Unit 6.2 Rotational, Vibrational and Raman Spectroscopy (Marks 20)

Rotational spectra of diatomic molecules – rigid rotator concept – determination of bond length – effect of isotopic substitution – spectra of non-rigid rotator. Vibrational spectra of diatomic molecules – harmonic and anharmonic oscillator model – Morse potential - calculation of force constants – effect of isotope - vibrations of polyatomic molecules, overtone and combination bands (H_2O, CO_2). Diatomic vibrating rotor – vibration rotation spectrum of CO. Principle of Raman spectroscopy – rotational and vibrational Raman spectra of linear molecules – rule of mutual exclusion.

Structure elucidation by IR spectroscopy – finger print region and group frequencies – effect of hydrogen bonding (alcohol, keto-enol) and coordination to metal.

ROTATIONAL SPECTRA OF RIGID DIATOMIC MOLECULE (RIGID ROTATOR MODEL)

A rigid diatomic molecule means that the distance between the atoms (bond length) does not change during rotation. No vibrational movement is taking place during rotation.

Let us consider a diatomic molecule A—B in which the atoms A and B having masses m1 and m2 are joined together by a rigid bond of length *r0 = r1 + r2 (figure 1). The molecule* A—B rotates about a point C, the centre of gravity: this is defined by the moment, or balancing, equation. The moment of inertia about C is defined by

$$m_1 r_1 = m_2 r_2 \qquad \ldots(1.1)$$

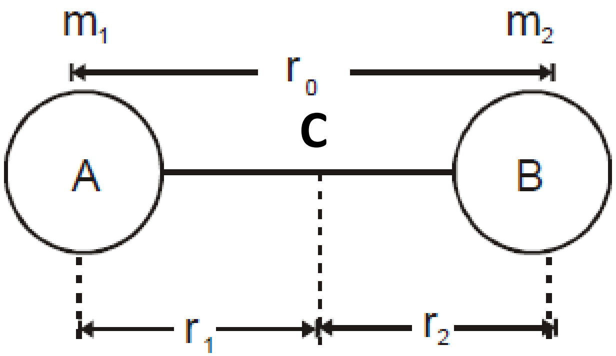


Fig. (1.1) : A rigid diatomic molecule A-B having atomic masses, m_1 and m_2, joined together by a rigid bond of length $r_0 = r_1 + r_2$ and rotates about a point C.

ROTATIONAL SPECTRA OF RIGID DIATOMIC MOLECULE (RIGID ROTATOR MODEL)

$$I = m_1 r_1^2 + m_2 r_2^2 \qquad \because \left[m_1 r_1 = m_2 r_2 \right]$$

$$= m_2 r_2 r_1 + m_1 r_1 r_2$$

$$= r_2 r_1 \left(m_1 + m_2 \right) \qquad \text{....(1.2)}$$

from eq$^{\underline{n}}$ (1) $m_1 r_1 = m_2 r_2 = m_2 \left(r_0 - r_1 \right)$

$$m_1 r_1 = m_2 r_0 - m_2 r_1$$

or $m_1 r_1 + m_2 r_1 = m_2 r_0$

or $r_1 \left(m_1 + m_2 \right) = m_2 r_0$

$\Rightarrow$ $r_1 = \dfrac{m_2 r_0}{m_1 + m_2}$ Similarly $r_2 = \dfrac{m_1 r_0}{m_1 + m_2}$ ...(1.3)

Putting the value of r_1 & r_2 from (3) in (2)

$$I = \frac{m_2 r_0}{\left(m_1 + m_2 \right)} \frac{m_1 r_0}{\left(m_1 + m_2 \right)} \left(m_1 + m_2 \right) = \frac{m_1 m_2 r_0^2}{m_1 + m_2} = \mu \, r_0^2 \qquad \text{...(1.4)}$$

where μ is the reduced mass of the system i.e.

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \qquad \text{...(1.5)}$$

ROTATIONAL SPECTRA OF RIGID DIATOMIC MOLECULE (RIGID ROTATOR MODEL)

Equation (1.4) defines the moment of inertia conveniently in terms of the atomic masses and the bond length.

By the use of the Schrödinger equation it may be shown that the rotational energy levels allowed to the rigid diatomic molecule are given by the expression

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \text{ Joules when } J = 0,\ 1,\ 2\ \ldots\ldots \qquad \ldots(1.6)$$

In this expression h is Planck’s constant, are *I is the moment of inertia,*either I_B *or* I_C, *since both are equal. The quantity J, which can take integral values from zero* upwards, is called the rotational quantum number and each level is (2J + 1) fold degenerate.

ROTATIONAL SPECTRA OF RIGID DIATOMIC MOLECULE (RIGID ROTATOR MODEL)

$$\varepsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 Ic} J(J+1) cm^{-1} \qquad \left[\frac{E}{hc} = \frac{1}{\lambda}\right]$$

$$= BJ(J+1) cm^{-1} \qquad \text{J = 0, 1, 2....} \qquad ...(1.7)$$

where B is the rotational constant and is given by

$$B = \frac{h}{8\pi^2 Ic} cm^{-1} = \frac{h^2}{8\pi^2 I}\ Joule$$

Denoting the lower state by J′′ and the upper state by J′

$$\Delta\varepsilon_J = \varepsilon_{J'} - \varepsilon_{J''}$$

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

$$B\left[J'(J'+1) - J''(J''+1)\right]$$

use of the selection rule $(\Delta J = \pm 1)$ or $J' - J'' = 1$ gives the frequency of the absorption line as

$$v_J = \Delta\varepsilon_J = B\left[(J''+1)(J''+2) - J''(J+1)\right]$$

$$B(J''+1)2 \qquad ...(1.8)$$

$$J \longrightarrow J+1$$

$$\varepsilon_{J+1} = B(J+1)(J+2)$$

$$\varepsilon_J = B\, J(J+1)$$

$$\overline{\Delta\varepsilon = B(J+1)(J+2-J)}$$

$$\Delta\varepsilon = 2B(J+1) cm^{-1} \quad where\ J = 0, 1, 2....$$

ROTATIONAL SPECTRA OF RIGID DIATOMIC MOLECULE (RIGID ROTATOR MODEL)

The rotational constant B is assumed to be the same in both lower and upper rotational states and double prime is dropped from equn (8). The allowed energy levels of a rigid diatomic rotor are illustrated in Fig. 1.2(a). Thus a step-wise raising of the rotational transitions result in an absorption spectrum consisting of spectral lines with a separation of 2 B, that is at 2B, 4B, 6B, ... (Fig. 1.2(b)). The lowering of stepwise energy results in identical emission spectrum. Fig. (a) allowed energy levels of a rigid diatomic rotor showing electric dipole allowed transitions and (b) the resulting absorption spectrum.

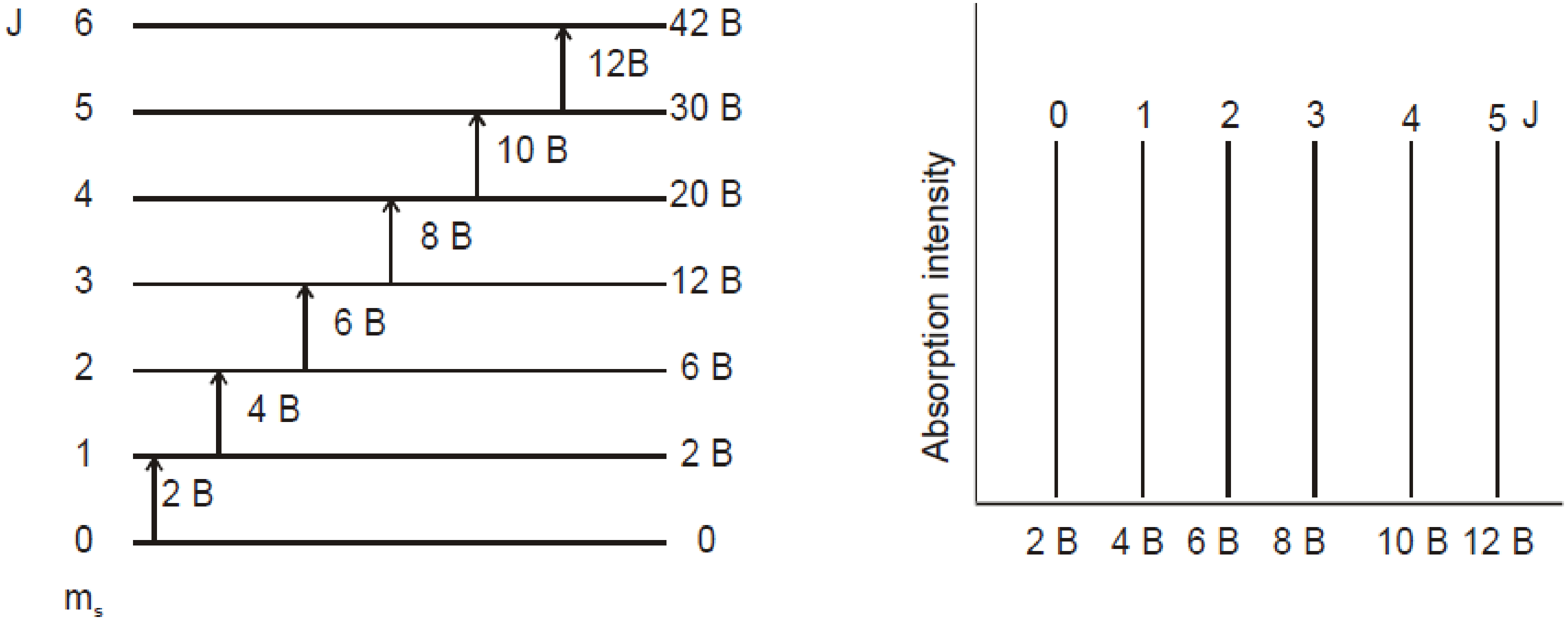


Fig. 1.2 (a)

Fig. 1.2(b)

Fig. 1.2(a) allowed energy levels of a right diatomic rotor showing electric dipole allowed transitions and 1.2(b) the resulting absorption spectrum.

Selection Rules

The selection rule for a transition between any two rotational states is quantum chemically given by

$$\mu_{ij} = \int \psi_i \mu \Psi_j d\tau$$

where ψ_i and Ψ_j are the wave functions for the rotational states i and j and μ is the permanent dipole moment of the molecule. The dipole moment being a vector quantity can be expressed by its three components along the Cartesian coordinates axes, $\mu = \vec{\mu}_x + \vec{\mu}_y + \vec{\mu}_z$ and $\mu^2 = \mu_x^2 + \mu_y^2 + \mu_z^2$. The transition moment integral can be split in terms of the components of the dipole moment,

$$\left[\mu_{ij}^x\right] = \int \mu_i x \, \mu_j \, d\tau$$

$$\left[\mu_{ij}^y\right] = \int \mu_i y \, \mu_j \, d\tau$$

$$\left[\mu_{ij}^z\right] = \int \mu_i z \, \mu_j \, d\tau$$

If atleast any one of the integrals is non zero, then the transition is allowed and forbidden otherwise. The intensity of an allowed rotational transition depends on the square of the

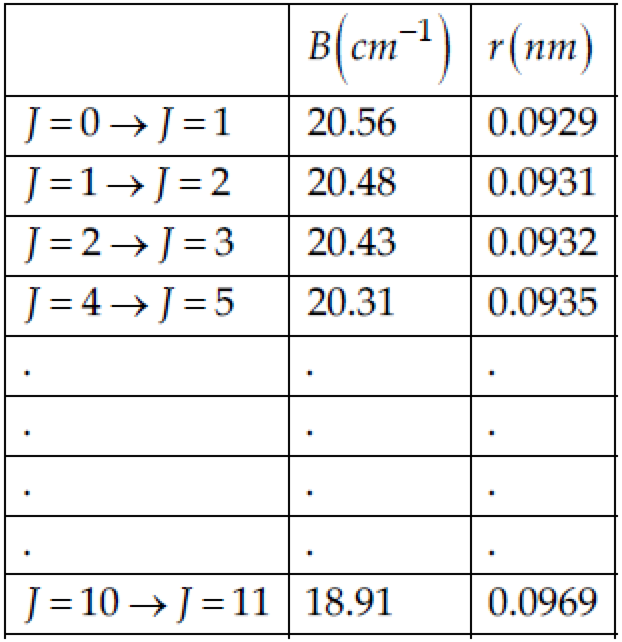
Selection Rules

transition dipole moment. Consequently, the intensity of the rotational line depends on the square of the permanent dipole moment of the molecule.

Schrödinger equation shows that for a diatomic rigid rotor (in the absence of an external electric or magnetic field) only transitions in which J changes by one unit, that is, $\Delta J = \pm 1$ are allowed and all other transactions are forbidden. Thus the selection rule for rotational spectra is $\Delta J = \pm 1$ (plus sign for absorption and minus sign for emission) and second, the molecule must have a permanent dipole moment (only hetronucelar diatomic molecules will exhibit the rotational spectrum since homonuclear diatomic molecules do not possess permanent dipole moment)

NON RIGID ROTOR

It is observed that in the pure rotational spectra of a diatomic molecule when the bond in it is considered as a rigid, the spacing between successive lines is same, i.e. 2B cm^{-1}. However, the assumption that the bond is rigid is only an approximation. Actual bond is not a rigid bond and the bond length is not constant. It increases with rotations and is elastic. In a rapidly rotating molecule, there is always a tendency of the bond to stretch due to centrifugal effects. Hence, the moment of inertia increases with the rotational energy. This causes rotational levels to be same what closer as the J value increases. For example, consider the spectrum of hydrogen fluoride

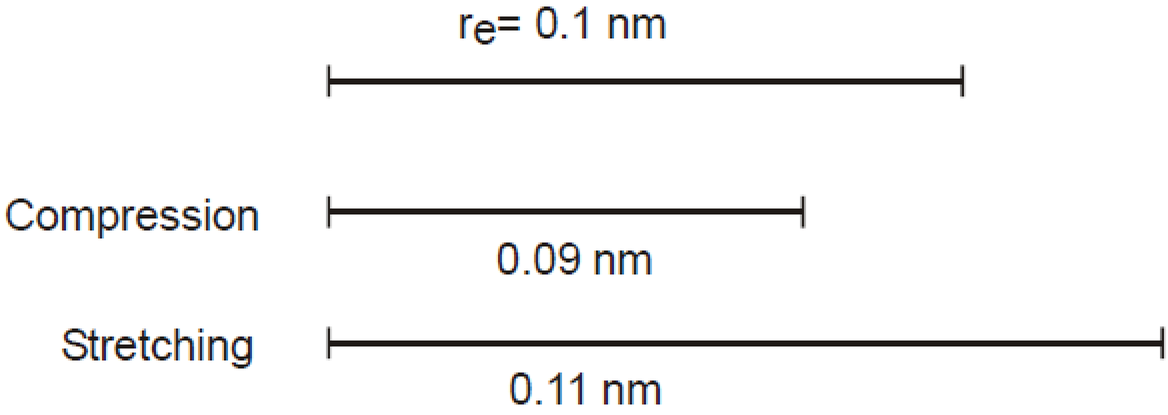


	$B\left(cm^{-1}\right)$	$r(nm)$
$J=0 \rightarrow J=1$	20.56	0.0929
$J=1 \rightarrow J=2$	20.48	0.0931
$J=2 \rightarrow J=3$	20.43	0.0932
$J=4 \rightarrow J=5$	20.31	0.0935
.	.	.
.	.	.
.	.	.
.	.	.
$J=10 \rightarrow J=11$	18.91	0.0969

It is evident that the separation between successive lines (and hence the apparent B value) decreases steadily with increasing J.

NON RIGID ROTOR

The reason for this decrease may be seen if we calculate internuclear distance from the B values. In simple harmonic motion a molecular bond is compressed and extended an equal amount on each side of the equilibrium distance and the average value of the distance is therefore unchanged, the average value for a bond of equilibrium length 0.1 nm vibrating between the limits 0.09 and 0.11 nm, we have



NON RIGID ROTOR

$$\langle r \rangle_{av} = \frac{0.09+0.11}{2} = 0.1\,nm = r_e$$

But we know $B = \frac{h}{8\pi^2 Ic} = \frac{h}{8\pi^2 c\mu r^2}$

$B \propto \frac{1}{r^2}$ [since all other quantities are independent of vibration

$$\left\langle \frac{1}{r^2} \right\rangle_{av} = \frac{\left(\frac{1}{0.09}\right)^2 + \left(\frac{1}{0.11}\right)^2}{2} = 103.05\,(nm)^2$$

$$\therefore \quad r_{av} = \sqrt{\frac{1}{103.5}} = 0.0985\,nm$$

The value differ from r_e*. The difference, through small, is not negligible compared* with the precision with which B can be measured spectroscopically. In fact the real situation is more different. For chemical bonds we know stretching is easier than compression, so the result r_{av} *being greater than* r_{eq} *. Thus the more vibration (i.e. higher J value), the difference* is more due to high rotation.

NON RIGID ROTOR

From Schrödinger equation for a non-rigid rotator in simple harmonic force field.

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

K = force constant

$$\varepsilon_J = \frac{E_J}{hc} = \frac{h^2}{8\pi^2 Ihc} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 Khc} J^2 (J+1)^2 \ cm^{-1}$$

Relationship between B & D

$$B = \frac{h^2}{8\pi^2 Ihc} = \frac{h}{8\pi^2 Ic}$$

$$K = 4\pi^2 c^2 \overline{w}^2 \mu$$

$$D = \frac{h^4}{32\pi^4 I^2 r^2 Khc} = \frac{h^3}{32\pi^4 I^2 r^2 Kc} = \frac{h^3}{8\times 2\times 4\times 8\pi^6 I^3 c^3} \frac{16\pi Ic^2}{Kr^2}$$

$$= B^3 \times \frac{16\pi^2 Ic^2}{Kr^2} = B^3 \times \frac{16\pi^2 \times \mu r^2 c^2}{4\pi^2 \overline{w}^2 c^2 \mu r^2} = \frac{B^3 \times 4}{\overline{w}^2} = \frac{4B^3}{\overline{w}^3}$$

$$\therefore \ \boxed{D = \frac{4B^3}{\overline{w}^2}}$$

$[\because \underset{frequency}{w} = \frac{\overline{w}}{c}$

$\omega =$ frequency

$\overline{\omega} =$ wave number

$\because \ \overline{\omega} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$

$\therefore \ k = 4\pi^2 \overline{\omega}^2 mc^2]$

$[\because \ B^3 = \frac{h^3}{8\times 8\times 8\pi^6 I^3 c^3}]$

$[\because I = \mu r^2 ; k = 4\pi^2 \overline{\omega}^2 \ c^2 \ \mu]$

NON RIGID ROTOR

If B = 10 cm^{-1} & $\overline{w} = 10^3\ \mathrm{cm}^{-1}$

$$D \approx \frac{\left(10\ cm^{-1}\right)^3}{\left(10^3\right)^2} = \frac{10^3}{10^6} \approx 10^{-3}\ cm^{-1}$$

So $D << B$

i.e. D is much smaller than B. For small values of J, the correction term is equation (1.9) is negligibly small. For higher values of J, say 10 or more the value of D may be appreciable. The selection rule $\Delta J = \pm 1$ is of course still valid. The spectral line given by the equation

$$BJ(J+1) - DJ^2(J+1)^2\ cm^{-1}$$

$$\varepsilon_J = B_J(J+1) - DJ^2(J+1)^2\ cm^{-1}$$

NON RIGID ROTOR

If D is neglected, the spectral lines occur at interval of 2B.

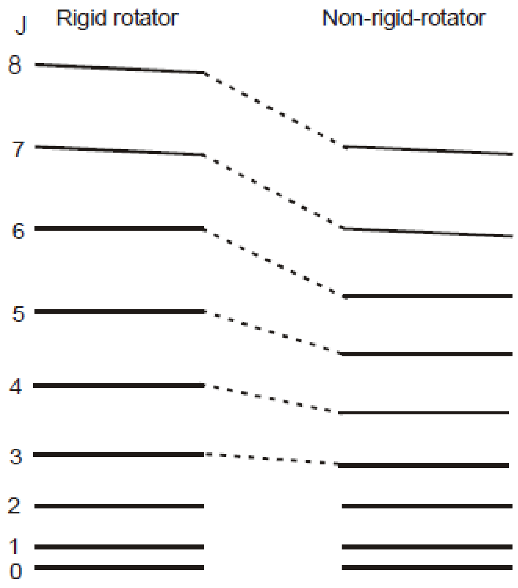


Fig. 1.3 (a)

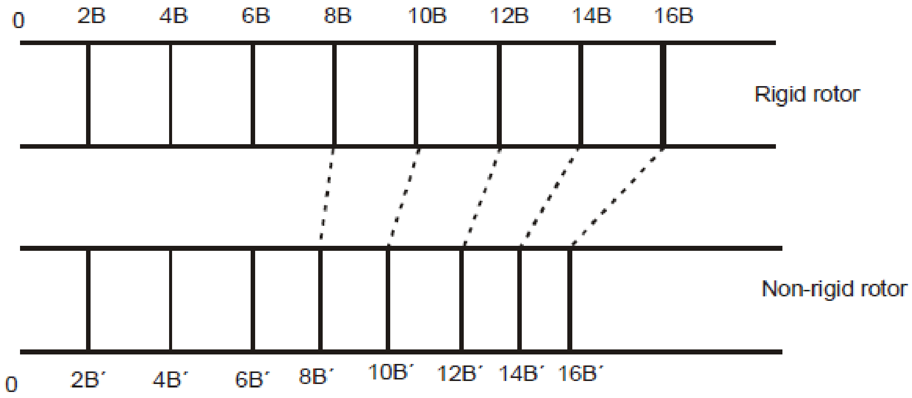


Fig. 1.3(b)

Fig. 1.3 (a) rotational energy levels and 1.3 (b) allowed spectral lines for rigid and non-rigid rotors.

NON RIGID ROTOR

For the an harmonic oscillator the expression (1.9) should be modified as

$$\varepsilon_J = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + KJ^4(J+1)^4 \ cm^{-1} \qquad \ldots(1.10)$$

where the constants H, K etc, are dependent on the molecule. These constants H, K etc. are very small compared to D and hence can be neglected.

The value of D is also given by

$$D = \frac{16B^3\pi^2\mu c^2}{K} = \frac{4B^3}{\bar{w}^2}$$

NON RIGID ROTOR

The spectral line $\overline{v}_J$ is given by the equation

$$E_{J+1} - E_J = \overline{v}_J = 2B(J+1) - 4D(J+1)^3 \ cm^{-1} \qquad \ldots(1.11)$$

If D is neglected, the spectral lines occur at intervals of 2B. The rotational spectrum of a diatomic molecule such as HF, CO etc. can be fitted to the equation (1.11).

Information from D

1. Determination of J value
2. Determination of vibrational frequency

$$D = \frac{4B^3}{\overline{w}^2}$$

$$\overline{w}^2 = \frac{4B^2}{D}$$

In HF B = 41.122 cm^{-1}

$$D = 8.52 \times 10^{-3} cm^{-1}$$

$$\overline{w}^2 = \frac{4 \times (41.122)^3}{8.52 \times 10^{-3} \ cm^{-1}} \left(cm^{-1}\right)^3 = 16.33 \times 10^6 \left(cm^{-1}\right)^2$$

$$\overline{w} = 4.050 \times 10^3 \ cm^{-1} = 4050 \ cm^{-1}$$

The accurate value is 4138.3 cm^{-1}. The 2% inaccuracy in the present calculation is due partly to the assumption of simple harmonic motion and partly to the very small and hence relatively inaccurate, value of D.

The force constant follow directly

$$K = 4\pi^2 c^2 \overline{w}^2 \mu = 960 \ Nm^{-1}$$

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