qquad \ldots (8)\end{aligned}$$

and is thus independent of the rotational constant, A.

We can find out the term values, $F(J, K)$, in the case of prolate and oblate type of symmetric top molecules on substituting the values of rotation constants. For example, for

Prolate Type : CH_3F molecule: $A = 5{\cdot}10\ \text{cm}^{-1}$

$B = 0{\cdot}85\ \text{cm}^{-1}$

Oblate Type : NH_3 molecule: $B = 9{\cdot}94\ \text{cm}^{-1}$

$C = 6{\cdot}31\ \text{cm}^{-1}$

The rotational energy level patterns for both these types of symmetric molecules are shown in Fig. 2.6.

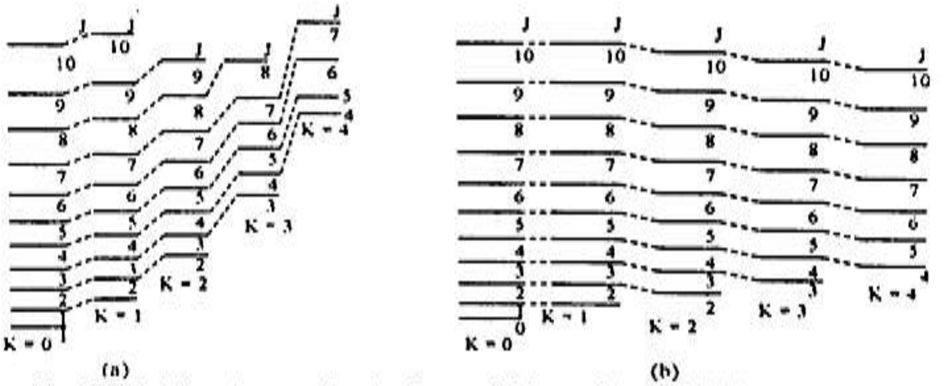

Fig. 2.6. Rotational energy level patterns : (a) for prolate, and (b) for oblate type.

Results Obtained from the Analysis of Spectra

The one value of B obtained from the spectrum (eq. 8) is insufficient for the determination of bond lengths and bond angles of a polyatomic molecule, since the molecule must have atleast two structural parameters in order to satisfy the condition of nonzero dipole moment. This value of B must, therefore, be combined with data from other sources, such as rotation-vibration spectra which can give a value of A or C.

(D) ASYMMETRIC MOLECULES

A molecule with three different moments of inertia is called asymmetric top molecule.

The rotational energy expression

$$E_r = \frac{p_a^2}{2I_a} + \frac{p_b^2}{2I_b} + \frac{p_c^2}{2I_c} \qquad \ldots (9)$$

can still be applied; but since, unlike the symmetric top case, no component of total angular momentum vector **J** is quantised, no quantum number other than **J** is available to characterise the rotational energy states. It is, therefore, impossible to give one simple expression for all the energy levels. The problem is treated in quantum mechanics by using the symmetric top wave-functions of either the limiting prolate top, with B and C replaced by $\frac{1}{2}(B+C)$, or the limiting oblate top, with A and B replaced by $\frac{1}{2}(A+B)$. Equation (9) then leads to a polynomial equation of $(2J+1)^{\text{th}}$ degree involving the rotational constants A, B and C for each J value. For first few levels, exact expressions for energy levels can then be given.

END OF PART II

Book: Elements of Spectroscopy – By: S L Gupta, V Kumar, R C Sharma, Pragati Prakashan; Meerut

QUESTION BANK 2020-21

Part: I: Multiple Choice Questions:

1. A transition between two Vibrational levels results in a radiation that falls in the_____________
   (a) Visible region. (b) Micro wave region.
   (c) Near infra red region. (d) Ultra violet region.
2. In practice, rotational spectra are observed in _____________
   (a) Absorption. (b) Adsorption
   (c) emission (d) All of above
3. When two atoms are brought nearer to form a stable molecule, the electronic energy _____________rapidly.
   (a) increases (b) decreases
   (c) remain same (d) none of above
4. A transition between two electronic levels results in a radiation that falls in the ___________.
   (a) Visible or infra red region (b) Visible or near infra red region
   (c) Visible or ultra violet region (d) Visible or microwave region
5. A transition between two rotational levels results in a radiation that falls in the ___________.
   (a) Visible or infra red region (b) ultraviolet or near infra red region
   (c) far infrared or ultra violet region (d) far infrared or microwave region
6. The homonuclear diatomic molecules do not exhibits_____________.
   (a) pure rotational spectra (b) pure vibration spectra
   (c) pure electronic spectra (d) rotational and vibration spectra
7. The hetronuclear diatomic molecules do exhibits _____________.
   (a) pure rotational spectra (b) pure vibration spectra
   (c) pure electronic spectra (d) rotational and vibration spectra
8. The reduced mass is given by, _______________.
   (a) m’= $\frac{m_1}{(m_1+m_2)}$ (b) m’= $\frac{m_2}{(m_1+m_2)}$
   (c) m’= $\frac{m_1 m_2}{(m_1+m_2)}$ (d) m’= $\frac{(m_1+m_2)}{m_1 m_2}$
9. The molecular spectra are also known as ________________.
   (a) line spectra (b) band spectra
   (c) absorption spectra (d) emission spectra
10. A band has sharp intense edge on one side called _____________.
    (a) band cap (b) band head
    (c) band border (d) band zone
11. The separation of the nuclear and electronic motion is embodies in the _________approximation.
    (a) Bohr (b) Ruther ford
    (c) Born OppenHeimer (d) None of above
12. The compete Hamiltonian operator is given by____________________

(a) $\frac{h}{8\pi^2 m}\nabla^2+V$ (b) $-\frac{h^2}{8\pi^2 m}\nabla^2+V+V$
(c) $\frac{h}{8\pi^2 Im}\nabla^2+V$ (d) $\frac{h}{8\pi^2 m}\nabla^2 - V$

13. Homo nuclear diatomic molecules do not exhibits ________________spectra.
(a) pure Vibrational (b) pure rotational
(c) visible (d) None of above

Part: II: Short Questions

1. Explain in brief salient features of rotational spectra.
2. Define rigid rotator.
3. Enlist various regions of the electromagnetic spectrum.
4. Write difference between rigid and non rigid rotator.
5. Explain principle of moment of inertia of assembly of N particles.

Part: III: Long Questions

1. Write theory to explain rotational spectra using rigid rotator model of molecule.
2. Discuss isotope effect in rotational spectra in detail.
3. Discuss diatomic molecule as a non rigid rotator.
4. Write a detail note on rotation spectra of poly atomic molecules.

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