## Unit - II

Molecular Spectroscopy :
Rotational and Vibrational Spectroscopy

## Objectives :

Calculate the bond lengths of diatomics
from the value of their rotational
Constant

① Outline the selection rules for
rotational and vibrational spectra
and rationalize the role of the
molecular dipole moment in
selection rules.

Distinguish bet^n the energy levels of
a rigid and non rigid rotors

Distinguish bet^n harmonic and
anharmonic vibrations

Sketch qualitatively rotational -
Vibrational spectrum of a diatomic,

Calculate relative populations of
rotational and vibrational energy
levels.

Identify the I.R. freq^n where
simple functional groups
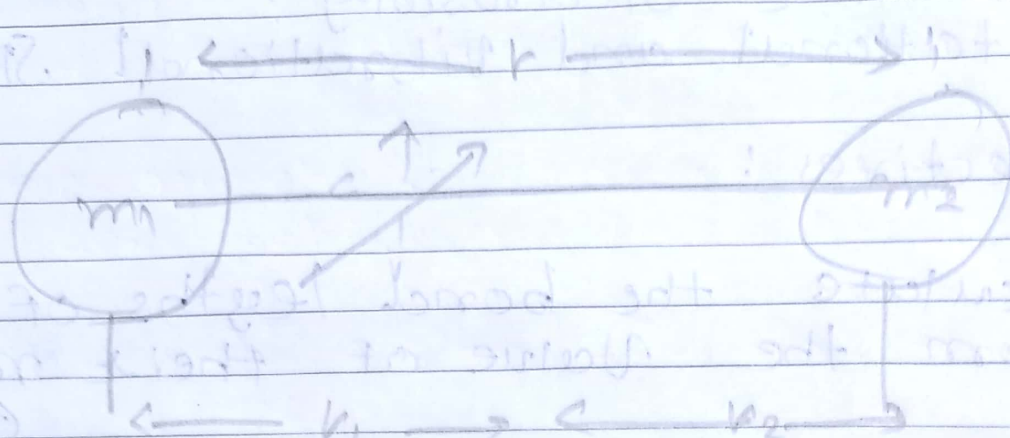absorb light

# Rotational Spectra of diatomics



Fig 1 : Rigid diatomic with masses $m_1$ and $m_2$ joined by a thin rod of length $r = r_1 + r_2$. the Centre of mass is at C.

The Centre of mass is defined by equating the moments on both segments of the molecular axis

$$m_1 r_1 = m_2 r_2$$

The moment of inertia is defined by

$$I = m_1 r_1^2 + m_2 r_2^2$$

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

$$= r_1 r_2 (m_1 + m_2)$$

Since $m_1 r_1 = m_2 r_2 = m_2 (r - r_1)$

$$(m_1 + m_2) r_1 = m_2 r.$$

Therefore,

$$r_1 = \frac{m_2 h}{m_1 + m_2} \qquad r_2 = \frac{m_1 r}{m_1 + m_2}$$

Substitute in eqn(1) we get

$$I = \frac{m_1 m_2 r^2}{(m_1 + m_2)} = \mu r^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

where $\mu$, the reduced mass is given

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

The rotation of a diatomic is equivalent to a "rotation" of a mass $\mu$ at a distance of $r$ from the origin C.

$$K.E = \frac{L^2}{2I} \qquad L, \text{ angular momen} = I\omega \text{ in radian/sec}$$

$$L^2 Y_{lm} = l(l+1) Y_{lm}$$

where $Y_{lm}$ are the spherical harmonics. The quantized rotational energy levels for this diatomic

$$E_J = \frac{h^2}{8\pi^2 I} (J(J+1))$$

energy diff$^n$ bet$^n$ two rotational
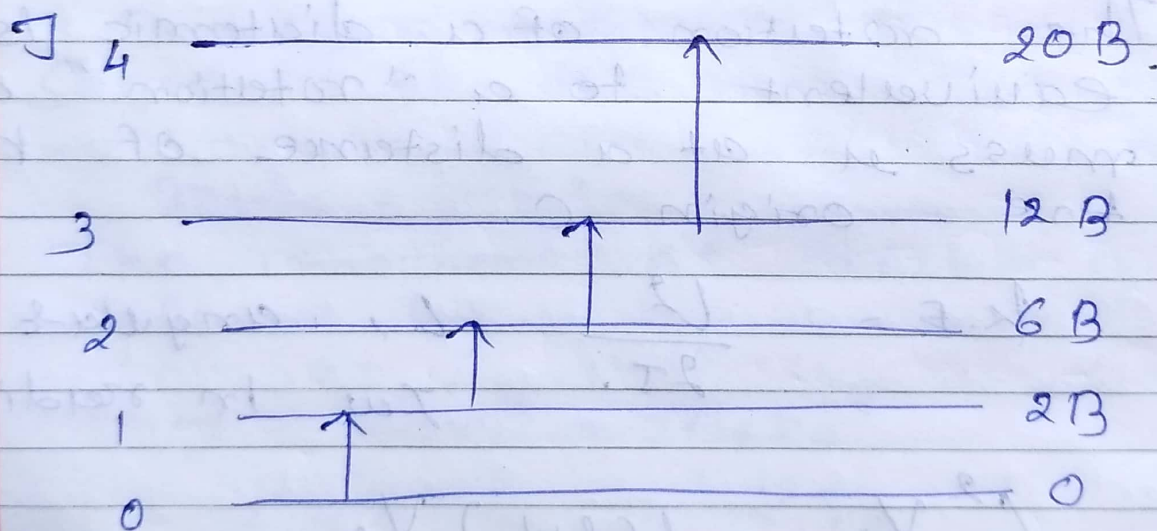level is usually expressed in cm$^{-1}$

wave number Corresponding to
given $\Delta E$ is given by

$$U = \frac{\Delta E}{hc} \quad cm^{-1}$$

$$E_J = B(J(J+1)) \quad where$$

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

rotational energy levels
of a diatomic molecule.



Rotational energy levels of a
rigid diatomic molecule and
the allowed transitions

$$\Delta J = \pm 1$$

molecule has to possess a dipole
moment,

dipolar molecule rotates, Rotating
dipole Constitutes the transition
dipole operator $\mu$.
Molecules such as HCl and CO will
Show rotational Spectra, while
$H_2$, $Cl_2$, and $CO_2$ will not

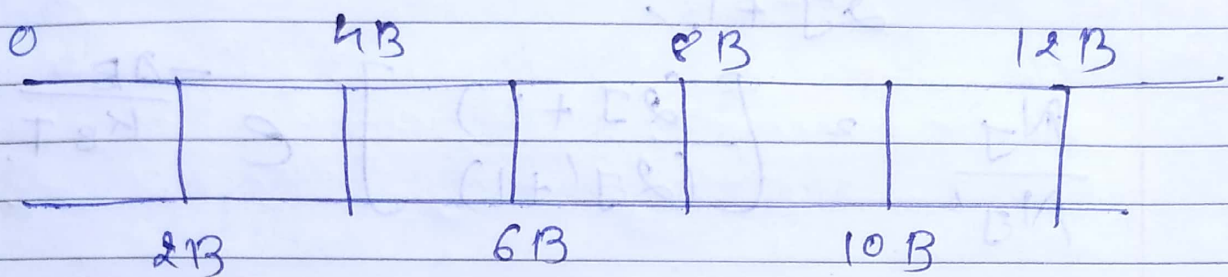| 0 | 4B | 8B | 12B |
|---|----|----|-----|
| 2B | 6B | 10B | |

fig: Rotational Spectra of a rigid diatomic
values of B are in $cm^{-1}$.

Example :
  calculate the value of I and
of CO , $B = 1.92118 \, cm^{-1}$

Sol$^n$ :
$$I = \frac{h}{8\pi^2 B c}$$

$$= \frac{6.626 \times 10^{-34}}{8 \times 3.1415^2 \times 1.92118 \times 3 \times 10^{10}}$$

$$= 1.45579 \times 10^{-46} \, Kg\,m^2.$$

$I = \mu r^2.$

$$r^2 = \frac{I}{\mu} = \frac{1.45579 \times 10^{-46}}{1.13826 \times 10^{-27}}$$

$\boxed{r = 1.131 \, \mathring{A}}$

The rotational levels are degenerate Just as there are three p orbitals for $J=1$, for $J=1$ there are 3 degenerate rotational states.

degeneracy for given value of J is $2J+1$.

$$\frac{N_J}{N_{J'}} = \left[\frac{(2J+1)}{(2J'+1)}\right] e^{\frac{-\Delta E}{K_B T}}$$

When molecules rotates with great speeds, they cannot not treated as a rigid any more. There are distortions due to Centrifugal and other forces.

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

Centrifugal distortion Constant D is given by

$$D = h^3/(32\pi^4 I^3 r^2 kc) \quad cm^{-1}$$

# Vibrational's and Rotations of a diatomic.

$$E_v = (u + \tfrac{1}{2}) h v \qquad v = 0, 1, 2, \ldots$$

The quantized Vibration energies $E_v$ of a harmonic oscillator are

→ The vibrational freq$^n$ $v$ realated to the force constant $k$ through.

$$v = \frac{1}{(2\pi)} \sqrt{\frac{k}{\mu}}, \quad Hz.$$

Vibrational motion occurs under the action of binding potential energy (P.E) curve for a harmonic Oscillator is given by
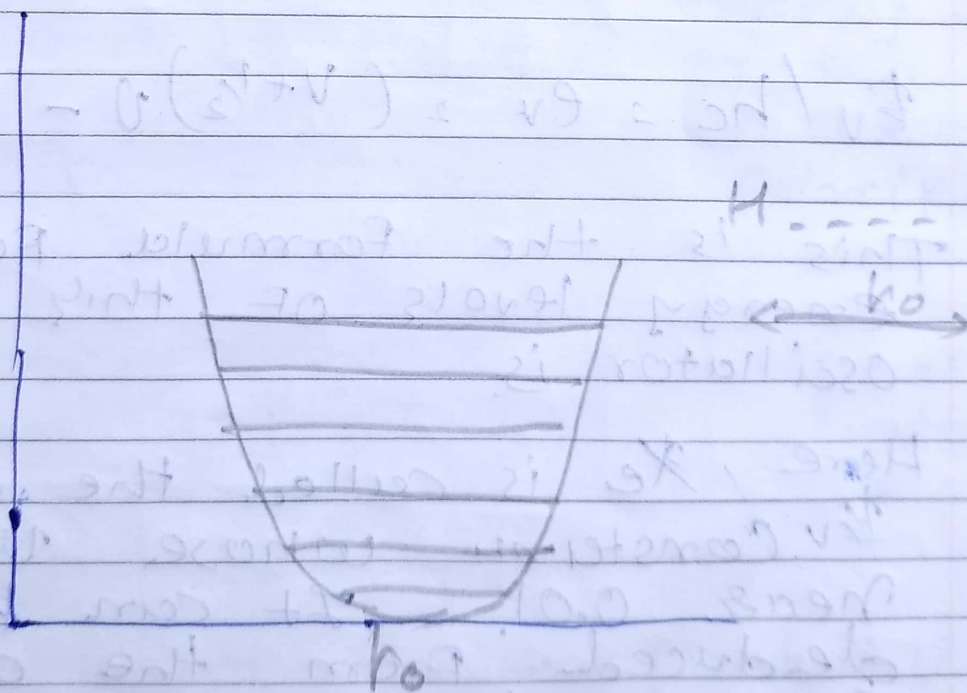


fig I: Potential energy of harmonic oscillator $V = k(r - r_0)^2$

→ on either sides of the equilibrium bond length, $r_0$, the PE rises as a symmetric quadric function.

→ Selection rules for the harmonic oscillator are

$$\Delta v = \pm 1.$$

In actual diatomic potential is anharmonic, A good description of a anharmonic oscillator is given by Morse function.

$$P.E = Deq \left[1 - exp. \{a(r_0 - r)\}\right]^2 \quad -2)$$

In eq (2), Dea is a depth of the P.E curve, $r_0$ is bond length.

$$E_v/hc = ev = (v+\tfrac{1}{2})\upsilon - \upsilon(v+\tfrac{1}{2})^2 \upsilon x_e$$
$$cm^{-1}.$$

This is the formula for the energy levels of this anharmonic oscillator is.

Here, $x_e$ is called the anharmonicity $E_v$ constant whose value is near 0.01. It can be easily deduced from the above formula that the vibrational energy levels for large $v$ start bunching together.

Dea

P.E.

3
2
1
0

$r_0$
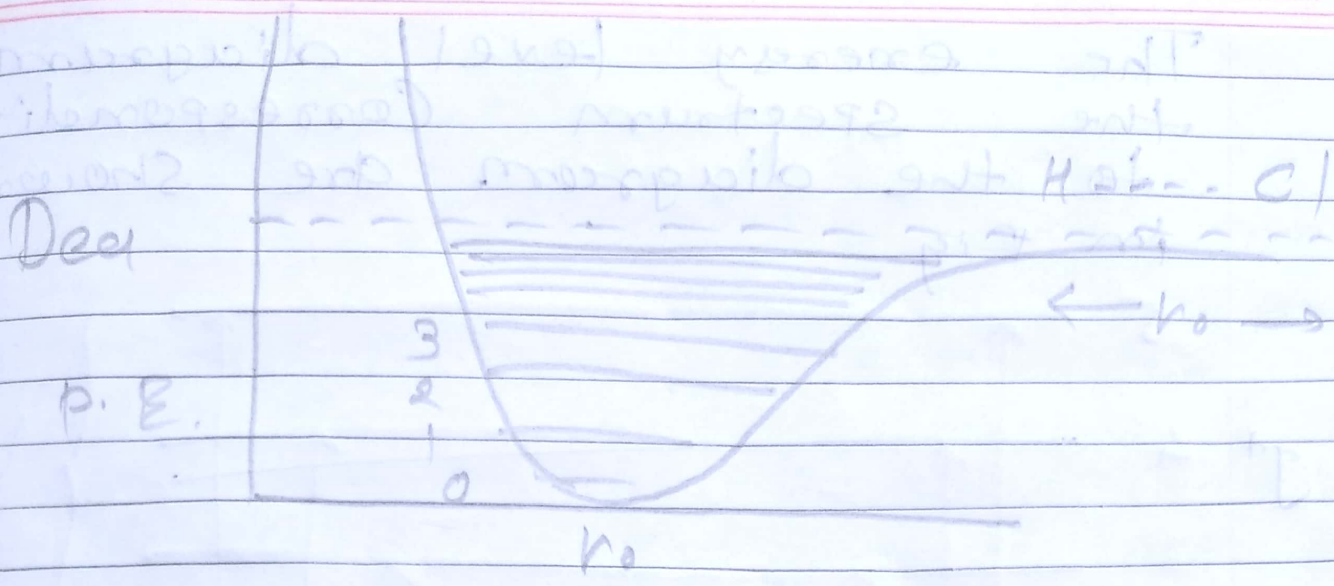
Morse Potential and the energy levels there in,

Note the difference bet$^n$ the dissociation energy Do and the depth Dea.

All molecules have a minimum of the zero point energy of $hv/2$ Corresponding to the $v=0$ state. This is a consequence of the uncertainty principle.
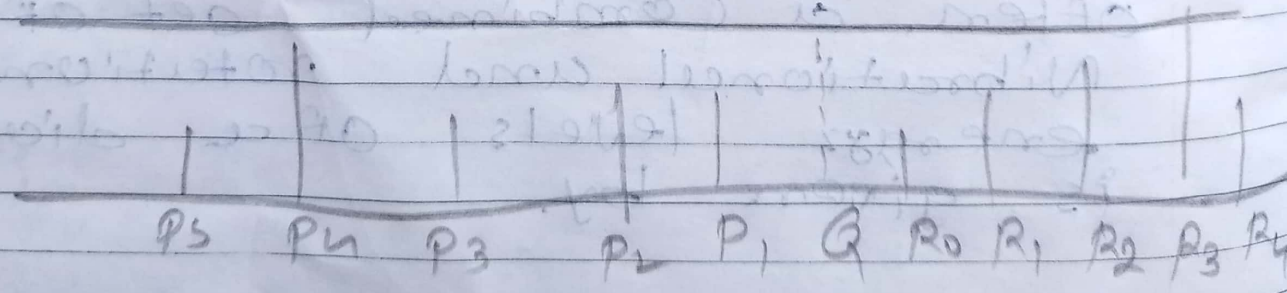
Often a Combined set of Vibrational and rotational energy levels of a diatomic is given by.

$$E_{total} = BJ(J+1) + (N+\tfrac{1}{2})v$$

$$- Xe (v+\tfrac{1}{2})^2 v, \ cm^{-1}$$

The energy level diagram and the spectrum corresponding to the diagram are shown in fig



$J^*$ 5 4 3 2 1 0

$J^*$ 5 4 3 2 1 0

Energy levels

The Spectra

P5  P4  P3  P2  P1  Q  R0  R1  R2  R3  R4
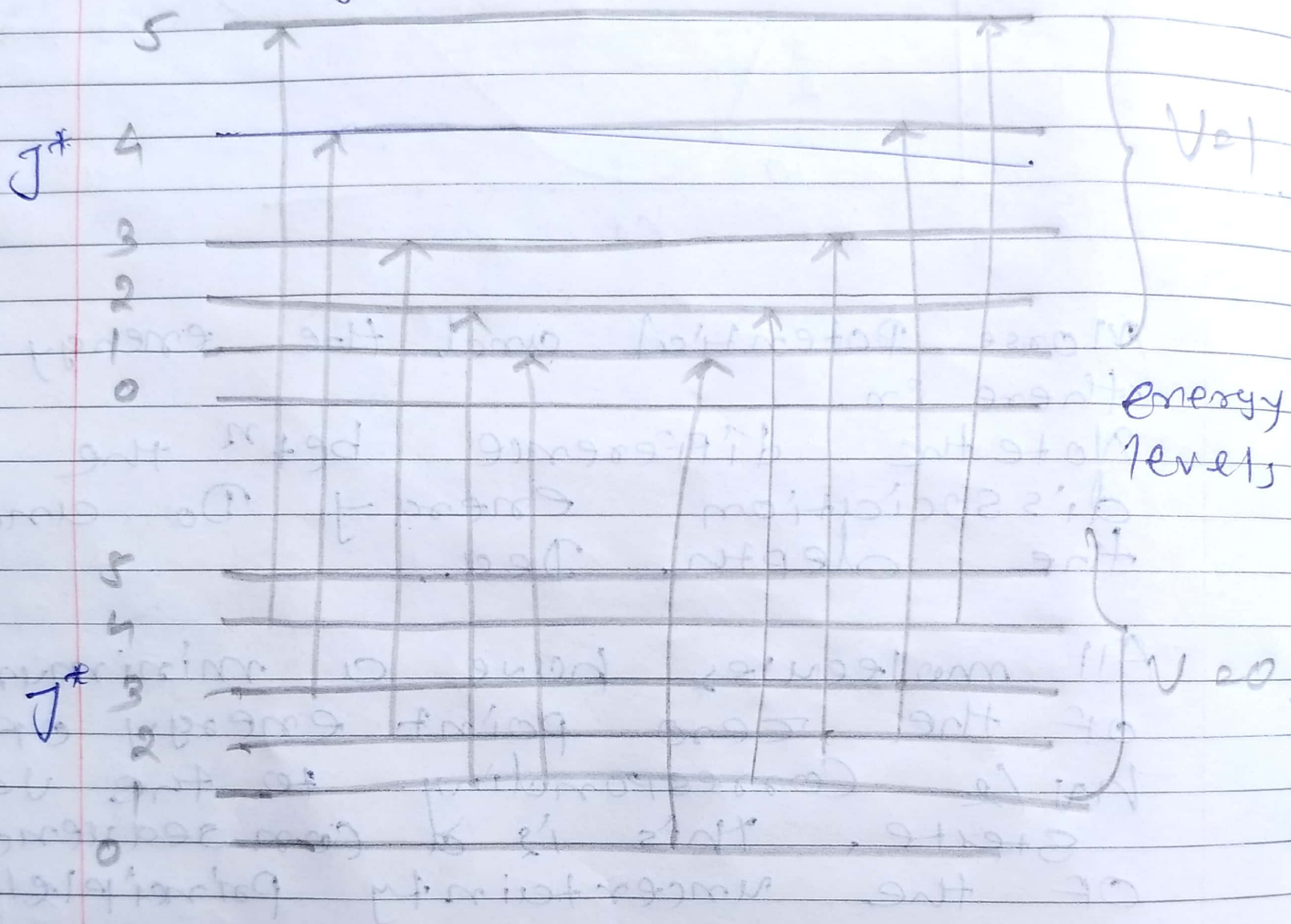
The Selection rules are.

$$\Delta v = \pm 1, \pm 2 \cdots$$

$$\Delta J = \pm 1, \quad \Delta J = \pm 1 \text{ Corresponds to the}$$

R branch. on the right at higher frequencies and.

$$\Delta J = J'' - J' = -1$$ Corresponds to the P branch. On the left

The dashed line Q for which $\Delta J = 0$, is not seen. the difference bet^n $R_0$ and $P_1$ is $4B$ and the diff^n bet^n adjacent R. lines, and adjacent. P lines is $2B$.