

ROTATIONAL SPECTRA

MICROWAVE SPECTROSCOPY

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Rotation Of Molecules

- ❑ Spectroscopy in the microwave region is concerned with the study of rotating molecules
- ❑ Rotation of 3D body may be quite complex
- ❑ Rotational components about three mutually perpendicular directions through the centre of gravity - the principal axis of rotation.
- ❑ Three principal moments of inertia I_A , I_B , and I_C designated.

Classification of molecules

(i) Linear molecules:

- ✓ Atoms are arranged in a straight line.
- ✓ e.g. HCl or OCS

The three directions of rotation may be taken as :

(a) about the bond axis,

(b) end-over-end rotation in the plane of the paper,

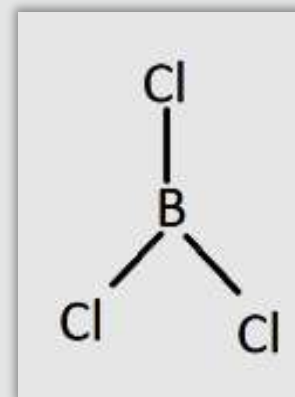
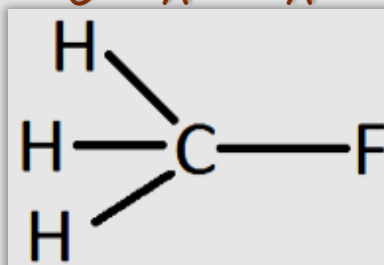
(c) end-over-end rotation at right angles to the plane. Here

$$I_A = 0 \text{ and } I_B = I_C$$

(ii) **Symmetric top:** Consider a molecule such as methyl fluoride, three hydrogen atoms are bonded tetrahedrally to the carbon

The moment of inertia about the C-F bond axis is now not negligible, however, because it involves the rotation of three comparatively massive hydrogen atoms of this axis

Symmetric tops: $I_B = I_C \neq I_A$ $I_A \neq 0$

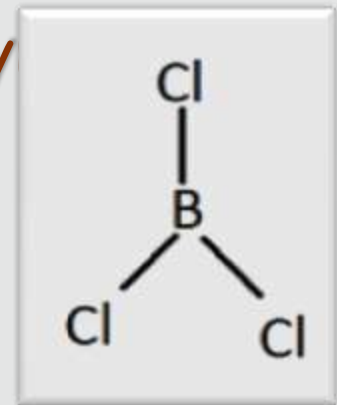


Two subdivisions of this class

- Methyl fluoride above, $I_B = I_C > I_A$, then the molecule is called *prolate symmetric top*
- If $I_B = I_C < I_A$, it is referred to as *oblate*

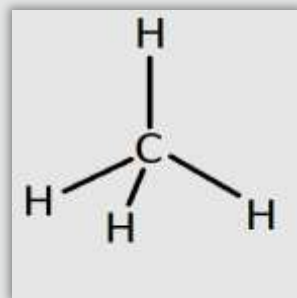
An example of the latter type is boron trichloride, which, as shown, is planar and symmetric

$$I_A = 2I_B = 2I_C$$



(iii) Spherical top: when a molecule has all three moments of inertia identical, it is called spherical tops.

e.g, CH₄

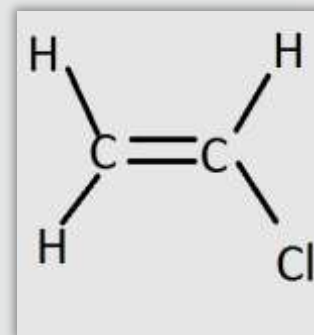
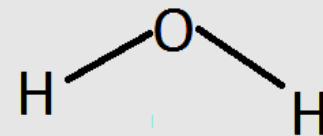


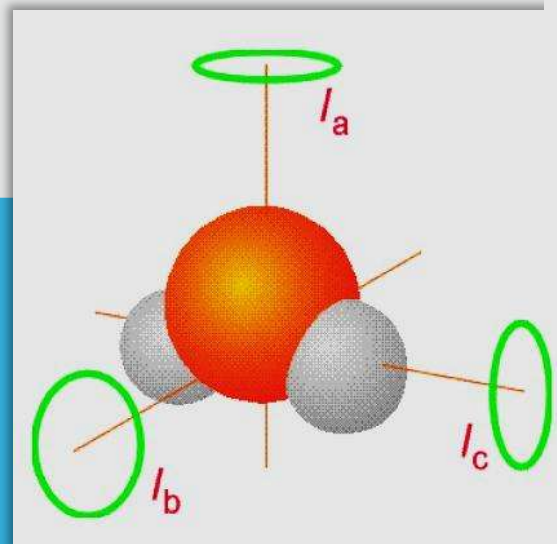
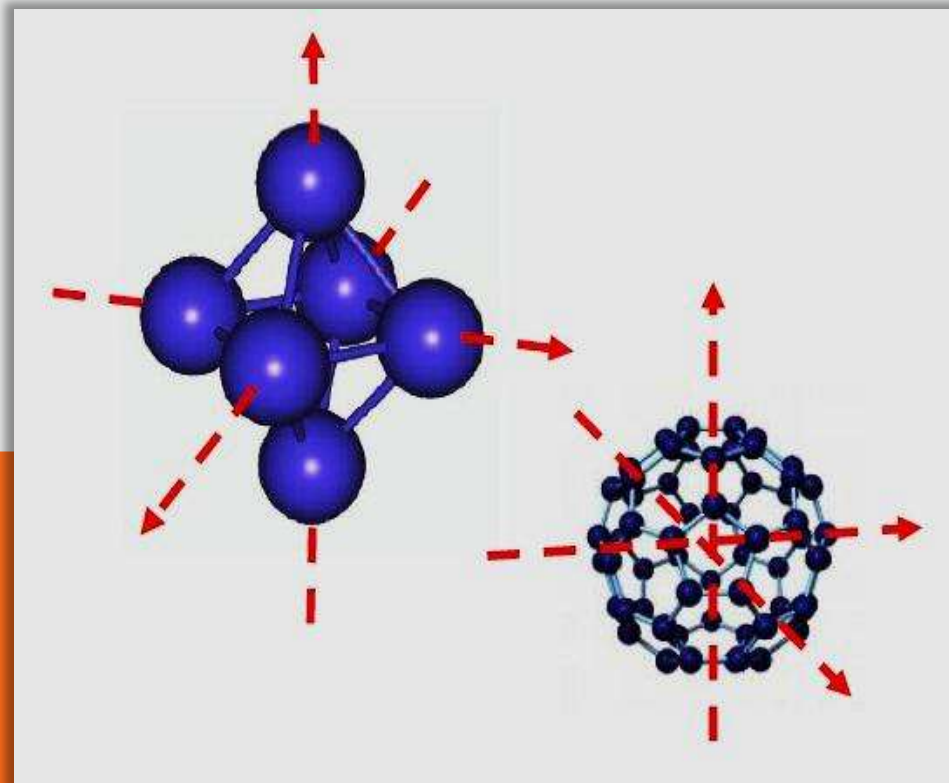
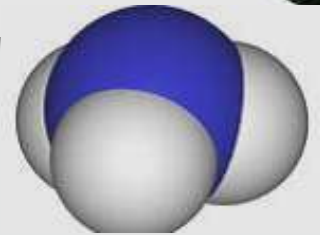
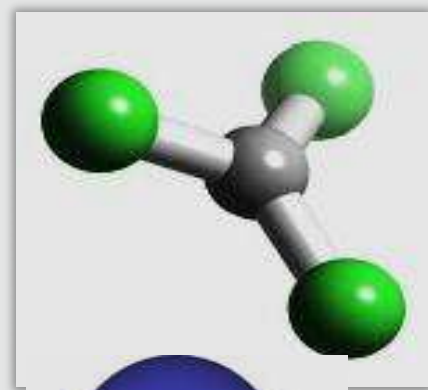
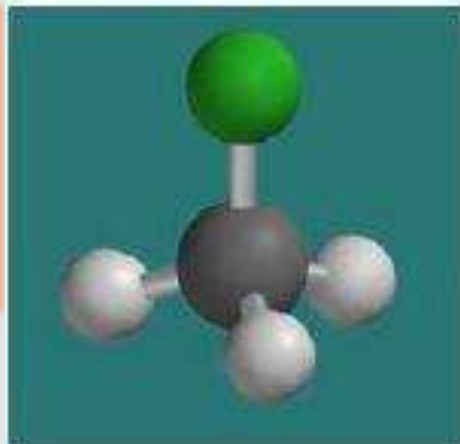
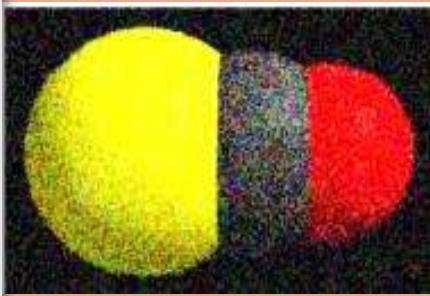
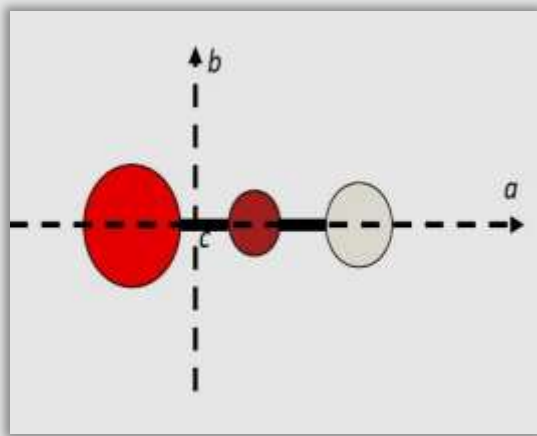
$$I_A = I_B = I_C.$$

(iv) Asymmetric top: These molecules, to which the majority of substance belong, have all three moments of inertia different:

$$I_A \neq I_B \neq I_C$$

Simple examples are H₂O and CH₂=CHCl





Rotational Spectra: Molecular Requirements

- ❑ Spectroscopy in the microwave region is concerned with the study of rotating molecules.
- ❑ Only molecules that have a permanent dipole moment can absorb or emit electromagnetic radiation in such transitions.
- ❑ In the rotation of HCl, fluctuation seen to be exactly similar to the fluctuating electric field of radiation.
- ❑ Thus interaction can occur, energy can be absorbed or emitted and the *rotation gives rise to a spectrum.*

WHICH TYPE OF MOLECULE DOESN'T SHOW ROTATIONAL SPECTRUM AND WHY.....???

- ❑ In homonuclear molecules like N_2 & O_2 , no change occur in dipole moment during the rotation.
- ❑ Linear diatomic molecules are rotationally inactive for rotation about the bond axis.
 - i. The moment of inertia is very small (zero) about the bond axis.
 - ii. No change in dipole occurs when it is rotating about bond axis.
- ❑ Homonuclear molecules, however show rotational Raman spectra (which is arises due to the polarisability of the molecules.)

Techniques And Instrumentation

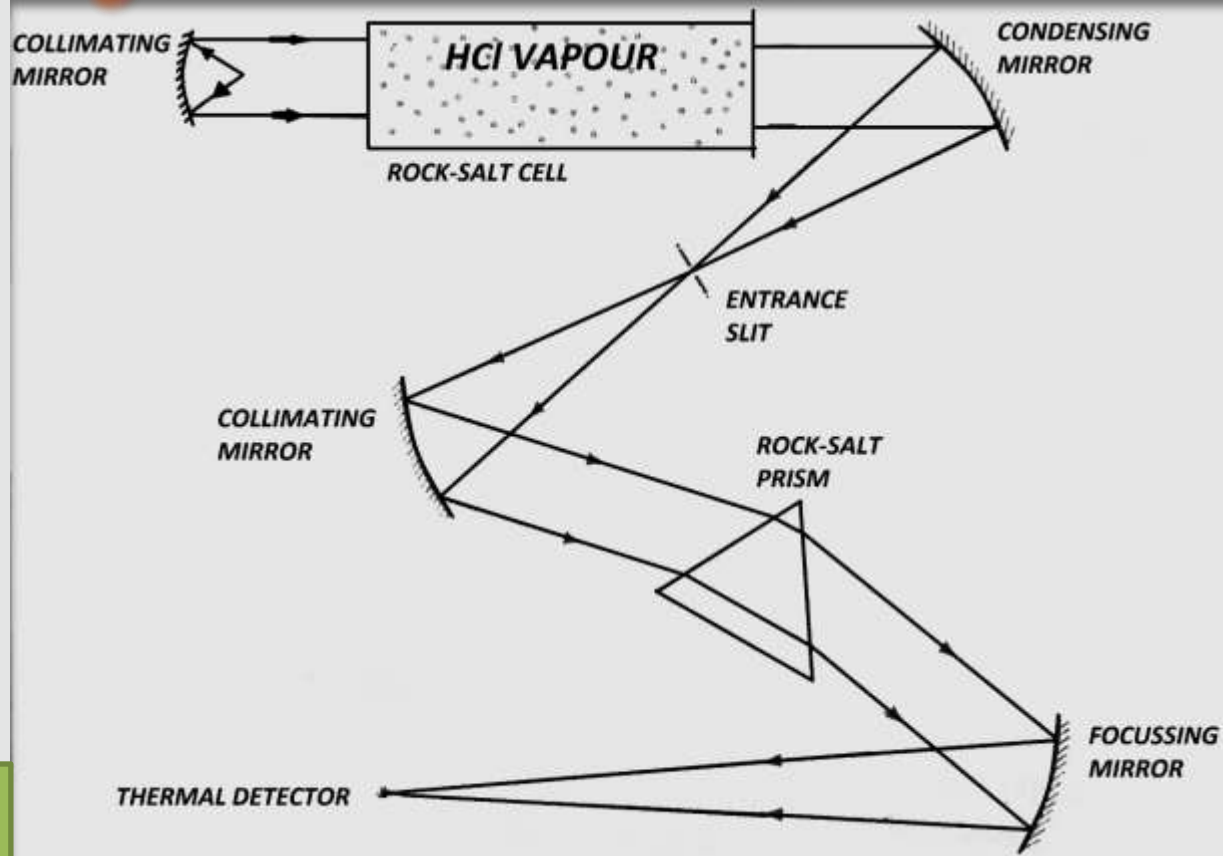
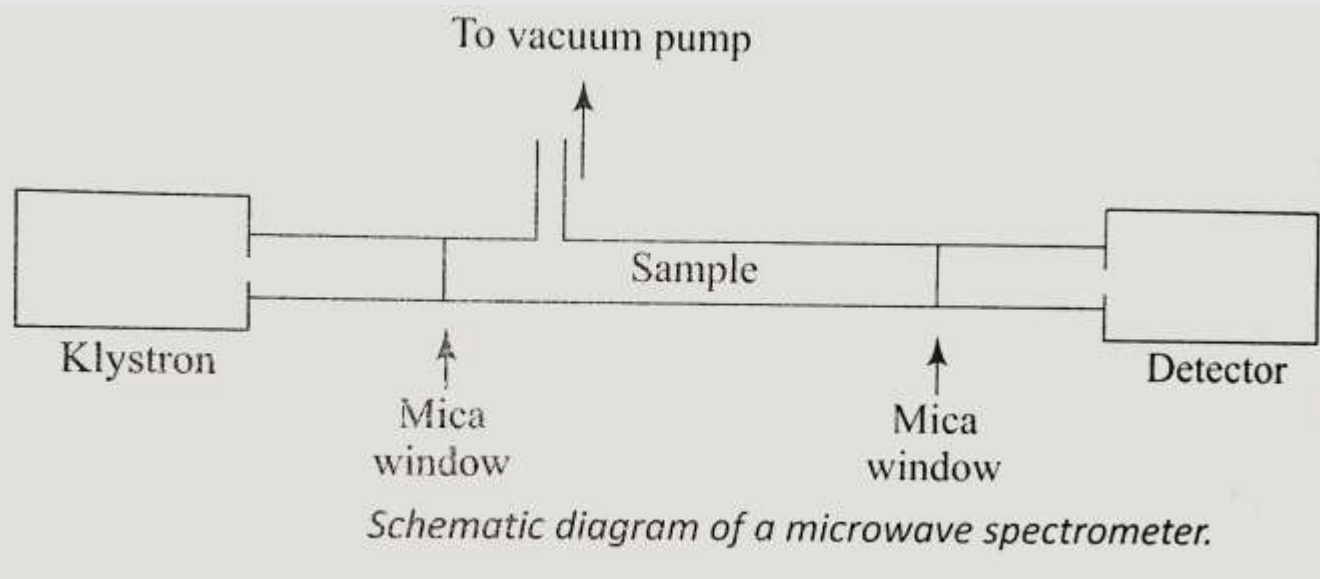


Fig.1

The basic requirements for observing pure rotational spectra in absorption are a source of continuous radiation in the proper infrared region, a dispersive device and a detector.

- ❑ Radiation from the source is taken, which passes through the HCl vapour
- ❑ The transmitted beam falls on a condensing mirror
- ❑ The collimated beam passes through a rock-salt prism and is brought to a focus at the thermal detector by means of a focusing mirror



I. Source and monochromator: Klystron valve is monochromatic source, emits radiation over only a very narrow freq. range.

II. Beam direction: Achieved by use of waveguides (rectangular) inside which radiation is confined.

III. Sample and sample space

IV. Detector

Molecule As A Rigid Rotator: Diatomic Molecule

The simplest model of a rotating molecule is
that of a rigid rotator

By the definition of Centre of mass, we have

$$M_1 r_1 = M_2 r_2$$

Also $r_1 + r_2 = r$

From these two equation, we have

$$r_1 = \frac{M_2}{M_1 + M_2} r \quad \text{and} \quad r_2 = \frac{M_1}{M_1 + M_2} r$$

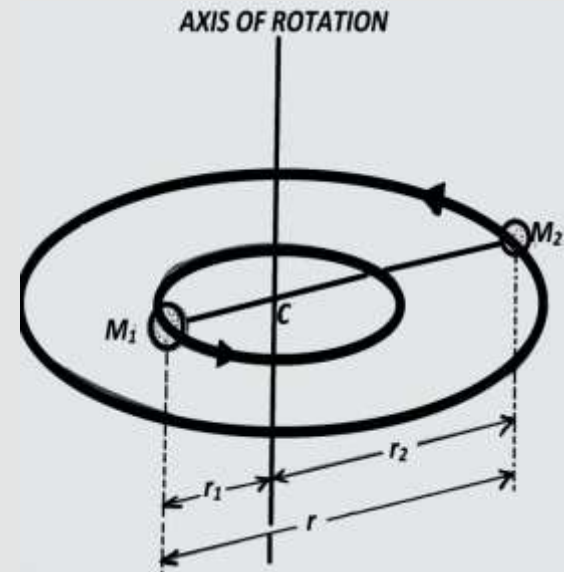


Fig.2

Now, the moment of inertia of the molecule about the axis of rotation is given by

$$\begin{aligned} I &= M_1 r_1^2 + M_2 r_2^2 \\ &= \frac{M_1 M_2}{M_1 + M_2} r^2 \end{aligned}$$

But $\frac{M_1 M_2}{M_1 + M_2}$ is the reduced mass μ of the molecule. Then

$$I = \mu r^2$$

Thus the diatomic molecule is equivalent to a single point mass μ at a fixed distance r from the axis of rotation. Such a system is called a *rigid rotator*.

Schrodinger equation for a rigid rotator, which is

$$\Delta^2 \psi + \frac{8\pi^2 \mu}{h^2} E \psi = 0$$

The potential energy term V has been taken zero because r is fixed.

In spherical polar coordinate system

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 \mu}{h^2} E \psi = 0 \quad \text{----- (i)}$$

Using separable variable method

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

On solving by separable variable method, we have two equations

$$\frac{d^2\Phi}{d\phi^2} = -M^2\Phi \quad \text{----- (ii)}$$

And,

$$\frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \left(\frac{8\pi^2 IE}{h^2} - \frac{M^2}{\sin^2\theta} \right) \Theta = 0 \quad \text{----- (iii)}$$

The solution of the Φ -equation

$$\Phi_m = \frac{1}{\sqrt{2\pi}} e^{iM\phi} \quad \text{----- (iv)}$$

On solving Θ -eq.

$$1-x^2 \frac{d^2P}{dx^2} - 2x \frac{dP}{dx} + \left(\frac{8\pi^2 IE}{h^2} - \frac{M^2}{1-x^2} \right) P = 0$$

This eq. is identical to the associated Legendre's differential equation, provided

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

Or,

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

In this expression, h is Planck's constant and I is moment of inertia, either I_B or I_C , since both are equal.

The quantity J , which takes integral values from zero upwards, is called the Rotational Quantum Number.

Spectrum Of Rigid Rotator

In the rotational region, spectra are usually discussed in terms of wave numbers.

$$\varepsilon = \frac{E_J}{hc} = \frac{h}{8\pi^2 Ic} J(J+1) \text{ cm}^{-1} \quad (J=0, 1, 2, \dots) \quad \text{----- (vi)}$$

Where c is velocity of light, I is here expressed in cm s^{-1} .

$$\varepsilon = BJ(J+1) \text{ cm}^{-1} \quad \text{----- (vii)}$$

Where B , *the rotational constant*, is given by

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

From eq.(vii) allowed energy levels

- For $J = 0$, ϵ is zero-molecule is not rotating
- For $J=1$, the rotational energy is $\epsilon_1 = 2B$ and a rotating molecule has its lowest angular momentum
- For increasing J values, ϵ_J may have no limit to the rotational energy

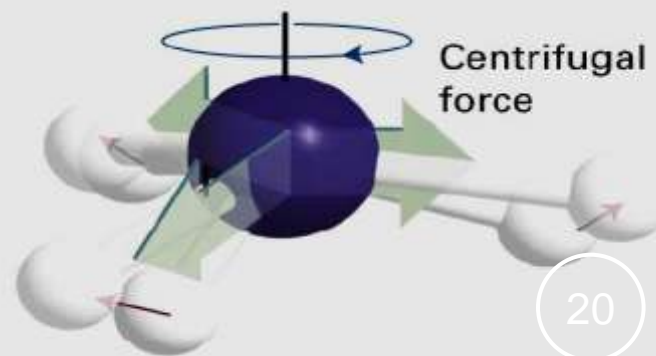
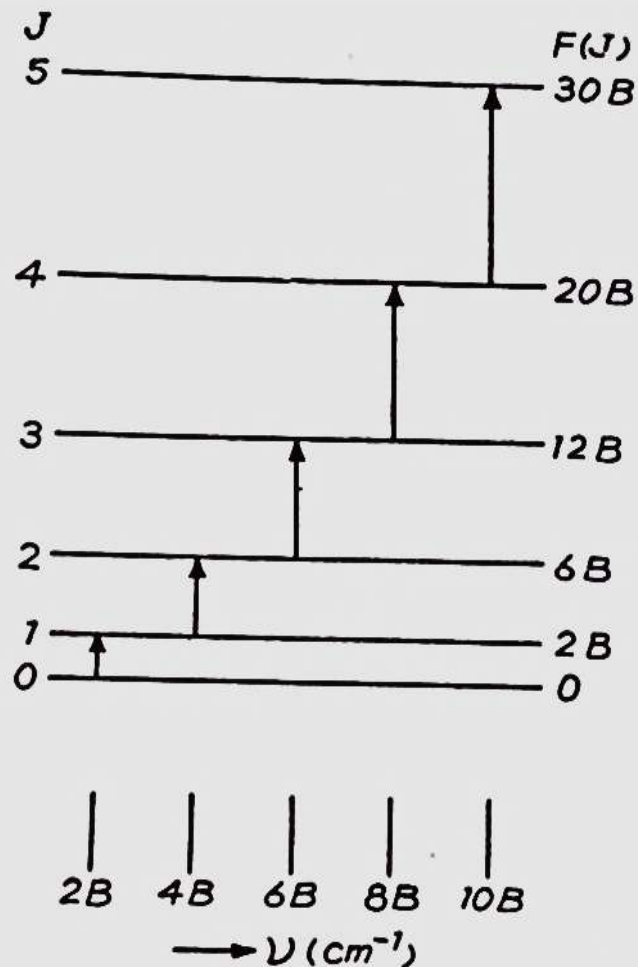


Fig.3

If we imagine the molecule to be in the the ground state, in which no radiation occurs

To raise the molecule to $J= 1$ state energy absorbed will be

$$\epsilon_{J1} - \epsilon_{J0} = 2B - 0 = 2B \text{ cm}^{-1}$$

$$\bar{\nu}_{J=0 \rightarrow J=1} = 2B \text{ cm}^{-1}$$

Further for $J=1$ to $J=2$

$$\bar{\nu}_{J=1 \rightarrow J=2} = 4B \text{ cm}^{-1}$$

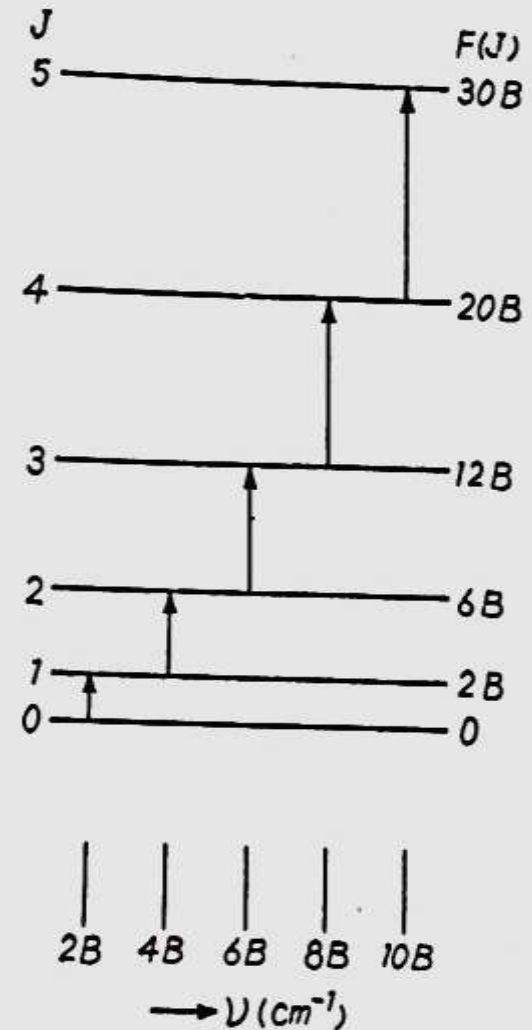


Fig.3.1

In general,

$$\bar{\nu}_{J \rightarrow J+1} = B [J+1(J+2) - BJ(J+1)]$$

Or,

$$\bar{\nu}_{J \rightarrow J+1} = 2B [J+1] \text{ cm}^{-1} \quad \text{-----(viii)}$$

Thus a step wise raising of the rotational energy results in an absorption spectrum consisting of lines at $2B, 4B, 6B, \dots \text{ cm}^{-1}$.

we need only consider transition in which J changes by one unit - all other transitions being *spectroscopically forbidden*, such a result, it is called a **selection rule**,

Selection rule: $\Delta J = \pm 1$

Quantization Of Rotational Energy

Energy and angular momentum of rotator

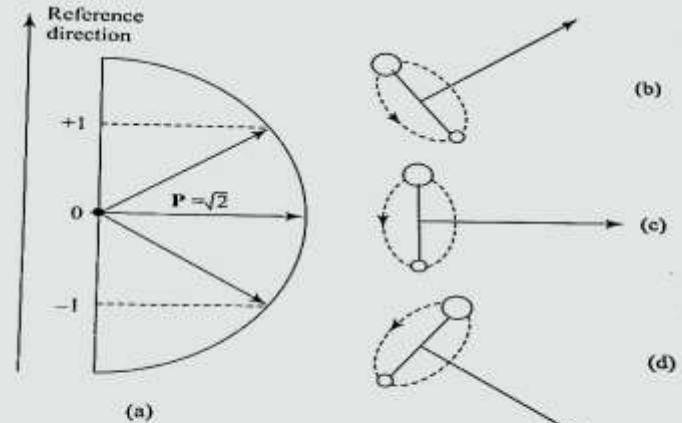
$$E = \frac{1}{2} I \omega^2 \quad P = I \omega$$

The energy level expression

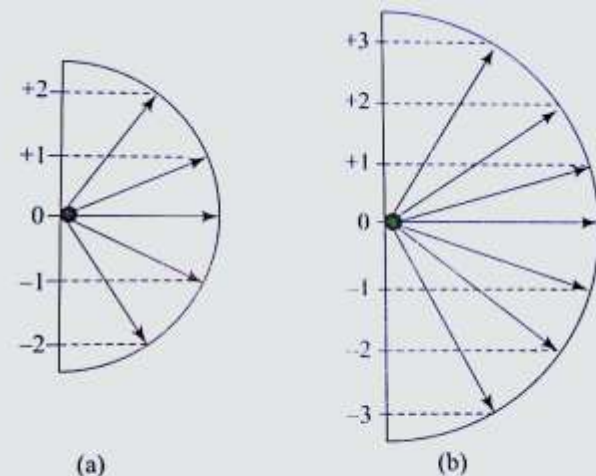
$$2EI = J(J+1) \frac{h^2}{4\pi^2}$$

Or,

$$P = \sqrt{J(J+1)} \text{ units}$$



The three degenerate orientations of the rotational angular momentum vector for a molecule with $J = 1$.



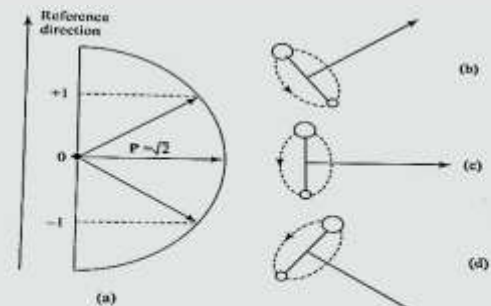
The five and seven degenerate rotational orientations for a molecule with $J = 2$ and $J = 3$, respectively.

Intensity Of Spectral Lines

□ For the transition other than $\Delta J = \pm 1$ (which are forbidden), the transition probability is zero.

And the probability of all changes with $\Delta J = \pm 1$ is almost the same.

□ This does not mean that all spectral lines will be equally intense.



The three degenerate orientations of the rotational angular momentum vector for a molecule with $J = 1$.

- ❑ In normal gas sample, there will be different numbers of molecule in each level therefore different total numbers of molecules will carry out transition between the various levels.
- ❑ Since the intrinsic probabilities are identical, the line intensities will be directly proportional to the initial numbers of molecules in each level.
- ❑ The first factor governing the population of the level is the Boltzmann distribution.

$$N_j/N_0 = \exp \left[-E_j/kT \right] = \exp \left[-BhcJ(J+1)/kT \right]$$

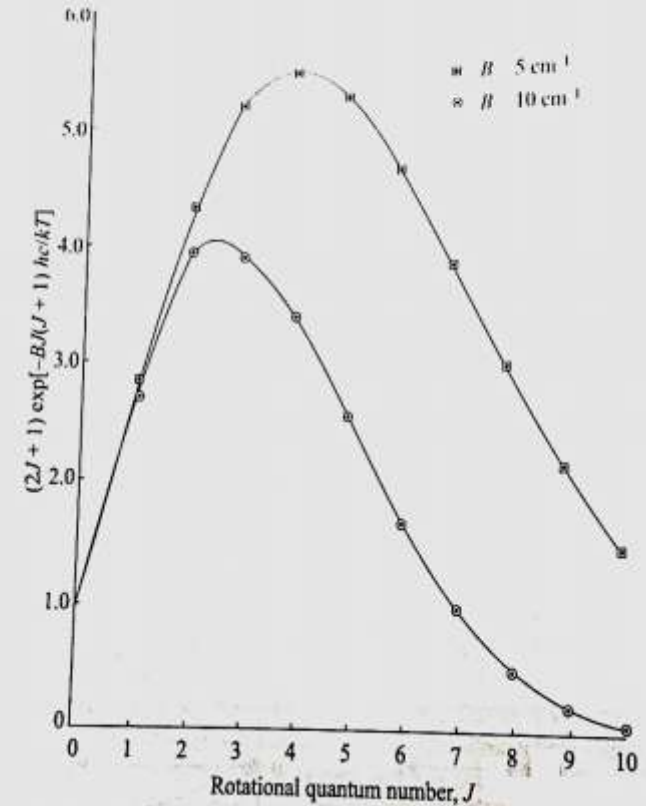
- ❑ The second factor governing the population of the levels is the possibility of degeneracy in the energy states.

- Each level J is $(2J+1)$ degenerate
- population is greater for higher J states.

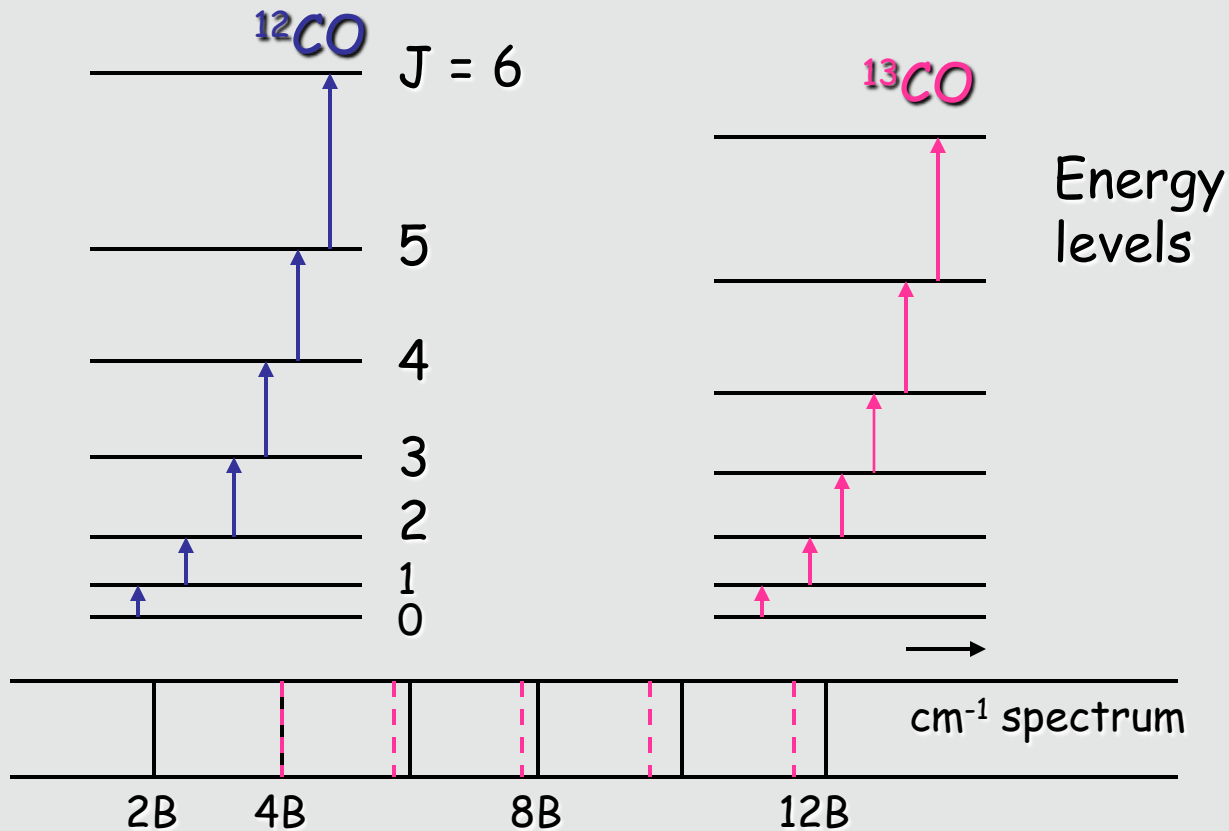
Total relative population at energy

$$E_J \propto (2J+1) \exp(-E_J / kT)$$

$$\text{Maximum population: } J = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$$



Effect Of Isotopic Substitution



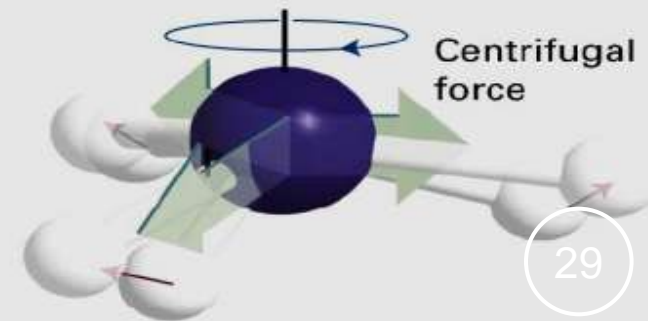
From $^{12}\text{C}^{16}\text{O} \rightarrow ^{13}\text{C}^{16}\text{O}$, mass increases, B decreases ($\propto 1/I$), so energy levels lower.

Non Rigid Rotator

- ❖ In practice, spectrum lines are not exactly equidistant; separation decreases with increasing J .
- ❖ Molecules stretched and become non rigid with increasing rotation.

A correction term, containing the centrifugal distortion constant, D , which corrects for the fact that the bond is

not rigid.



Spectrum Of Non-rigid Rotator

The Schrodinger eq. may set up for non rigid rotator

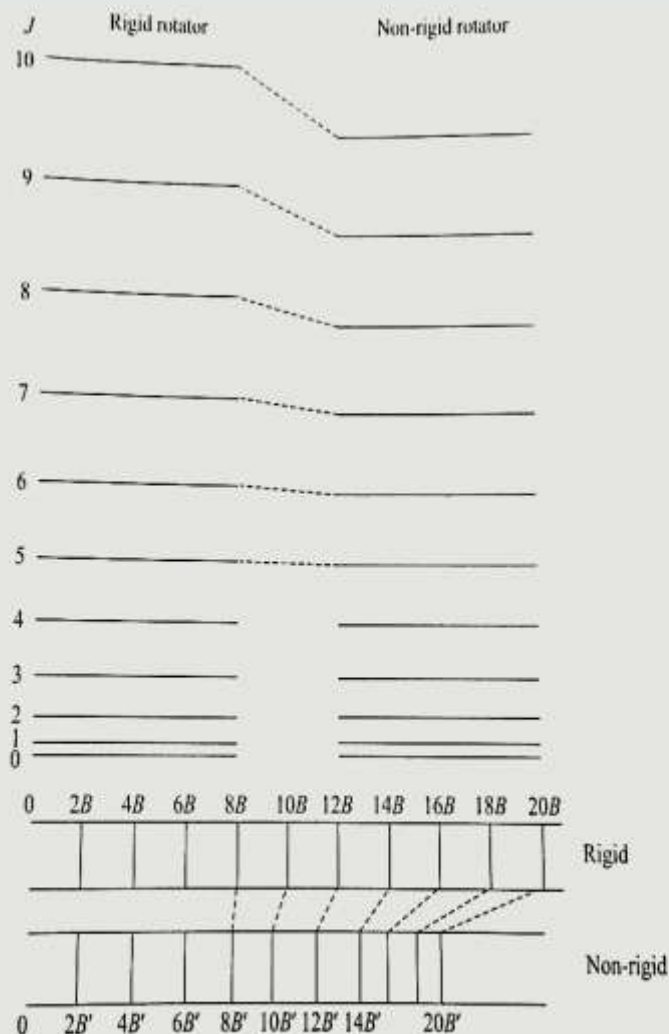
$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^2 I^2 r^2 k} J^2(J+1)^2 J$$

Or,

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

Where D is centrifugal distortion constant, given by,

$$D = \frac{h^3}{32\pi^4 I^2 r^2 k c} \text{ cm}^{-1}$$



The change in rotational energy levels and spectrum when passing from a rigid to a non-rigid diatomic molecule. Energy levels on the right are calculated using $D = 10^{-3} B$.

Applications Of Microwave Spectroscopy

Chemical analysis by microwave spectroscopy

- ❑ The rotational spectrum of a substance at room temperature can be examined accurately.

Molecular identification in space

- ❑ Electronic spectroscopy has been able to detect the presence of various atoms, ions and few radicals in the light of stars but recently simple stable molecules in space detected by using microwave spectroscopy.
- ❑ 130 molecules / ions have been identified in interstellar space by their rotational emission spectra (rf-astronomy).

H ₂	C ₃	c-C ₃ H	C ₅	C ₅ H	C ₆ H	CH ₃ C ₃ N	CH ₃ C ₄ H	CH ₃ C ₅ N?	HC ₉ N	CH ₃ OC ₂ H ₅	<u>HC₁₁N</u>
AlF	C ₂ H	l-C ₃ H	C ₄ H	l-H ₂ C ₄	CH ₂ CHCN	HCOOCH ₃	CH ₃ CH ₂ CN	(CH ₃) ₂ CO			
AlCl	C ₂ O	C ₃ N	C ₄ Si	C ₂ H ₄	CH ₃ C ₂ H	CH ₃ COOH?	(CH ₃) ₂ O	NH ₂ CH ₂ COOH			
C ₂	C ₂ S	C ₃ O	l-C ₃ H ₂	CH ₃ CN	HC ₅ N	<u>C₇H</u>	CH ₃ CH ₂ OH	<u>CH₃CH₂CHO</u>			
CH	CH ₂	C ₃ S	c-C ₃ H ₂	CH ₃ NC	HCOCH ₃	<u>H₂C₆</u>	HC ₇ N				
CH ⁺	HCN	C ₂ H ₂	CH ₂ CN	CH ₃ OH	NH ₂ CH ₃	<u>CH₂OHCO</u>	C ₈ H				
CN	HCO	CH ₂ D ⁺	CH ₄	CH ₃ SH	<u>c-C₂H₄O</u>	<u>CH₂CHCHO</u>					
CO	HCO ⁺	HCCN	HC ₃ N	HC ₃ NH ⁺	<u>CH₂CHOH</u>						
CO ⁺	HCS ⁺	HCNH ⁺	HC ₂ NC	HC ₂ CHO							
CP	HOC ⁺	HNCO	HCOOH	NH ₂ CHO							
CSi	H ₂ O	HNCS	H ₂ CHN	C ₅ N							
HCl	H ₂ S	HOCO ⁺	H ₂ C ₂ O	<u>HC₄N</u>							
KCl	HNC	H ₂ CO	H ₂ N ₂ CN								
NH	HNO	H ₂ CN	HNC ₃								
NO	MgCN	H ₂ CS	SiH ₄								
NS	MgNC	H ₃ O ⁺	H ₂ COH ⁺								

NIST & National Radio Astronomy Lab.

Microwave oven

Do you know what is the basic principle of cooking in microwave oven????

- Its mode of operation depends entirely upon the absorption by the food of microwave radiation.

THANK YOU