V P & R P T P SCIENCE COLLEGE-VALLBH VIDYANAGAR

Course code: US06CPHY22 Unit 3

ATOMIC AND MOLECULAR SPECTROSCOPY

INFRARED SPECTROSCOPY:

SALIENT FÉATURES OF VIBRATIONAIL-ROTATIONAL SPECTRA

(1) When there are transitions between vibrational states of the same electronic state of molecule, we get vibrational-rotational molecular spectra. Such a spectra is observed in near infra-red region (1 -100 u) of electromagnetic spectrum.

(ii) Vibrational-rotational spectra, like pure rotational spectra, are observed only for molecules that have permanent dipole moment such as HCl, HCN, HF-the hetero nuclear diatomic molecules.

(i) The internuclear distance changes when the nuclei of these molecules vibrate relative to each other. Thus these molecules possess an oscillating dipole moment, which according to classical Fundamental electrodynamics, emits radiations of frequency that fall in near band infra-red region. Conversely, if an electromagnetic radiation falls on such a molecule then oscillating dipole interacts with the Overtones incident radiation and can absorb radiation of frequency of near infra-red region.

(iv) In practice, vibration al-rotational spectra are observed in absorption.

HCl MOLECULE :

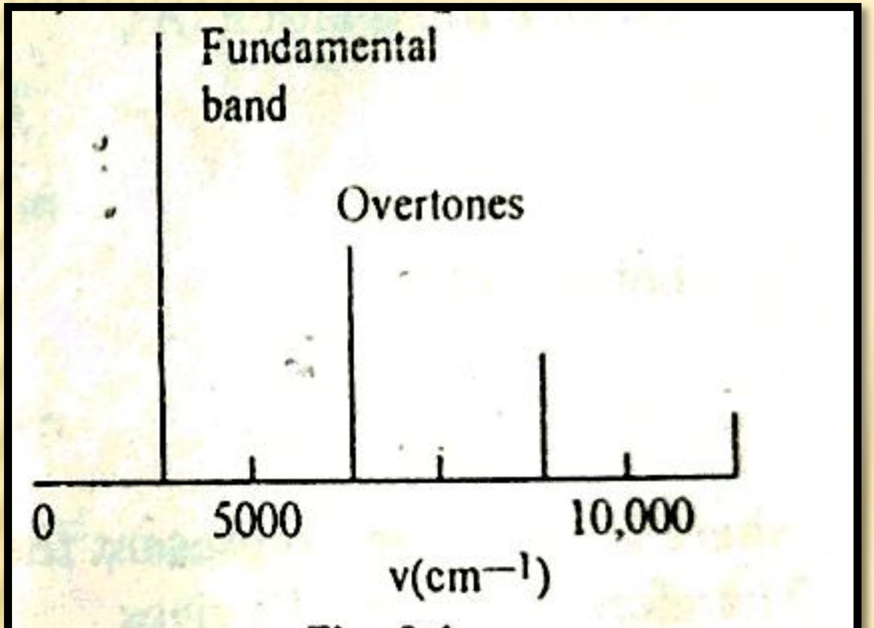


Fig. 3.1.

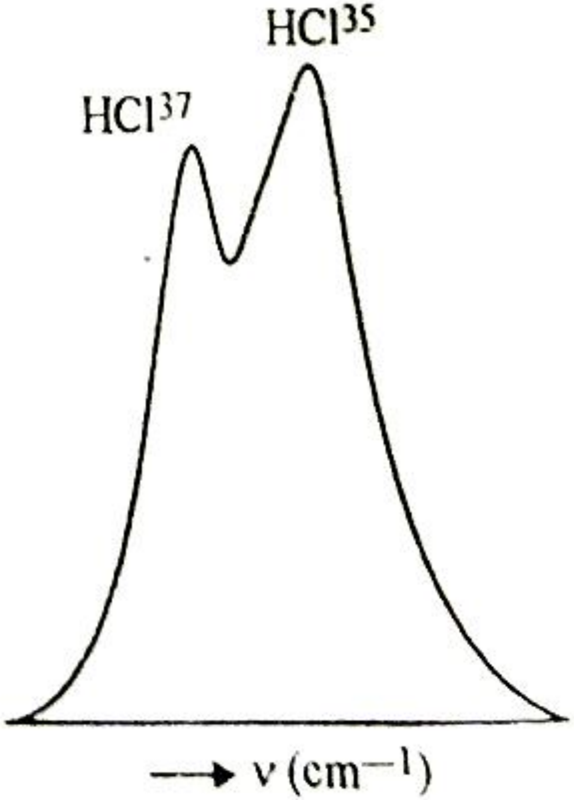


Fig. 3.2.

Infra red spectroscopy:

For HCl Molecule:

(a) Spectrum for a molecule has intense band (called fundamental band,

(b) Spectrum consists weak bands (overtones) that appear at wave numbers approximately double, triple, .. . of the fundamental band.

(c) On close examination, the fundamental band is found to consist of two close maxima which is an isotope effect.

(d) (i) Under high resolution, it is found that each band consists of a series of lines that are not equidistant.

ii) A line is found missing in the centre of the band and is called null line or zero gap.

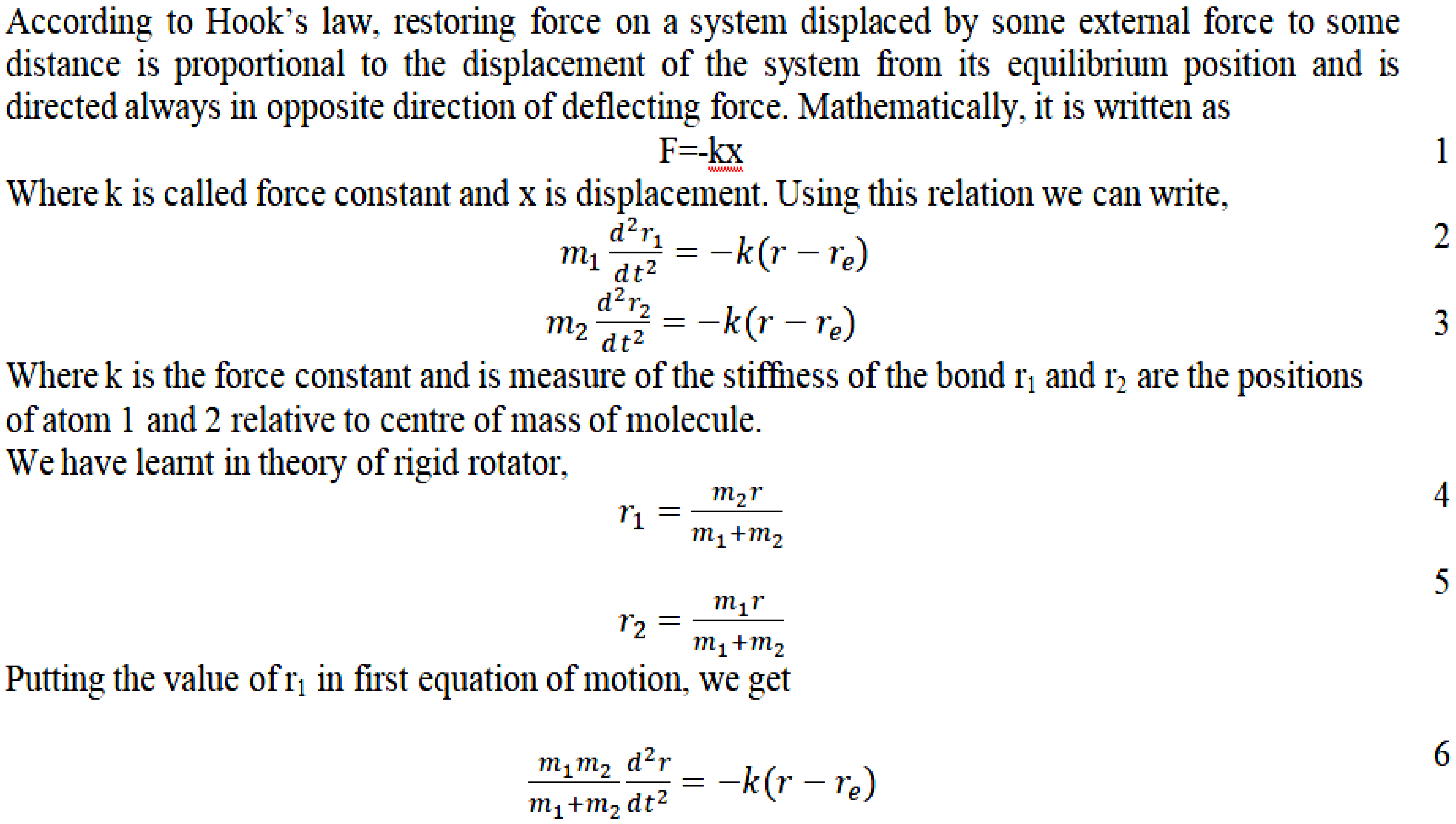
(i11) Lines seem to converge towards high wave number side and the

band is said to be degraded towards the low wave number side i.e., v (cm-) towards the red.

Infra red spectroscopy:

VIBRATING DIATOMIC MOLECULE AS A HARMONIC OSCILLATOR

Frequency of Vibration: A vibrating diatomic molecule can be approximated to a linear harmonic oscillator, whose frequency of vibration can be calculated on the classical lines using Newton's equation of motion. Suppose the bond distorted from its equilibrium length r, to a new O length r; then restoring forces on each atom of a diatomic molecule are



According to Hook's law, restoring force on a system displaced by some external force to some distance is proportional to the displacement of the system from its equilibrium position and is directed always in opposite direction of deflecting force. Mathematically, it is written as

$$F=-kx \tag{1}$$

Where k is called force constant and x is displacement. Using this relation we can write,

$$m_1 \frac{d^2 r_1}{dt^2} = -k(r - r_e) \tag{2}$$

$$m_2 \frac{d^2 r_2}{dt^2} = -k(r - r_e) \tag{3}$$

Where k is the force constant and is measure of the stiffness of the bond r_1 and r_2 are the positions of atom 1 and 2 relative to centre of mass of molecule.

We have learnt in theory of rigid rotator,

$$r_1 = \frac{m_2 r}{m_1 + m_2} \tag{4}$$

$$r_2 = \frac{m_1 r}{m_1 + m_2} \tag{5}$$

Putting the value of r_1 in first equation of motion, we get

$$\frac{m_1 m_2}{m_1 + m_2} \frac{d^2 r}{dt^2} = -k(r - r_e) \tag{6}$$

Infra red spectroscopy:

Since, r_e is constant its differentiation with respect to t will be zero. So we can write

$$\frac{d^2r}{dt^2} = -k(r-r_e) \tag{7}$$

Substituting this value in equation 6,

$$\frac{m_1m_2}{m_1+m_2}\frac{d^2(r-r_e)}{dt^2} = -k(r-r_e) \tag{8}$$

Let us put

$$r\text{-}r_e = x \quad \text{and} \quad \frac{m_1m_2}{m_1+m_2} = m'$$

Where x is the displacement of the bond length from equilibrium position

Thus equation 8 gives,

$$m'\frac{d^2x}{dt^2} = -kx \qquad \text{OR}$$

$$\frac{d^2x}{dt^2} + \frac{k}{m'}x = 0 \qquad \text{OR}$$

$$\frac{d^2x}{dt^2} + \omega^2 x = 0 \tag{9}$$

This is the equation of simple harmonic motion with frequency of vibration, expressed in cm^{-1}

$$= \frac{1}{c}\sqrt{\left(\frac{k}{m'}\right)} = \frac{1}{2\pi c}\sqrt{\left(\frac{k}{m'}\right)}\ \text{cm}^{-1} \tag{10}$$

Energy levels

Vibrational energies, like other molecular energies are quantised and the permitted vibrational energies for any particular system can be calculated from Schrödinger equation. The eigen values for the energy of a linear harmonic oscillator are of the type

$$\boxed{E_v = \left(v + \frac{1}{2}\right) hc\omega} \qquad \ldots (1)$$

where v is the *vibrational quantum number*, equal to zero or an integer, and ω is the vibrational frequency of the oscillator expressed in wave numbers. We shall now derive it using Schrödinger wave equation.

A vibrating diatomic molecule is approximated as a harmonic oscillator. The potential energy function under the influence of which nuclei vibrate is then parabolic and is of the form given by

$$V(r) = \tfrac{1}{2} k(r - r_e)^2 = \tfrac{1}{2} kx^2$$

where x is the displacement from the mean position or equilibrium position. Then Schröedinger wave equation can be written as

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m'}{h^2} (E_v - \tfrac{1}{2} kx^2)\psi = 0$$

where m' is the reduced mass of the diatomic molecule. If we put

$$\alpha = \frac{8\pi^2 m' E_v}{h^2} \quad \text{and} \quad \beta = \sqrt{\left(\frac{4\pi^2 m' k}{h^2}\right)} = 2\pi \sqrt{\left(\frac{m'k}{h^2}\right)}$$

then

$$\frac{d^2\psi}{dx^2} + (\alpha - \beta^2 x^2)\psi = 0.$$

Further we introduce a dimensionless independent variable

$$\xi = \sqrt{(\beta)} \cdot x \quad \text{so that} \quad \frac{d^2}{dx^2} = \beta \frac{d^2}{d\xi^2}$$

in the above equation. Thus

$$\beta \frac{d^2\psi}{d\xi^2} + \left(\alpha - \beta^2 \frac{\xi^2}{\beta}\right)\psi = 0$$

or

$$\frac{d^2\psi}{d\xi^2} + \left(\frac{\alpha}{\beta} - \xi^2\right)\psi = 0$$

If we try a solution of this equation in the form

$$\psi(\xi) = CU(\xi)\, e^{-\xi^2/2}$$

then equation, on putting for the ψ and $d^2\psi/d\xi^2$, becomes

$$\frac{d^2U}{d\xi^2} - 2\xi \frac{dU}{d\xi} + \left(\frac{\alpha}{\beta} - 1\right)U = 0$$

which will become Hermite differential equation provided we put

$$\left(\frac{\alpha}{\beta} - 1\right) = 2\upsilon \quad \text{or} \quad \frac{\alpha}{\beta} = 2\upsilon + 1$$

so that we can replace $U(\xi)$ by Hermite polynomial $H_\upsilon(\xi)$. Thus

$$\frac{d^2H_\upsilon(\xi)}{d\xi^2} - 2\xi \frac{dH_\upsilon(\xi)}{d\xi} + 2\upsilon\, H_\upsilon(\xi) = 0$$

Therefore solution of Schrödigner equation becomes

$$\psi = CH_{\upsilon}(\xi)\, e^{-\xi^2/2}$$

and is valid only for $\upsilon = 0, 1, 2, \ldots$. The restriction on υ also restricts energy values E.

Finally, writing

$$\frac{\alpha}{\beta} = 2\upsilon + 1$$

or

$$\frac{8\pi^2 m' E_{\upsilon}/h^2}{2\pi\sqrt{(m'k/h^2)}} = 2\upsilon + 1 = 2\left(\upsilon + \frac{1}{2}\right)$$

or

$$E_{\upsilon} = \frac{h}{2\pi}\sqrt{\left(\frac{k}{m'}\right)}\left(\upsilon + \frac{1}{2}\right)$$

$$= h\nu\left(\upsilon + \frac{1}{2}\right)$$

$$= hc\omega\left(\upsilon + \frac{1}{2}\right)$$

where ω is the vibrational frequency of the vibrating diatomic molecule *expressed in wavenumber.* The above equation gives the allowed energies for the harmonic oscillator. Significance of above equation lies in predicting the existence of zero point energy, equal to $\frac{1}{2}\, hc\omega$ ($\upsilon = 0$).

If we transform energy value to *term value* (on dividing by hc), we obtain for vibrational terms

$$G(v) = \frac{E_v}{hc} = \omega(v + \tfrac{1}{2}) \qquad \boxed{\qquad \ldots (2)}$$

Putting $v = 0, 1, 2, \ldots$ we get

$$G(v) = \frac{\omega}{2}, \frac{3}{2}\omega, \frac{5}{2}\omega, \frac{7}{2}\omega, \ldots$$

Thus we have a series of equispaced discrete vibrational levels (Fig. 3.3), the common separation being ω cm^{-1}. The spacing between vibrational levels is considerably larger than the spacing between rotational levels of a molecule.

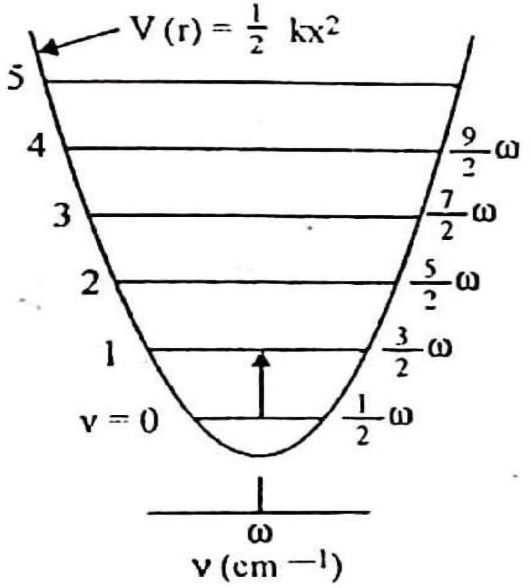


Fig. 3.3. Equispaced discrete vibrational levels.

Spectrum: Suppose a transition occurs from an upper vibrational level, in which the quantum number is v', to a lower state, with quantum number v''. The change in vibrational energy will be

$$E'_v - E''_v = (v' - v'')hc\omega.$$

The frequency ν_v of the radiation, in wave numbers, accompanying the vibrational transition, would be

$$\begin{aligned} \nu_v &= \frac{E'_v - E''_v}{hc} = (v' - v'')\omega \\ &= G(v') - G(v''). \end{aligned} \qquad \ldots (3)$$

Suppose a transition occurs between $v' = 1$ and $v'' = 0$; then

$$\begin{aligned} (\Delta E)_{1,0} &= E'_1 - E''_0 \\ &= hc\omega. \end{aligned}$$

The frequency of this transition will be

$$(\nu_v)_{1,0} = \frac{(\Delta E)_{1,0}}{hc} = \omega \text{ cm}^{-1}$$

$$= \frac{1}{2\pi c}\sqrt{\left(\frac{k}{m'}\right)}\,\mathrm{cm}^{-1}$$

Therefore we can write

$$(\Delta E)_{1,0} = hc(\nu_0)_{1,0}.$$

Thus vibrational spectrum is expected to consist of a single band at ω cm^{-1}. Thus an intense band in infrared spectrum is to be concluded as vibrational spectrum, owing its origin to harmonic vibrations of the nuclei along internuclear axis. However, infra-red spectrum also consists some weak bands (called overtones) at frequencies slightly lesser than 2ω, 3ω, . . . etc. Their appearance suggests that vibrations deviate from being harmonic and analysis should be made by treating the vibrating diatomic molecule as anharmonic oscillator

The vibrational spectra are known only in absorption. Electromagnetic radiations can induce transitions among the vibrational energy levels. *For the transference of energy between the radiation and the vibrating molecule, an electrical coupling must be present.* If the vibrating molecule produces an oscillating dipole moment, then the desired coupling results due to the interaction of this dipole moment with electric field of radiation. *Consequently, homonuclear diatomic molecules like* H_2, N_2 *and* O_2 *that possess a zero dipole moment for any bond length will not interact with the radiation.* On the other hand, molecules like HF, HCl, HBr, HCN have a dipole moment, which is some function of internuclear distance, (and consequently gives rise to an oscillating dipole moment) will exhibit vibrational spectra.

Let us take a specific case, say of HCl molecule. For HCl molecule, the frequency of spectral line arising due to transition between $\upsilon = 0$ and $\upsilon = 1$ states is

$$(\nu)_{1,0} = 2{,}890 \text{ cm}^{-1}$$

so that

$$(\Delta E)_{1,0} = hc\nu_{10}$$

$$= 6{\cdot}62 \times 10^{-27} \times 3 \times 10^{10} \times 2890$$

$$= 5{\cdot}75 \times 10^{-13} \text{ erg.}$$

representing the energy of a molecule in $\upsilon = 1$ state compared with one in $\upsilon = 0$ state. The Boltzmann distribution at 25°C gives the ratio of population of these two states as:

$$\frac{N_1}{N_0} = e^{-\Delta E/kT}$$

$$= 8 \times 10^{-7},$$

which shows that population N_0 in $\upsilon = 0$ state, the lowest state, is much greater than the population N_1 in $\upsilon = 1$ state, or in other words, only a very small fraction of the molecules populate the higher vibrational levels at ordinary temperature. This means that most of the molecules are in the lowest allowed vibrational state. In a spectroscopic study, therefore, one investigates the absorption of radiation by these $\upsilon = 0$ states' molecules.

Thus main vibrational transition in absorption is $\upsilon = 1 \leftarrow \upsilon = 0$.

Transition Rule

For the probability of any given transition, it is essential to assume that the diatomic molecule has a permanent dipole moment. For a linear harmonic oscillator the eigen functions are of the form

$$\psi_n = N_n e^{-q^2/2} H_n(q),$$

where $q = x\sqrt{b}$ (in which x is the displacement of the particle from the equilibrium position and

$b = \frac{4\pi^2 \nu m}{h}$, where ν is the frequency of oscillation of the particle of mass m), N_n is a normalising factor and $H_n(q)$ represents a Hermite polynomial of degree n defined by

$$H_n(q) = (-1)^n e^{q^2} \frac{d^n e^{-q^2}}{dq^n}.$$

By inserting the appropriate eigen function in the equation

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

we find that the result differs from zero only if the change in the vibrational quantum number in the two states, between which transition is to occur, is equal to unity. Therefore for a harmonic oscillator, selection rule is

$$\Delta \upsilon = \pm 1.$$

Putting this condition in equation (3), we get

$$\nu_\upsilon = \omega,$$

predicting that for a harmonic oscillator the frequency ν_υ of the radiation emitted or absorbed should be equal to the mechanical frequency, ω, of vibration of the system. *Thus we find that, like classical theory, quantum theoretically the frequency of radiated light is equal to the frequency* ν_{osc} (= ω) *of the oscillator, no matter what the* υ *value of the initial state is.* In Fig. 3.4 the allowed transitions are indicated by vertical lines. It is obvious from the figure that they all give rise to the same frequency.

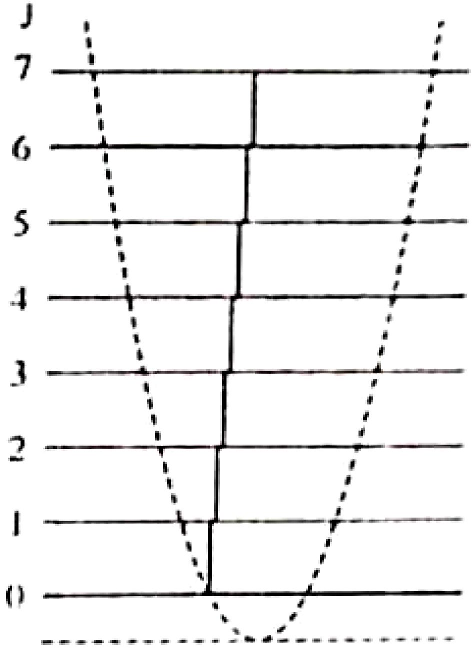


Fig. 3.4. Potential energy curve, Energy Levels and Infrared transition of the Harmonic Oscillator.

3.2. VIBRATING DIATOMIC MOLECULE AS ANHARMONIC OSCILLATOR

For a strictly harmonic oscillator, change in vibrational quantum number is restricted to unity ($\Delta \upsilon = \pm 1$) and hence each mode of vibration would yield one band only. But actual investigation of the vibration rotation spectrum (since we are speaking here about band, it is necessary to mention change in rotational energy and hence the name vibration-rotation spectrum) shows that there is one strong band with one or two other bands called *overtones* or *harmonics*. Appearance of these latter bands corresponds to the frequencies which are possible if the change in vibrational quantum number is 2, 3 etc.

Thus we infer that

(*i*) Overtones occur because selection rule $\Delta \upsilon = \pm 1$ is not strictly obeyed but transitions corresponding to $\Delta \upsilon > 1$ do take place. It means dipole moment of the molecule is *not* strictly linear with respect to the internuclear displacement, $x = (r - r_e)$ and so points to anharmonicity of the molecule.

(*ii*) Further overtones (weak bands) appear not exactly at 2ω, 3ω but at lesser and lesser values. It indicates that vibrational energy levels are not exactly equally spaced but converge slowly. This is attributed to the fact that for an actual molecule, the potential energy curve is not strictly parabolic (except near the minimum). It means potential energy function is not merely quadratic but we have to include a cubic term at least, *i.e.*,

$$V(r) = \frac{1}{2!} \frac{\partial^2 V(r)}{\partial r^2}\bigg|_{r = r_e} (r - r_e)^2 + \frac{1}{3!} \frac{\partial^3 V(r)}{\partial r^3}\bigg|_{r = r_e} (r - r_e)^3 + \dots$$

$$= f(r - r_e)^2 - g(r - r_e)^3$$

$$= fx^2 - gx^3$$

where $g \ll f$. On putting this value of $V(r)$ in the Schrödinger equation and solving by perturbation method, we arrive at the energy values given by the forthcoming eq. (2).

Thus real molecules do not obey exactly the laws of simple harmonic motion; real bonds, although elastic, are not homogeneous as to obey Hooke's law. Fig. 3.5 shows the energy curve for a typical diatomic molecule undergoing anharmonic extensions and compressions together with (dotted) the ideal simple harmonic parabola.

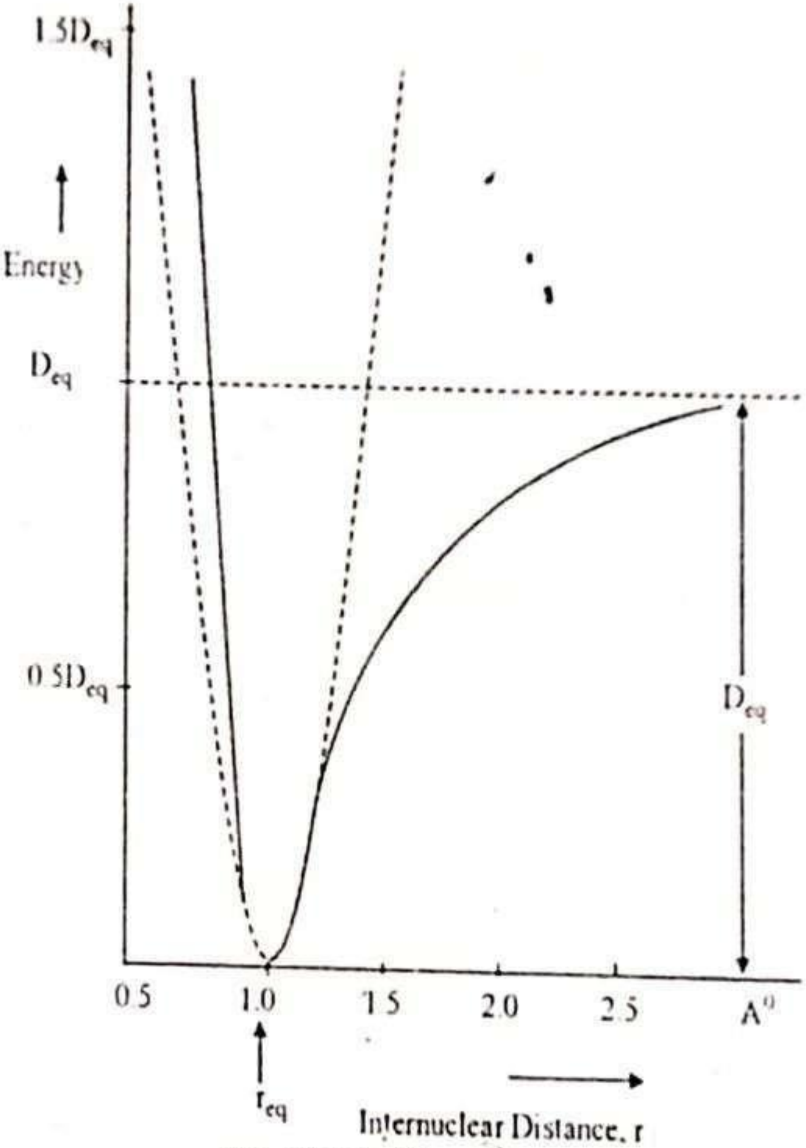


Fig. 3.5. The Morse Curve

To explain this curve, P.M. Morse gave a purely empirical expression called Morse function as:

$$E = D_{eq}[1 - \exp\{a(r_{eq} - r)\}]^2 \quad \ldots (1)$$

where D_{eq} is the dissociation energy, a is constant for a particular molecule, r_{eq} is the value of internuclear distance r that corresponds to the minimum of Morse curve (potential energy curve).

Energy Levels :

(Eigen values for the energy)

When equation (1) is substituted in the Schrödinger equation eigen values for the energy, *i.e.*, allowed vibrational energy levels are found to be

$$E_v = (v + \tfrac{1}{2})hc\omega_e - (v + \tfrac{1}{2})^2 hcx\omega_e + (v + \tfrac{1}{2})^3 hcy\omega_e + \ldots, \qquad \ldots(2)$$

where x, y, etc are the anharmonicity constants; ω_e is called the equilibrium frequency of the molecule expressed in wave numbers and is the value for small displacements. In *term values*, we obtain for vibrational terms

$$G(v) = (v + \tfrac{1}{2})\omega_e - (v + \tfrac{1}{2})^2 x\omega_e + (v + \tfrac{1}{2})^3 y\omega_e + \ldots \qquad \ldots(3)$$

The quantity ω_e is the spacing (in cm^{-1}*) of energy levels that would occur if the potential energy curve were a parabola, $\omega_e x$ is the 'anharmonicity constant' which is much smaller than ω_e and is always positive. Eq.* (3) *shows that the energy levels of an arharmonic oscillator are not equidistant, but their separation decreases slowly with increasing v. (See Fig.* 3.6.*)*

When the molecule receives energy more than that corresponding to the uppermost vibrational level, it dissociates into atoms and the excess energy appears as unquantised kinetic energy of these atoms. Hence a continuum joins the uppermost level. (See Fig. 3.6).

Transition Rules :

The use of eigen value equation (2) alters the corresponding eigenfunctions and the alteration in eigenfunction when applied to the function

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

leads to the result that the matrix component, which determines the probability of transition, is no longer zero for all transitions other than those for which the change in vibrational quantum number is unity. The selection rules for the anharmonic oscillator are found to be

$$\Delta\upsilon = \pm 1, \pm 2, \pm 3, \ldots \qquad \ldots (4)$$

The transitions from,

$\upsilon = 1$ to $\upsilon = 0$ gives Fundamental Band,
$\upsilon = 2$ to $\upsilon = 0$ gives First overtone (second harmonic),
$\upsilon = 3$ to $\upsilon = 0$ gives Second Overtone (third harmonic), etc.

Spectrum: Frequency of Vibration :

Now suppose a transition occurs from the upper state υ' to the lower state υ''; then the energy change will be

$$E_\upsilon' - E_\upsilon'' = (\upsilon' - \upsilon'')hc\omega_e - \{\upsilon'(\upsilon' + 1) - \upsilon''(\upsilon'' + 1)\}hcx\omega_e$$

or the corresponding frequency of radiation resulting from the transition will be

$$\nu_\upsilon = \frac{E_\upsilon' - E_\upsilon''}{hc} = G(\upsilon') - G(\upsilon'')$$

$$= (\upsilon' - \upsilon'')\omega_e - \{\upsilon'(\upsilon' + 1) - \upsilon''(\upsilon'' + 1)\}x\omega_e \qquad \ldots (5)$$

The vibrational quantum number in the final state is always zero, it follows that

$$\upsilon_\upsilon \rightarrow 0 = \upsilon\omega_e - \{\upsilon(\upsilon + 1)\}x\omega_e$$

$$= \{1 - (\upsilon + 1)x\}\upsilon\omega_e, \qquad \ldots (6)$$

where υ is the vibrational quantum number in the initial state.

Thus

$$\left.\begin{array}{lll} \text{for fundamental band} & : & \upsilon = 1 \text{ to } \upsilon = 0, \\ & & \nu_1 = (1 - 2x)\omega_e \quad \ldots(a) \\ \text{for first overtone band} & : & \upsilon = 2 \text{ to } \upsilon = 0, \\ & & \nu_2 = (1 - 3x)2\omega_e \quad \ldots(b) \\ \text{for second overtone band} & : & \upsilon = 3 \text{ to } \upsilon = 0, \\ & & \nu_3 = (1 - 4x)3\omega_e, \quad \ldots(c) \end{array}\right\} \qquad \ldots(7)$$

where ν_1, ν_2 and ν_3 are frequencies of the origins (or centres) of the *fundamental*, *first* and *second overtone bands* respectively. Since the frequencies of first and second overtone bands are approximately 2 to 3 times the frequency of the fundamental band, they appear in regions of the shorter wavelengths than do the fundamental. The intensity of bands falls off with increasing value of $\Delta\upsilon$ due to which it is difficult to detect the overtone band beyond the third. Overtone bands are sufficiently weak in intensity but even then they can be studied experimentally due to their appearance in shorter wavelength region.

Vibration bands are almost invariably observed in absorption. The equation (7) would also represent the frequency for absorption fundamental and overtone bands with the difference that now transition will occur from $\upsilon = 0$ to $\upsilon = 1$, $\upsilon = 0$ to $\upsilon = 2$ and $\upsilon = 0$ to $\upsilon = 3$, *i.e.*, they are reversed. The three absorption transitions are shown in Fig. 3.6. *At room temperature nearly all the molecules in a particular sample have only the zero point vibrational energy and exist in $\upsilon = 0$ state. The absorption of radiation must, therefore, result in transitions starting from $\upsilon = 0$.*

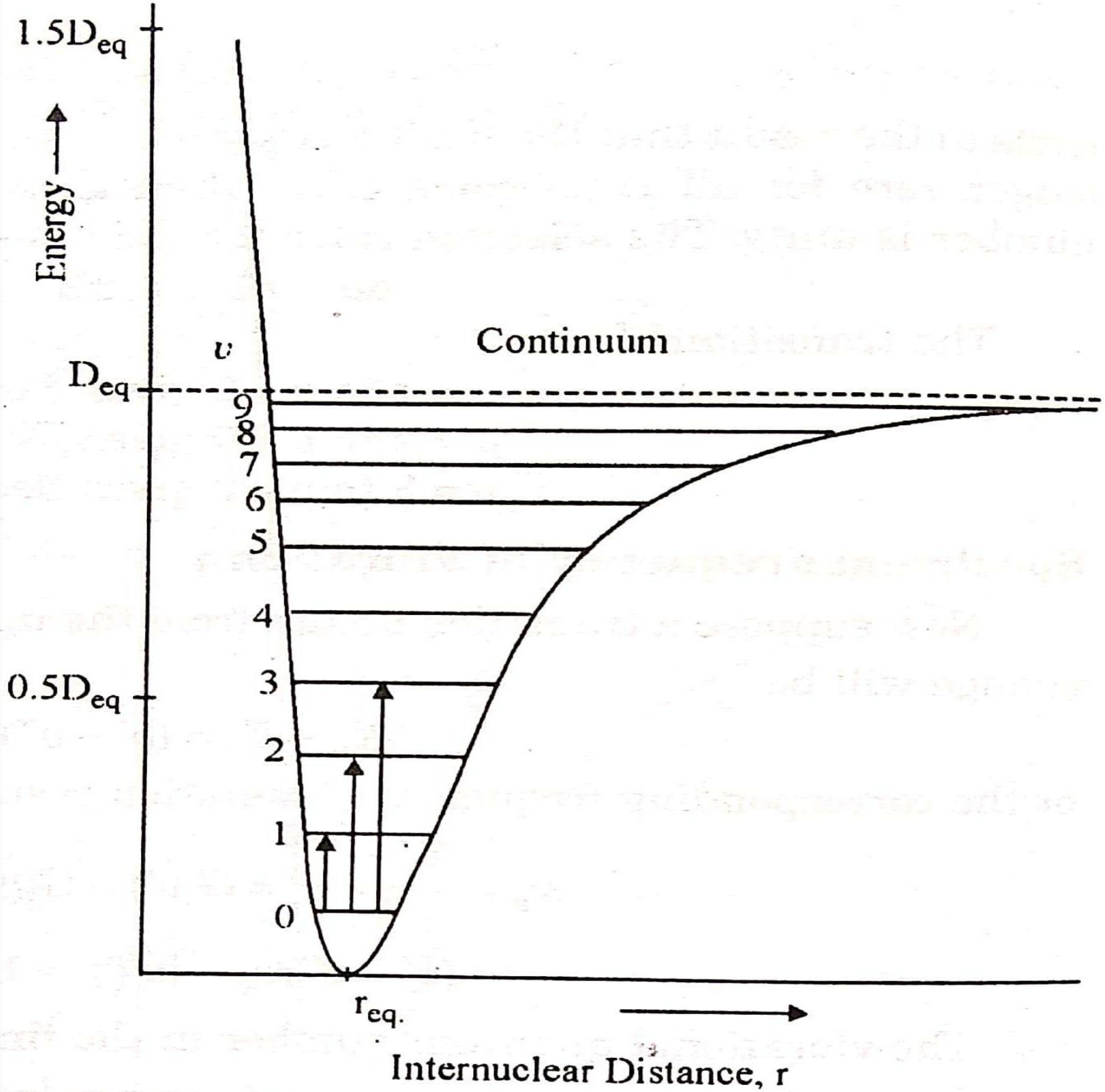


Fig. 3.6. The allowed vibrational energy levels and some transitions between them for a diatomic molecule undergoing anharmonic oscillations.

PART - 2

3.3. MOLECULE AS A VIBRATING ROTATOR: FINE STRUCTURE OF INFRA-RED BANDS: IGNORING INTERACTION OF VIBRATIONAL AND ROTATIONAL ENERGIES

So far we have considered rotation and vibration quite separately. Observed fine structure of the rotation bands gives ample evidence that a simultaneous rotation and vibration do occur.

(A) Diatomic molecule as rigid rotator and harmonic oscillator :

The near infra-red spectra of molecules consist of bands (not lines), each band being composed of close lines arranged in a particular manner. This observed fine structure suggests that in a vibrational transition the molecule also changes its rotational energy state, that is, it must be treated as a vibrating rotator. As a first approximation, we consider that a diatomic molecule can execute rotations and vibrations quite *independently*, *i.e.*, there is no interaction between rotational and vibrational energies. We can then take the combined rotational vibrational energy to be simply the sum of the separate energies, *i.e.*

$$E_{\text{total}} = E_{\text{rot}} + E_{\text{vib}} \text{ (ergs)}. \qquad \ldots (1)$$

If we first assume that diatomic molecule to be behaving as a linear harmonic oscillator and a rigid rotator, the combined energy will be

$$E_{vr} = \{G(v) + F(J)\}\, ch$$

$$E_{vr} = (v + \tfrac{1}{2})hc\omega + \frac{h^2}{8\pi^2 I} J(J+1) \quad \text{(Eq. 2 art. 3.1 and Eq. 14 art. 2.1]}$$

Suppose a simultaneous transition from the vibrational level v' to the level v'' and from the rotational level J' to the level J'' occurs. Then change in energy, on using above equation, ①

$$E'_{vr} - E''_{vr} = (v' - v'')hc\omega + \frac{h^2}{8\pi^2 I}[J'(J' + 1) - J''(J'' + 1)]$$

and the corresponding frequency of radiation arising due to this transition will be

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

$$= (v' - v'')\omega + B[J'(J' + 1) - J''(J'' + 1)] \qquad \ldots(2)$$

where $$B = \frac{h}{8\pi^2 Ic} = \frac{h}{8\pi^2 m' r^2 c}$$

(B) Diatomic molecule as a non-rigid rotator and anharmonic oscillator :

If we consider the diatomic molecule as the non-rigid rotator and anharmonic oscillator, then the combined energy will be [using equation (2) of art. 3.2 and equation (2) of art. 2.2],

$$E_{rv} = G(v) + F(J)$$

$$= hc[BJ(J + 1) - DJ^2(J + 1)^2 + HJ^3(J + 1)^3 + \ldots + (v + \tfrac{1}{2})\omega_e - x(v + \tfrac{1}{2})^2\omega_e].$$

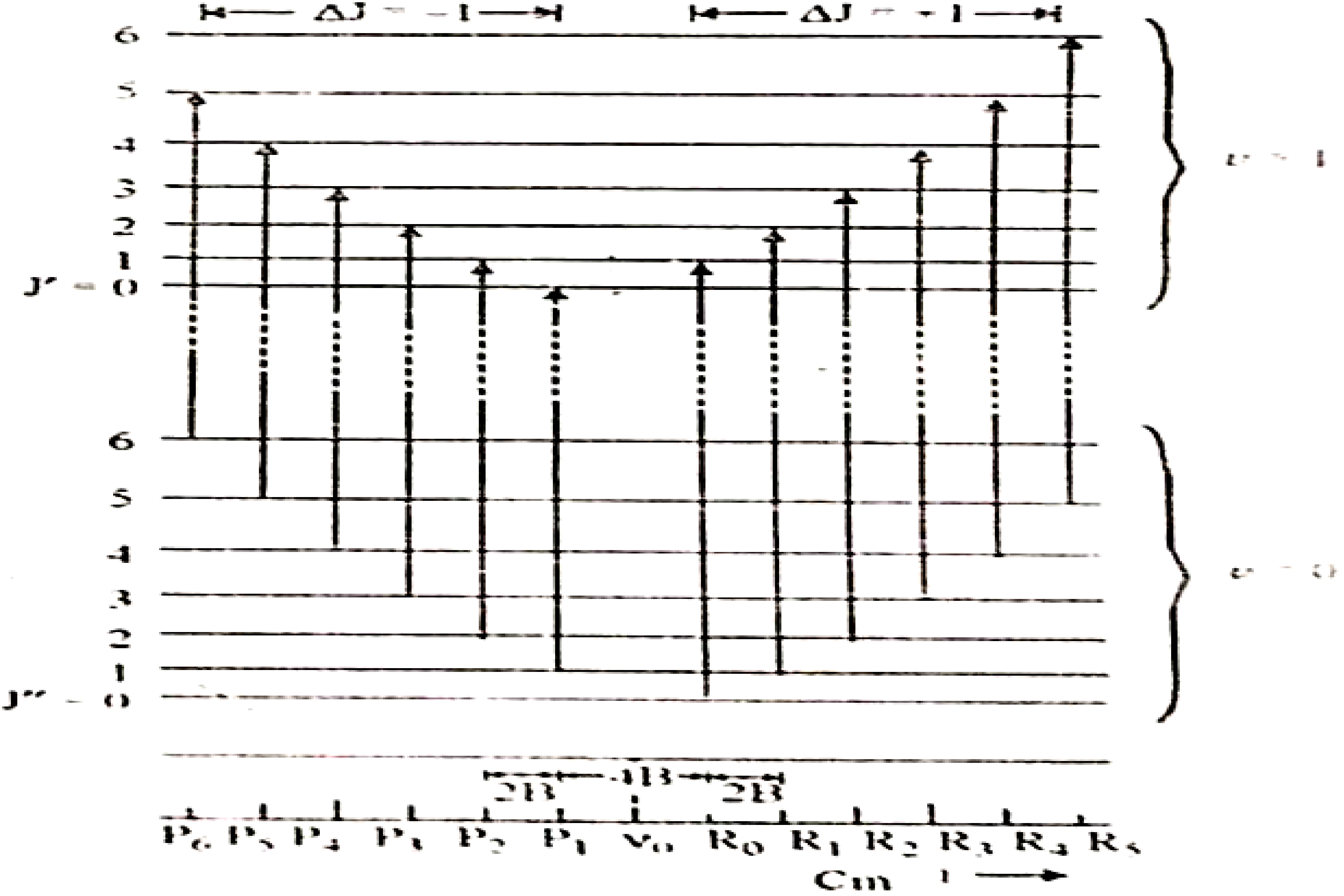
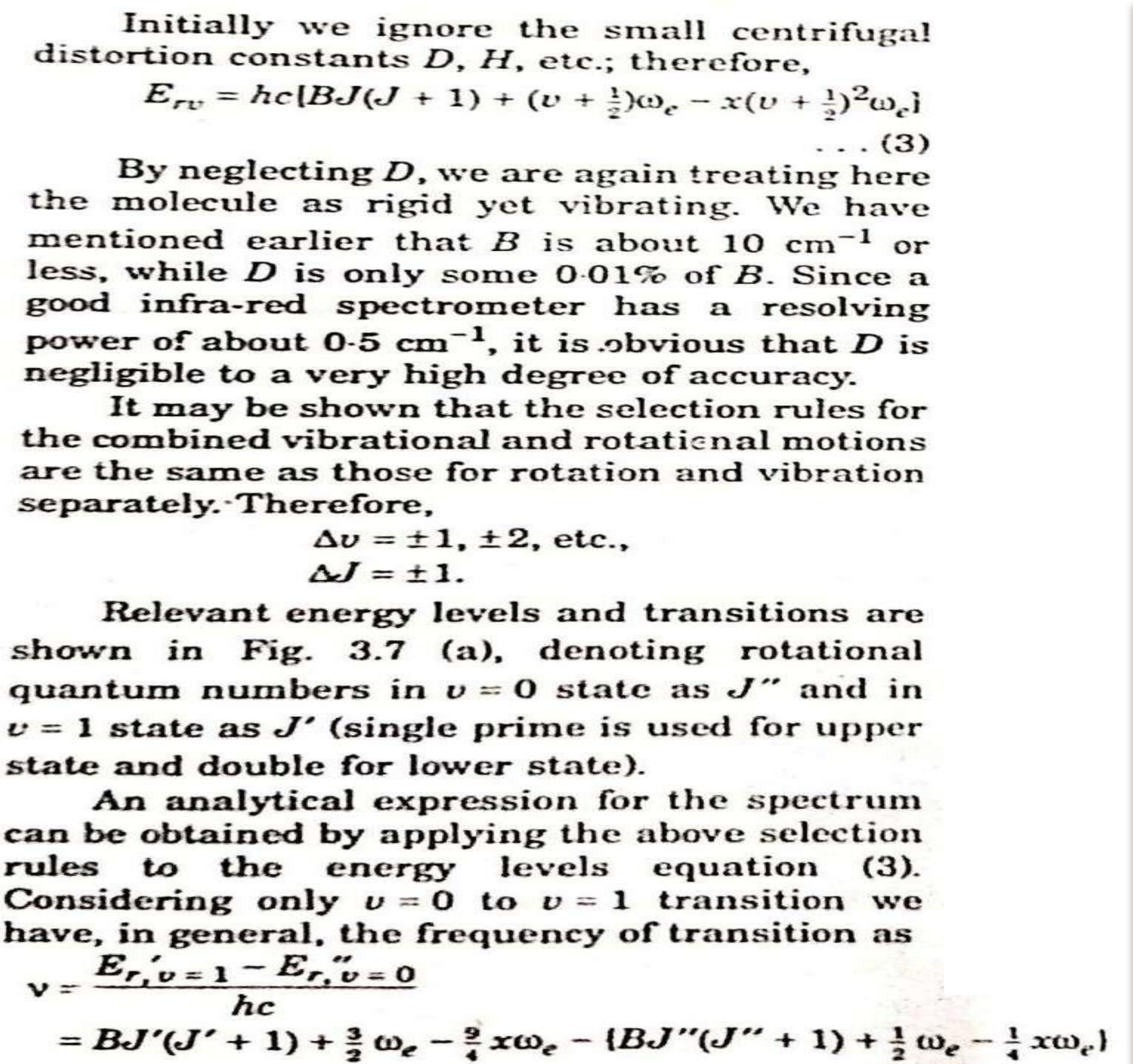


Fig. 3.7(a). Some transitions between the rotational vibrational energy levels of a diatomic molecule together with the spectrum arising from them (absorption spectrum). Note that lines in *P* and *R* branches are shown equidistant.



Initially we ignore the small centrifugal distortion constants D, H, etc.; therefore,

$$E_{rv} = hc\{BJ(J+1) + (v+\tfrac{1}{2})\omega_e - x(v+\tfrac{1}{2})^2\omega_e\} \quad \ldots (3)$$

By neglecting D, we are again treating here the molecule as rigid yet vibrating. We have mentioned earlier that B is about 10 cm^{-1} or less, while D is only some 0·01% of B. Since a good infra-red spectrometer has a resolving power of about 0·5 cm^{-1}, it is obvious that D is negligible to a very high degree of accuracy.

It may be shown that the selection rules for the combined vibrational and rotational motions are the same as those for rotation and vibration separately. Therefore,

$$\Delta v = \pm 1, \pm 2, \text{ etc.},$$
$$\Delta J = \pm 1.$$

Relevant energy levels and transitions are shown in Fig. 3.7 (a), denoting rotational quantum numbers in $v = 0$ state as J'' and in $v = 1$ state as J' (single prime is used for upper state and double for lower state).

An analytical expression for the spectrum can be obtained by applying the above selection rules to the energy levels equation (3). Considering only $v = 0$ to $v = 1$ transition we have, in general, the frequency of transition as

$$\nu = \frac{E_{r,v=1}' - E_{r,v=0}''}{hc}$$
$$= BJ'(J'+1) + \tfrac{3}{2}\omega_e - \tfrac{9}{4}x\omega_e - \{BJ''(J''+1) + \tfrac{1}{2}\omega_e - \tfrac{1}{4}x\omega_e\}$$

$$= \nu_0 + B(J' - J'')(J' + J'' + 1) \text{ cm}^{-1}, \qquad \ldots (4)$$

where for $\omega_e(1 - 2x)$ we have written ν_0. It is the wavenumber of the pure vibrational transition (for which $J' = J'' = 0$) which is not allowed (as $\Delta J \neq 0$) and correspond to the missing line in the band. ν_0 is known as the wavenumber of the 'band origin' [see point (i) of discussion].

Because we have taken rotation to be independent of vibrational changes, B will remain same in the upper and lower vibrational states.

Now we can have

R branch: $\Delta J = +1$, *i.e.*, $J' = J'' + 1$ or $J' - J'' = +1$; hence

$$\boxed{\nu(R) = \nu_0 + 2B(J'' + 1) \text{ cm}^{-1}, J'' = 0, 1, 2, \ldots} \qquad \ldots (5)$$

P branch: $\Delta J = -1$, *i.e.*, $J'' = J' + 1$ or $J' - J'' = -1$; hence

$$\nu(P) = \nu_0 - 2B(J' + 1) \text{ cm}^{-1}, \quad J' = 0, 1, 2.$$

$$\boxed{\nu(P) = \nu_0 - 2BJ'', \quad J'' = 1, 2, 3} \qquad \ldots (6)$$

Discussion: Equations (5) and (6) can be combined in the form

$$\boxed{\nu = \nu_0 + 2Bm \text{ cm}^{-1}} \qquad \ldots (7)$$

with $m = \pm 1, \pm 2, \pm 3, \ldots$

(*i*) *m cannot be zero* since this would imply values of J' or J'' to be -1. The frequency ν_0 is usually called the *band origin*.

Equation (7) represents the combined vibration-rotation spectrum. Such a spectrum will thus consist of *equally spaced lines, with a spacing* $2B$, on each side of the band origin ν_0 but since $m \neq 0$, the *line at* ν_0 *itself will not appear (absence of Q branch).*

(*ii*) **P branch:** Equation (7) gives a series of lines, with a constant frequency separation of $2B$ cm^{-1}, lying on the *lower frequency* (longer wavelength) side of the centre of the band (of frequency ν_0) when m has negative values. These lines constitute the fine structure of what is known as the *P branch* of the vibration-rotation band. The frequencies of this branch are given by equation (6).

(*iii*) **R branch:** For positive values of m, a similar series of lines, with a constant frequency separation of $2B$ cm^{-1}, appears *on the higher frequency* (shorter wavelength) side of the centre of the band. This series is termed as *R branch* of vibration-rotation band. The frequencies of this branch are given by equation (5).

We note that the value of m in equation (7) cannot be zero, so that the *line of frequency corresponding to the centre of the band should be absent.* Thus lines arising from

	$\Delta J =$	-2	-1	0	1	$+2$
are called		*O*	*P*	*Q*	*R*	*S* branches

These theoretical predictions are in agreement with the experimental. In Fig. 3.7 (b) rotation-vibration bands of hydrogen chloride (HCl) are shown. It is found to consist of a number of lines with an approximately constant frequency separation of $2B$ cm^{-1}. As expected, there is a gap at the centre of the band, and therefore spacing between the lines immediately on each side of the centre is thus $4B$ cm^{-1}.

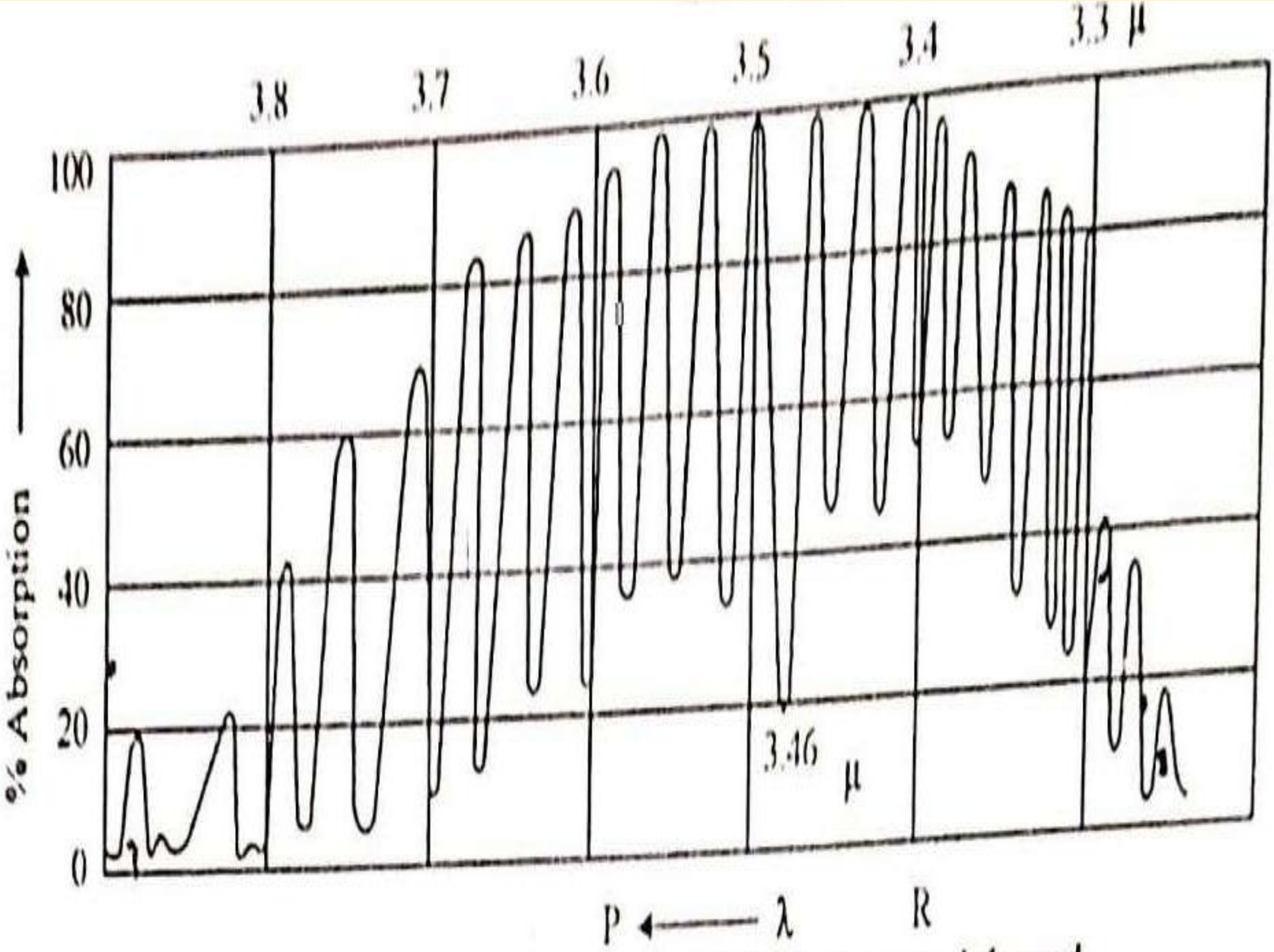


Fig. 3.7. (b). Principal absorption band of HCl in the near infra-red.

VIBRATIONAL AND ROTATIONAL ENERGIES: FINE STRUCTURE OF ROTATION-VIBRATION BANDS

If we do not take interaction of vibrational and rotational energies into consideration, R branch lines and P branch lines are equidistant. That is, these lines form two branches of *equidistant* lines. But in practice it is not observed. In fact, the separation between the lines of one branch slowly decreases (R-branch) and of other branch slowly increases (P-branch) as we move towards higher and higher lines of the branch. This is attributed to vibration-rotation interaction.

Though it is assumed that vibration and rotation can proceed quite independently of each other but it is not so. As a molecule vibrates some 10^3 times during the course of a single motion, the bondlength also changes continually during the motion. A change in bondlength will also change the moment of ineritia and constant B $\left(\text{since } I = m'r^2 \text{ and } B = \dfrac{h}{8\pi^2 Ic}\right)$. Thus interaction between the two energies occurs. An increase in vibration energy is accompanied by an increase in the vibrational amplitude. Since B, the rotational constant, depends on $\left(\dfrac{1}{r^2}\right)$ (r represents internuclear distance or bondlength), it will depend upon the vibrational quantum number v. *An increase in vibration energy will lead to an increase in the average bondlength r_{av}, rotational constant B is smaller in the upper vibrational state than in the lower.* An equation of the form

$$B_v^* = B_e\dagger - \alpha(v + \tfrac{1}{2}) + \ldots \qquad \ldots(1)$$

gives the values of B_v, the rotational constant in vibrational level v, in terms of the equilibrium

The expression gives the frequencies of the lines constituting P and R branches of a vibrational band, *i.e.*,

$$J - 1 \text{ to } J;\ \nu(P) = \nu_0 - (B_\upsilon' + B_\upsilon'')J + (B_\upsilon' - B_\upsilon'')J^2 + 4D_eJ^3 + \ldots \qquad \ldots(6)$$

$$J \text{ to } J - 1;\ \nu(R) = \nu_0 + (B_\upsilon' + B_\upsilon'')J + (B_\upsilon' - B_\upsilon'')J^2 - 4D_eJ^3 + \ldots \qquad \ldots(7)$$

where $J = 1, 2, 3, \ldots$

The constants B_υ' and B_υ'' are the values of B_υ in the initial (upper) and final (lower) states involved in the vibrational transition. ν_0 is the frequency of the centre of the band. For $\upsilon = 1$ to $\upsilon = 0$, $\nu_0 = (1 - 2x)\,\omega_e$

If we ignore D_e then eqs. (6) and (7) can be written as

$$\boxed{\nu_{P,R} = \nu_0 + (B_\upsilon' + B_\upsilon'')m + (B_\upsilon' - B_\upsilon'')m^2 \text{ cm}^{-1}}$$

where $m = +1, +2, +3, \ldots$ **for R branch**

and $m = -1, -2, -3, \ldots$ **for P branch.**

Discussion :

(*i*) As we know that average internuclear distance (r_e) increases with vibrational energy, the vibrational constant B_υ ($= h/8\pi^2Ic = h/8\pi^2m'r_e^2c$) is small in the upper vibrational state than in the lower. Since B_υ'' denotes lower state we have that *always* $B_\upsilon' < B_\upsilon''$. *It means band head appears in R branch on the high wave number side of the origin.* Such a band is said to be *degraded towards the red. Thus in vibration-rotation spectra bands are degraded to red only.*

But later in electronic spectra, we shall observe that since $B_\upsilon' - B_\upsilon''$ would belong to different electronic states, $(B_\upsilon' - B_\upsilon'')$ may be negative or positive, that is, $B_\upsilon' > B_\upsilon''$ or $B_\upsilon' < B_\upsilon''$ both are possible. Therefore, in electronic band system, both red and violet degraded bands have been observed.

The expression gives the frequencies of the lines constituting P and R branches of a vibrational band, *i.e.*,

$$J-1 \text{ to } J;\ \nu(P) = \nu_0 - (B'_\upsilon + B''_\upsilon)J + (B'_\upsilon - B''_\upsilon)J^2 + 4D_eJ^3 + \dots \qquad \dots(6)$$

$$J \text{ to } J-1;\ \nu(R) = \nu_0 + (B'_\upsilon + B''_\upsilon)J + (B'_\upsilon - B''_\upsilon)J^2 - 4D_eJ^3 + \dots \qquad \dots(7)$$

where $J = 1, 2, 3, \dots$

The constants B'_υ and B''_υ are the values of B_υ in the initial (upper) and final (lower) states involved in the vibrational transition. ν_0 is the frequency of the centre of the band. For $\upsilon = 1$ to $\upsilon = 0$, $\nu_0 = (1-2x)\,\omega_e$

If we ignore D_e then eqs. (6) and (7) can be written as

$$\boxed{\nu_{P,R} = \nu_0 + (B'_\upsilon + B''_\upsilon)m + (B'_\upsilon - B''_\upsilon)m^2 \text{ cm}^{-1}}$$

where $m = +1, +2, +3, \dots$ **for R branch**

and $m = -1, -2, -3, \dots$ **for P branch.**

Discussion :

(*i*) As we know that average internuclear distance (r_e) increases with vibrational energy, the vibrational constant B_υ $(= h/8\pi^2Ic = h/8\pi^2m'r_e^2c)$ is small in the upper vibrational state than in the lower. Since B''_υ denotes lower state we have that *always* $B'_\upsilon < B''_\upsilon$. *It means band head appears in R branch on the high wave number side of the origin.* Such a band is said to be *degraded towards the red. Thus in vibration-rotation spectra bands are degraded to red only.*

But later in electronic spectra, we shall observe that since $B'_\upsilon - B''_\upsilon$ would belong to different electronic states, $(B'_\upsilon - B''_\upsilon)$ may be negative or positive, that is, $B'_\upsilon > B''_\upsilon$ or $B'_\upsilon < B''_\upsilon$ both are possible. Therefore, in electronic band system, both red and violet degraded bands have been observed.

(*ii*) If a molecule possesses a resultant angular momentum so that there is a probability of the transition for which ΔJ is zero, then the expression for the frequency of Q branch is (J to J):

$$\nu(Q) = \nu_0 + (B_v' - B_v'')J + (B_v' - B_v'')J^2, \qquad \ldots (8)$$

where $J = 0, 1, 2, 3, \ldots$

which accounts for the fact that Q branch is observed to have a number of *very closely spaced lines.* When vibrational quantum numbers v' and v'' differ by 3 or 4 at most, the difference $(B_v' - B_v'')$ must be small and hence the lines be closely spaced.

(*iii*) From equations (6) and (7), we find that the frequency separation $\Delta\nu$ of successive lines in the P and R branches as respectively given by

$$\left.\begin{aligned} \Delta\nu(P) &= 2B_v' - (B_v' - B_v'')2J + \ldots \\ \text{and} \quad \Delta\nu(R) &= 2B_v' + (B_v' - B_v'')2J + \ldots \end{aligned}\right\} . \qquad \ldots (9)$$

which show that *the frequency separation of successive lines in the vibration band will not be constant in either branch.*

As for both P or R branch we have $B_v' < B_v''$, the separation between lines of R branch will decrease with increasing J values whereas separation between lines of P branch will increase with increasing J values (see Fig. 3.8).

B_v' refers to the upper and B_v'' to the lower state. Further, $B_v' < B_v''$; factor B_v decreases slightly with increasing v, the spacings *between the rotational levels* associated with vibrational state $v = 1$ are slightly smaller than those between the rotational levels associated with vibrational state $v = 0$ (see Fig. 3.8).

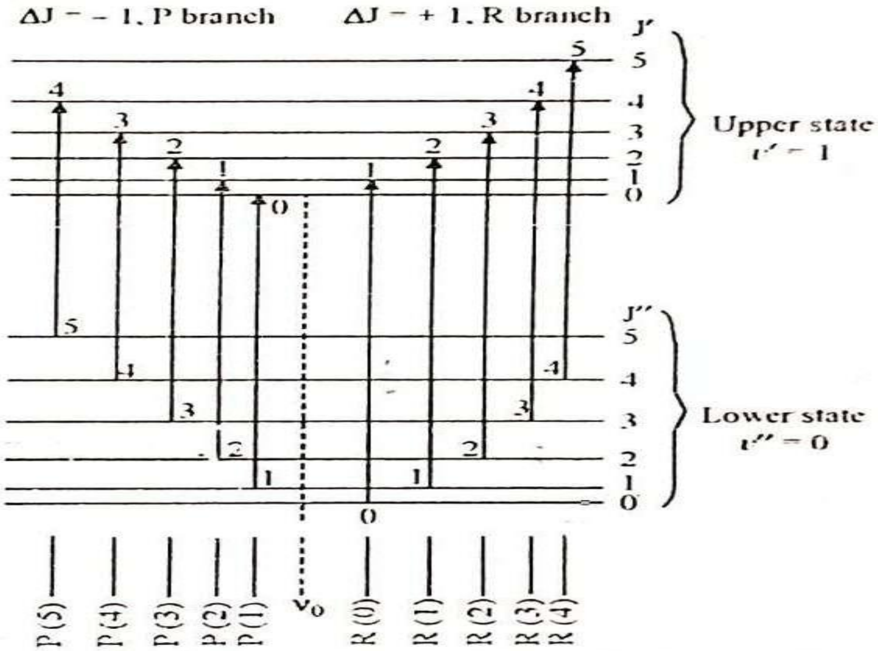


Fig. 3.8. *P* & *R* branches of rotation-vibration spectra. Note that lines in *R* branch & also in *P* branch are not equidistant. Also rotational levels in $v = 0$ state have more separation compared to that of $v = 1$ state.

Applications: We can evaluate, with the help of rotation vibration spectra, the equilibrium moments of inertia I_e and corresponding nuclear separations, r_e. For this, B_v values for two or three vibrational levels are determined from the analysis of the frequencies of the lines in P and R branches of the various vibration-rotation bands of given diatomic molecule. From there, the value of rotation constant, B_e, is calculated on using the *equation* (1). B_e, then provides the value of I_e since $B_e = \dfrac{h}{8\pi^2 I_e c}$. Further $I_e = m' r_e^2$ and hence r_e, the internuclear distance in the equilibrium state of the molecule can be determined. The data for most abundant isotopic form of each of the hydrogen halides are given in the table below:

Table: Internuclear distance from vibration-rotation spectra

Substance	B_e **(cm^{-1})**	I_e **(gm cm^2) × 10^{-40}**	r_e **(cm) × 10^{-8}**
HF	20·967	1·335	0·9266
HCl	10·591	2·644	1·747
HBr	8·471	3·304	1·414
HI	65·51	4·272	1·604

3.5. ISOTOPE EFFECTS IN VIBRATIONAL BANDS

The two isotopic forms of the same molecule have different reduced masses but force constants would remain same. From the expression, $k = 4\pi^2\omega_e^2 m'c^2$, for force constant, it is evident that equilibrium vibration frequencies of the two forms will differ. Let ω_1 and ω_2 be the values of ω_e for two isotopic forms, and m_1' and m_2' be their respective reduced masses; then from the rotation force constant $k = 4\pi^2\omega_e^2 m'c^2$, it follows that

$$\frac{\omega_2}{\omega_1} = \left(\frac{m_1'}{m_2'}\right)^{1/2} = \rho \qquad \ldots (1)$$

or

$$\omega_2 = \rho\omega_1.$$

Anharmonicity constant x, from theoretical considerations, is proportional to the equilibrium frequency so that we can write

$$x_2 = \rho x_1 \qquad \ldots (2)$$

Now we know that equation (6) of § 3.2 gives the general expression for the frequency of the centre of any band involving lower vibration level of $v = 0$. Writing that equation,

$$\nu_{v \to 0} = v\omega_e - \{v(v+1)\}x\omega_e,$$

which, with the aid of equations (1) and (2), gives

$${}_1\nu_{v \to 0} = v\omega_1 - \{v(v+1)\}x_1\omega_1$$

and

$${}_2\nu_{v \to 0} = v\rho\omega_1 - \{v(v+1)\}\rho^2 x_1\omega_1.$$

The subscripts 1 and 2 refer to the isotopic forms of the same molecule.

The frequency difference of the centres of the two isotopic bands, called isotopic shift, $\Delta\nu_i$, is then

$$= (1-\rho)\{1-(\upsilon+1)(1+\rho)x_1\}\upsilon\omega_1, \qquad \ldots(3)$$

The relation gives the isotopic shift for

(i) fundamental band ($\upsilon = 1$ to $\upsilon = 0$)

(ii) first overtone band ($\upsilon = 2$ to $\upsilon = 0$)

(iii) second overtone band ($\upsilon = 3$ to $\upsilon = 0$)

$$\left.\begin{aligned}
\Delta\nu_i(1) &= (1-\rho)\{1-2(1+\rho)x_1\}\omega_1\\
\Delta\nu_i(2) &= (1-\rho)\{1-3(1+\rho)x_1\}2\omega_1,\\
\Delta\nu_i(3) &= (1-\rho)\{1-4(1+\rho)x_1\}3\omega_1.
\end{aligned}\right\} \qquad \ldots(4)$$

Thus we find that if x_1 and ω_1 are known for one isotopic form of the molecule, it is possible to calculate the frequency shift corresponding to another isotopic form of the same diatomic molecule. The isotopic shift depends upon the factor $(1 - \rho)$ and since $\rho = \left(\dfrac{m_1'}{m_2'}\right)^{1/2}$, the former also depends upon the ratio of the reduced masses. Isotopic shift increases with the increase in $(1 - \rho)$.

Isotopic exchange, as we have seen, changes the frequency of the centre (origin) of the band. Further from the equations (5) and (6) of § 3.3 or equations (6) and (7) of § 3.4, we note that the rotational lines in the band involve the frequency of origin (ν_0) as the constant term and thus a shift in the frequency of the origin will result in the shifting of all the lines by the same amount as a whole. If $\rho > 1$, isotopic shift $\Delta\nu_i$ is in the direction of lower frequency, whereas if $\rho < 1$, the shift is in the opposite direction.

The vibrational isotope effect, expected according to theory, was first noticed by Loomis and independently by Kratzer in the rotation-vibration spectrum of HCl. Since Cl has two isotopes

Cl^{35} and Cl^{37}, two bands should appear in the spectrum of HCl, one corresponding to HCl^{35} and another to HCl^{37}. The band belonging to HCl^{37} should be shifted by a small amount toward longer wavelengths with respect to the band belonging to HCl^{35}. Experimental investigation of the rotation-vibration bands of HCl actually shows *doubling of all the lines.* Every line has a companion of weaker intensity to the wavelength side with a constant frequency separation of Δv_i to a first approximation (Fig. 3.9). The observed isotopic frequency shift have been found to be in good agreement with those calculated. Observed and calculated vibrational isotopic shift for the infra-red HCl are tabulated here.

Table—Observed and Calculated Vibrational Isotopic Displacement for the Infra-red HCl Bands

Band	$\Delta v_{obs.}$	$\Delta v_{calc.}$
1–0	2·01	2·105
2–0	4·00	4·053
3–0	5·834	5·845

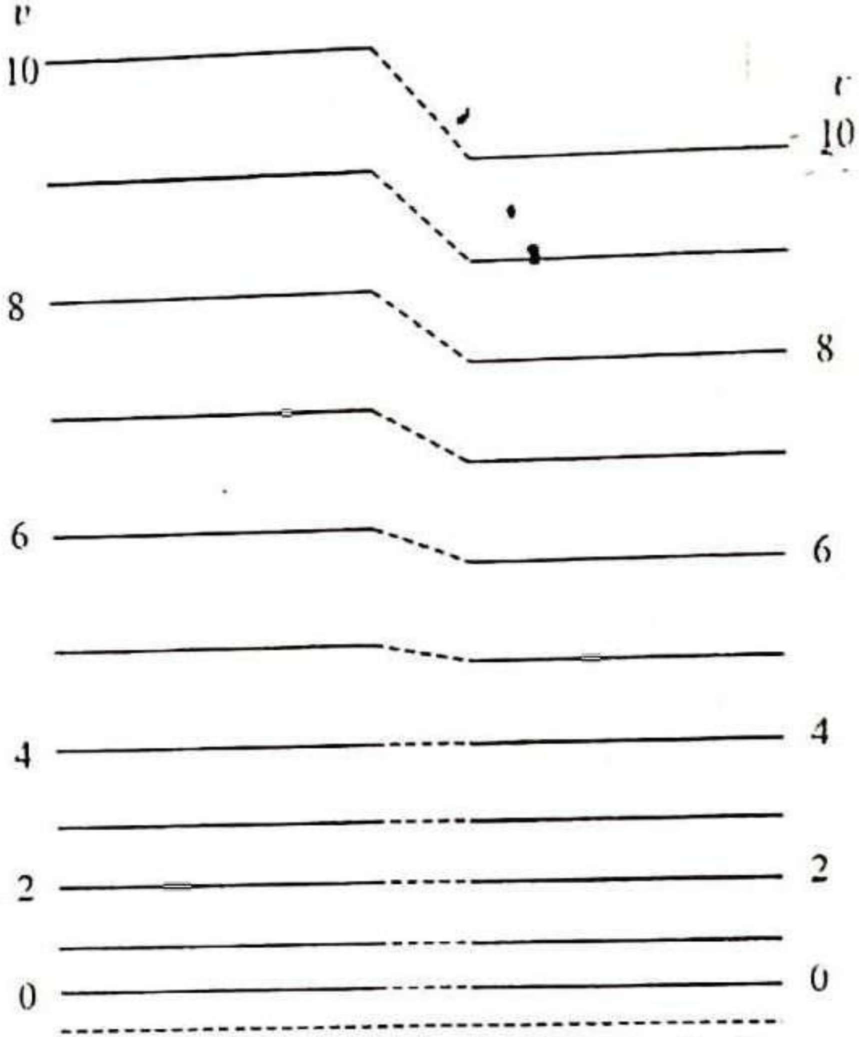


Fig. 3.9. Vibrational levels of two isotopic molecules.

3.6. APPLICATIONS OF VIBRATIONAL SPECTROSCOPY

(*i*) *Determination of force constant:* The force constant, which is a measure of stiffness of the bond of a molecule, can be evaluated.

(*ii*) *Determination of moments of inertia:* The moment of inertia can be deduced from the rotational structure of the vibrational band.

(*iii*) *Determination of molecular shape:* The molecular shape (whether linear or bent) can sometimes be deduced from the number of absorption bands observed in the vibrational spectra of the molecule.

(*iv*) *Indication of the presence of certain groups in the molecule:* Bonds or groups within a large molecule sometimes vibrate with a frequency that is little affected by the rest of the molecule. Therefore these groups will show absorption at their characteristic frequencies or conversely, absorption at a frequency that is characteristic of a particular group, can be taken as an indication of the presence of that group in the compound under study. For example, all compounds with single carbon-hydrogen bonds show a bond near 3·5 μ due to a C—H stretching mode and all compounds containing a carbonyl group have a bond due to a C=O stretching mode near 6 μ. Thus study of infra-red absorption spectrum of a large molecule gives the indication of a particular group being present.

(*v*) *Identification of unknown compound by matching:* The vibrational spectra are used in verifying the identity of a compound by matching its infra-red spectrum to that of a known sample. If the infra-red spectra of two substances are identical, the compounds are also identical. The complex spectra (above 7 μ, called finger print region) due to large molecules are used in such attempts of matching.

3.7. GENERAL EXPERIMENTAL ARRANGEMENT FOR STUDYING INFRA-RED SPECTRA

Infra-red spectra that are of chief practical significance lie in the region $2{\cdot}5\ \mu$ to $25\ \mu$. For spectroscopic study of the spectra, the basic requirements are a source, a dispersion element, and a detector. The choice depends upon the wavelength region under consideration. The block diagram of the arrangement used to observe absorption spectra is shown in Fig. 3.10.

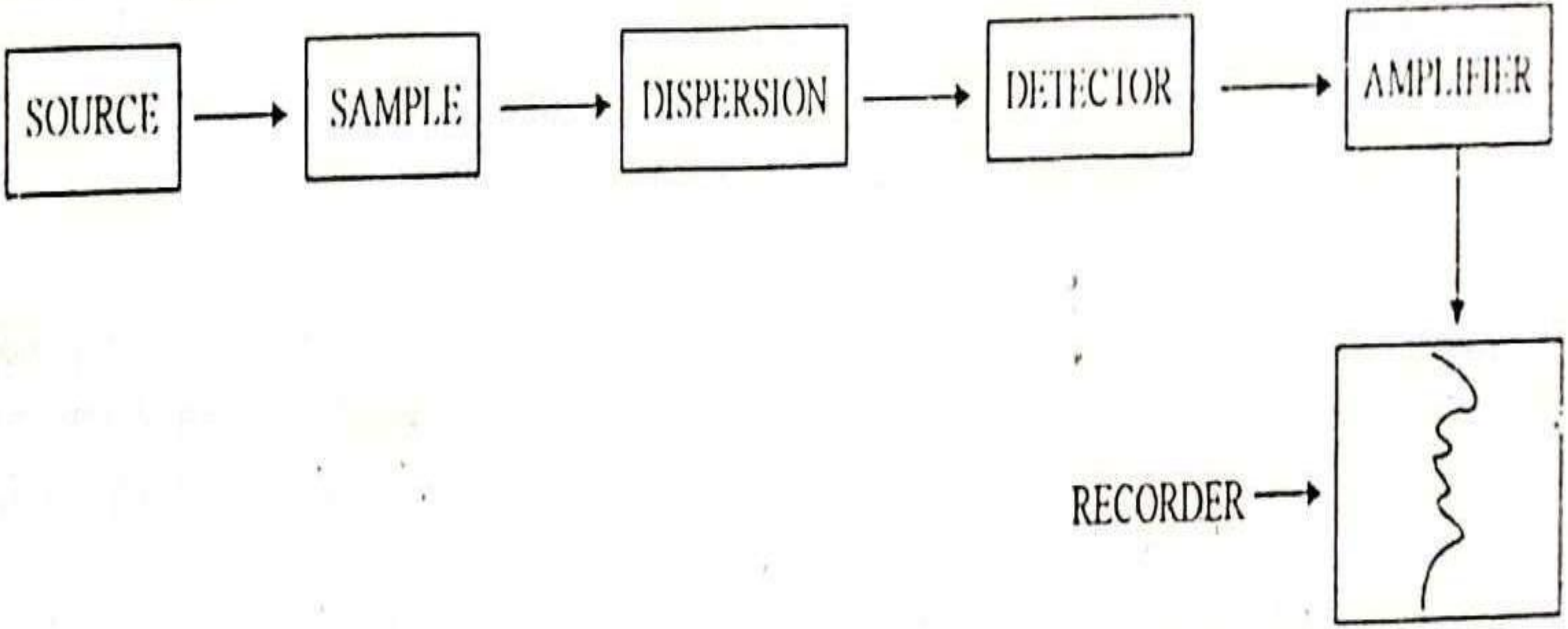


Fig. 3.10. Arrangement for observation of absorption spectra-single beam.

For absorption spectra, a source that emits all wavelengths over a useful interval of wavelengths is used and radiation is focussed on to the entrance slit of monochromator* through a convenient thickness of an absorbing sample. The recorder then shows the graph that predicts the energy reaching the detector at each wavelength. To determine absorption, wavelength interval is covered again without absorbing sample. Source and detectors should remain stable for the period of two scans (*i.e.*, with and without sample).

We shall now discuss the parts of the arrangements for infra-red region.

(i) **Radiation source:** A hot strip of material emitting all frequencies in accordance with black body radiation law is preferred as an infra-red source. The emission maximum lies in the near infra-red. The energy at each frequency increases with source temperature.

There are two common sources:

(*a*) *Nernst Filament (Glower):* It is a mixture of zirconium and yttrium oxides which is formed into small hollow rods about 2 mm in diameter and 80 mm in length. The filament is heated to surface temperatures 1500°C and 2000°C. It furnishes maximum radiation at about 1·4 μ.

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*The term monochromator applies to those instruments in which a second slit is placed in the focal plane. This slit isolates a particular narrow band of wavelength of radiation which is refocussed on to a detector whose output is a measure of the energy at the chosen wavelength band.

(b) Glober Source: It is a rod of sintered silicon carbide about 50 mm in length and 4 mm in diameter. It is self-starting and is heated to 1300°C–1700°C. The maximum radiation occurs about 1·9 μ. This is more satisfactory for work at wavelengths longer than 15 μ because its radiant energy output decreases less rapidly compared to Nernst source.

(ii) Sample: Gas samples are studied in glass cells that are about 10 cm in length, closed at their ends with rock salt† windows. The cell is evacuated and the sample is filled through a stop cock or needle valve. The window material, which is transparent over infra-red region to all the radiations to enter the sample, should be inert. Sodium chloride is transparent at wavelengths as long as 16μ, potassium chloride can be used up to 20 μ and cesium iodide to 40μ.

Samples that are liquid at room temperature are usually scanned in their pure form. The sample thickness should be chosen so that the transmittance lies between 15 and 70 per cent. For most liquids this will represent a very thin layer of the order of 0·01–0·05 mm.

Solid samples‡, whenever possible, are dissolved and examined as dilute solutions. However, not all substances can be dissolved in reasonable concentration in a solvent which is nonabsorbing in the regions of interest. For the range 2·5–15·4μ, a mixture of cabon tetrachloride and carbon disulphide is satisfactory. There is also KBr pellet technique which involves mixing the finely ground sample and potassium bromide and pressing the mixture into a transparent disc in an evacuable dye under high pressure.

Some window materials are listed in table.

(iii) Mirrors: Mirrors are used for collimating and focussing of radiations in infra-red region. The advantage of mirrors over lenses in this region is that:

(a) they do not require focussing. If the mirror is focussed for sodium *D* lines, the spectrum will be in focus to farthest infra-red and

(b) they can be used up to farthest infra-red where even fluorite and rock salt absorb the radiations.

(iv) The dispersing media: Media used for dispersion are prisms of suitable material, gratings or their combination. The choice of prism material depends upon the region of spectrum under investigation. Some prism and window materials for infra-red region are tabulated in table:

Table
Prism and Window Materials for Infra-Red

Material	Suitable range for window	Optimum range as prisms
Glass*	3000 mμ to 2·6 μ	3000 mμ to 2·0 μ
Fused Silica**	185 mμ to 4·0 μ	185 mμ to 3·5 μ
Lithium Fluoride	115 mμ to 7·0 μ	600 mμ to 6·0 μ
Calcium Fluoride*	125 mμ to 10·0 μ	200 mμ to 9·0 μ
Barium Fluoride*	200 mμ to 13·5 μ	300 mμ to 13·0 μ
Zinc sulphide* (Iriran 2)	150 mμ to 13·0 μ	—
Sodium Chloride*	200 μ to 17·0 μ	200 mμ to 15·4 μ
Silver Chloride	10 to 25 μ	—
Potassium Bromide	200 mμ to 26 μ	10 to 25 μ
Cesium Iodide	1 to 40 μ	10 to 38 μ

Higher dispersion can be obtained from a reflection grating substituted in place of the prism in the Littrow mount. Gratings are unstable only over a short spectral range.

(v) Detectors: Thermopiles, Bolometers and Golay cells are used as detectors. They measure the radiant energy by virtue of its heating effect.

Thermopile is a series of thermocouples linked together and thus acts on the principle of thermocouple *i.e.* an e.m.f. is generated when one of the two metal junctions is heated by radiant energy; e.m.f. developed is proportional to the radiant energy falling on hot junction.

Bolometers give an electrical signal as a result of the change in resistance of a metallic conductor with temperature.

Golay cell consists of a small metal cylinder, closed by a blackened metal plate at one end and by a flexible metallised diaphragm at the other. This cylinder is filled with xenon and sealed. When the radiations fall on backened plate, gas expands and deforms the metallised diaphragm. Light from a lamp inside the detector housing can be focussed upon the diaphragm which reflects the light on to a photo cell. The motion of diaphragm moves the light beam across the photo cell surface and changes the photocell output.

A double beam arrangement: In double beam arrangement, two equivalent beams are taken from the source. One beam passes through the sample while the other beam, called as reference beam, passes through a variable and calibrated attenuator. Then both beams are presented to monochromator-detector system on alternate half cycles by means of a rotating mirror. As the monochromator scans the wavelength range, the detector and amplifier system notes and discriminates between two signals. Any difference between them, as will occur because of the absorption by the sample, is used by the servo amplifier to actuate a motor to drive the

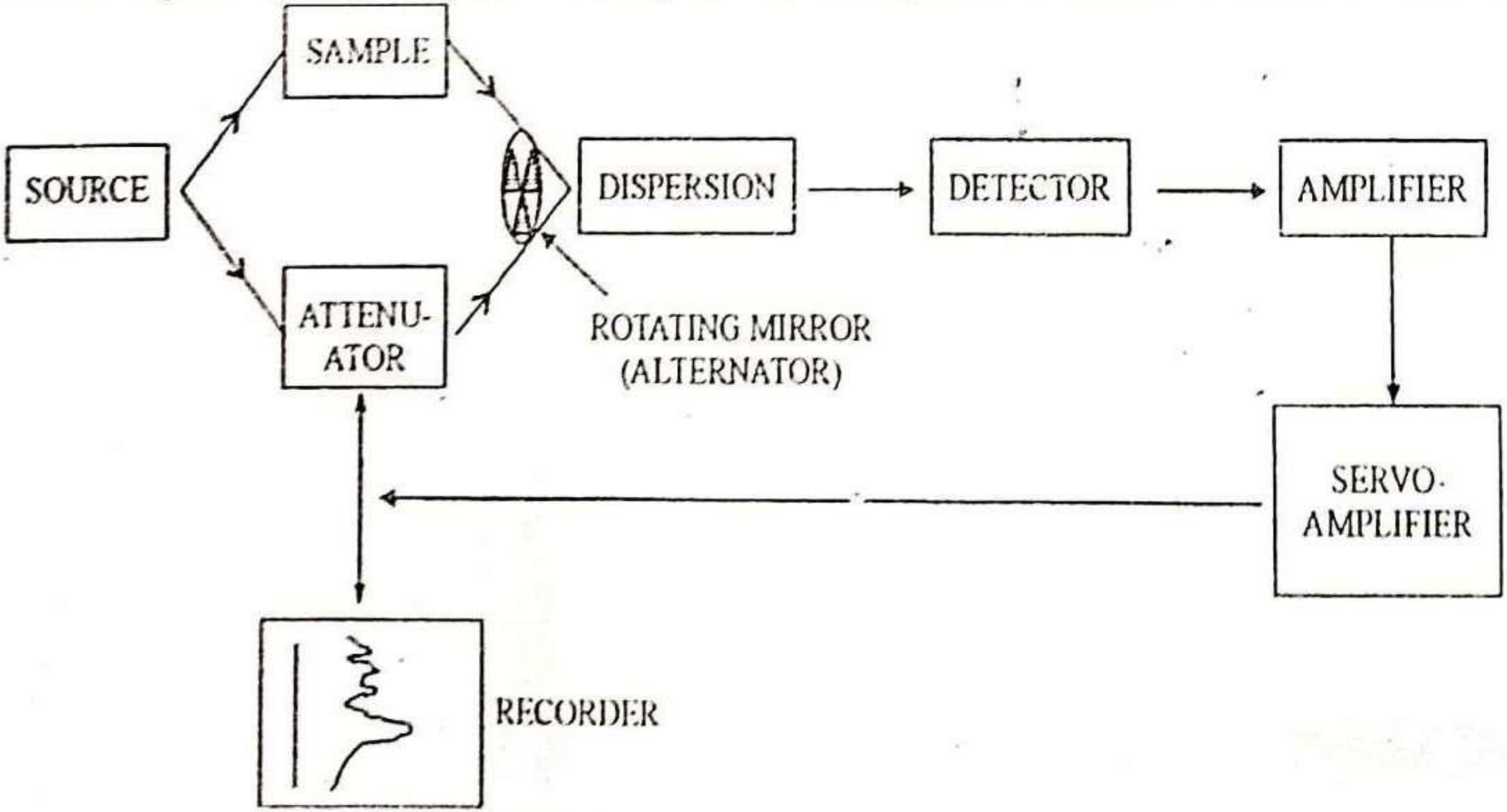

Fig. 3.11. Double beam spectrometer arrangement.

attenuator into the reference beam. This results in the reduction of comparison beam such that there is no difference between the two beams. Servo amplifier always acts in a direction as to correct for any difference between the two beams and thus maintains a balance. The absorption by the sample is given by the position of the attenuator at each wavelength. An electrical or mechanical connection between attenuator and recorder enables a curve to be drawn on a paper moving forward as the wavelength changes. Fig. 3.11 shows the arrangement.

THANK YOU