

B.Sc. III year Physical Chemistry

# Molecular Spectroscopy

Dr. Pokalwar R. U.  
Assistant Professor  
Degloor College, Degloor

***Spectroscopy is that branch of science which deals with the study of interaction of electromagnetic radiations with matter.***

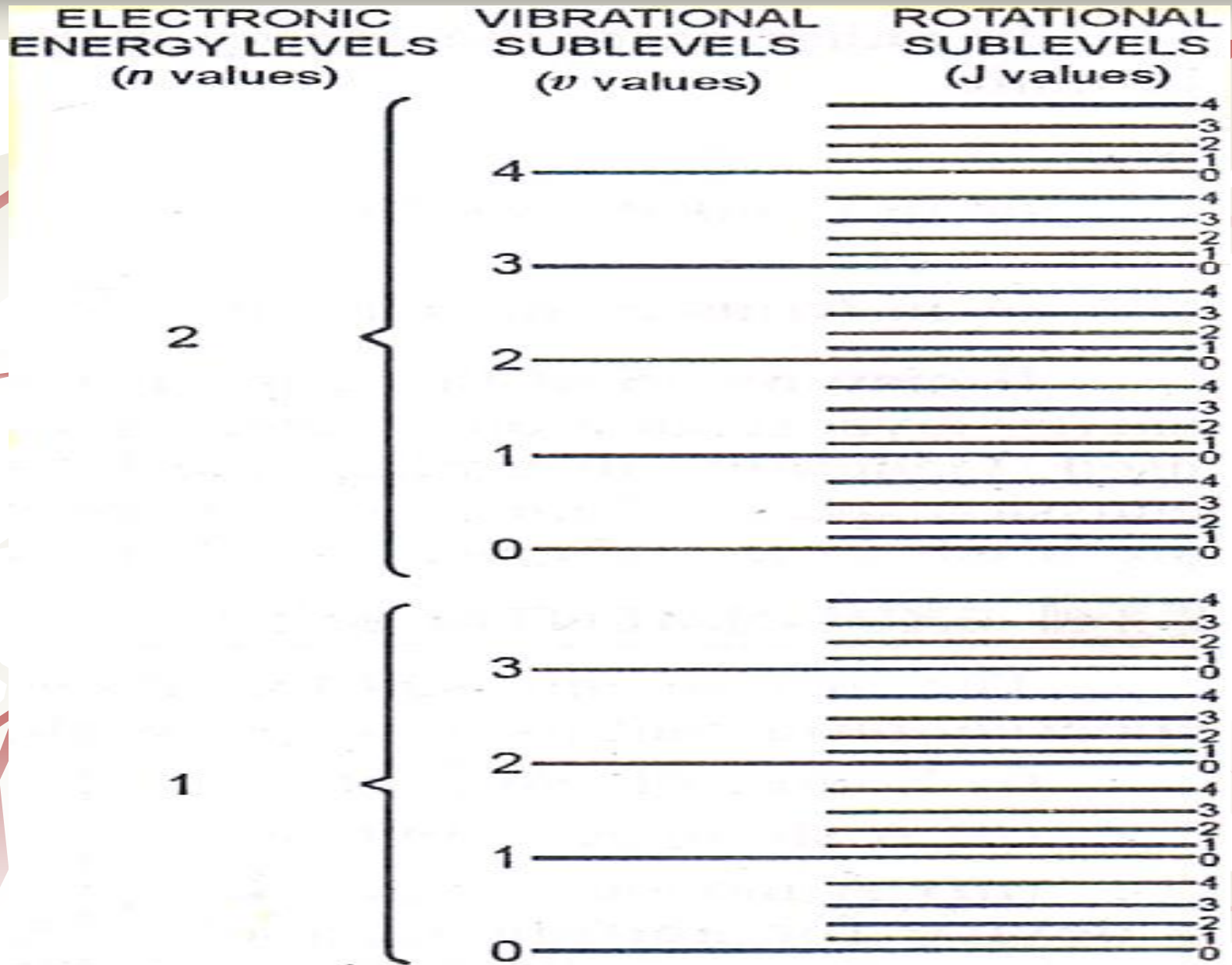
## **ELECTROMAGNETIC RADIATION**

The term electromagnetic radiation represents the radiant energy emitted from any source in the form of light, heat etc. Some important characteristics of these electromagnetic radiations are given below :

- (i) They have dual character i.e. particle character as well as wave character. For example, a beam of light is a stream of particles called photons moving through the space in the form of waves.
- (ii) These waves are associated with electric and magnetic fields oscillating perpendicular to each other and also perpendicular to the direction of propagation.
- (iii) All electromagnetic radiations travel with the velocity of light.

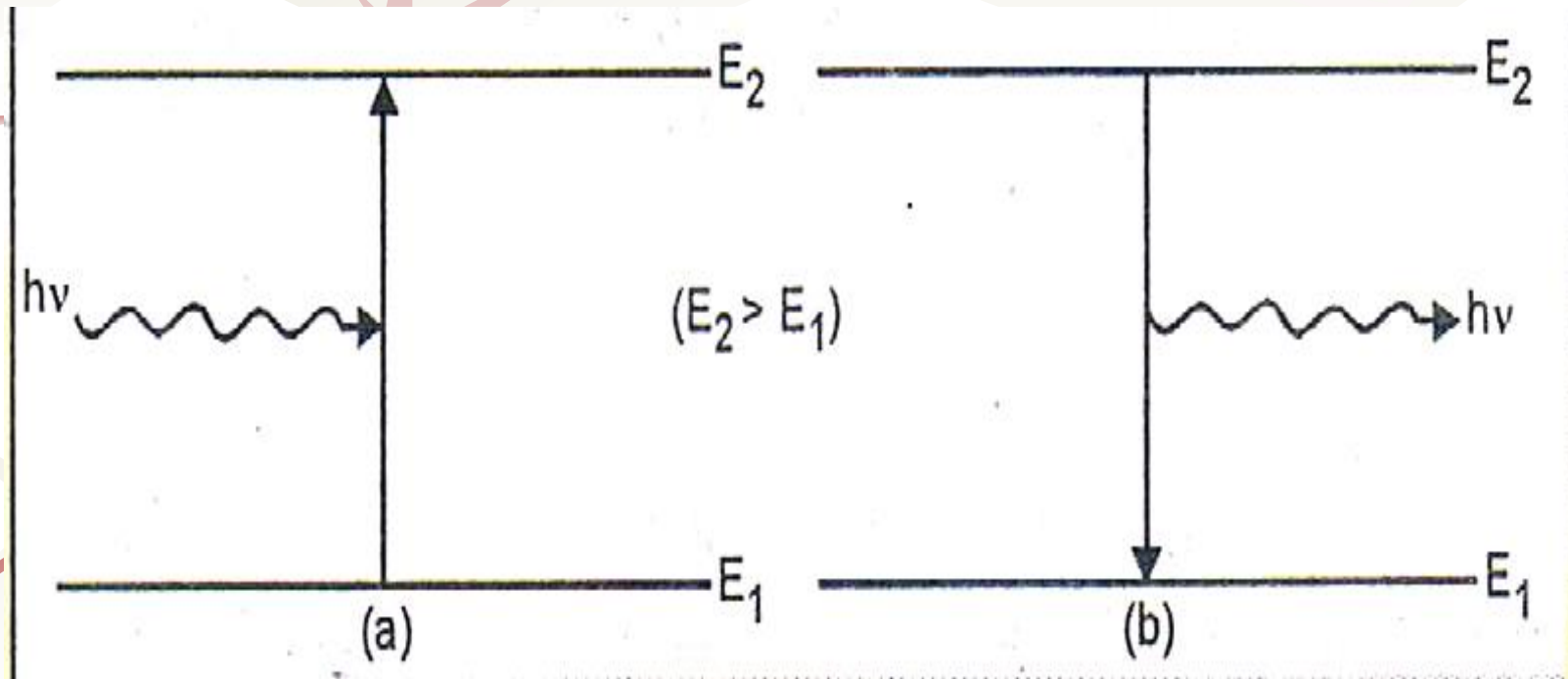
# REGIONS OF ELECTROMAGNETIC SPECTRUM

<i>Electromagnetic radiation</i>	<i>Wavelength range in Å (1 Å = 10<sup>-10</sup> m)</i>	<i>Frequency range in cycles/sec or Hertz or sec<sup>-1</sup></i>	<i>Source</i>
Cosmic rays	0 to 0.001	$\infty$ to $3 \times 10^{21}$	Present in the outer space.
Gamma rays	0.0001 to 0.1	$3 \times 10^{22}$ to $3 \times 10^{19}$	Radioactive substances.
X-rays	0.001 to 100	$3 \times 10^{20}$ to $3 \times 10^{12}$	Bombardment of certain metals with cathode rays.
Ultraviolet rays	1 to 3800	$3 \times 10^{12}$ to $7.9 \times 10^{14}$	Hydrogen or Deuterium discharge tube or a component of sun's rays.
Visible light	3800 to 7600	$7.9 \times 10^{14}$ to $4 \times 10^{14}$	Sun or any incandescent solid.
Infrared rays	7600 to $3 \times 10^7$	$4 \times 10^{14}$ to $1 \times 10^{11}$	By vibration of molecules e.g., by heating rods of special materials.
Microwaves	$3 \times 10^8$ to $3 \times 10^{11}$	$1 \times 10^{10}$ to $1 \times 10^7$	By the oscillations of electrons in a wire i.e., from alternating electric current.
Radiowaves or TV waves	$3 \times 10^7$ to $3 \times 10^{14}$	$1 \times 10^{11}$ to $1 \times 10^4$	



**MOLECULAR ENERGY LEVELS**

# ABSORPTION AND EMISSION SPECTROSCOPY



- (a) Transition Involving absorption of photon  
(b) Transition involving emission of photon.

According to Born-Oppenheimer approximation, the total energy of a molecule is the sum of translational, rotational, vibrational and electronic energies, i.e.

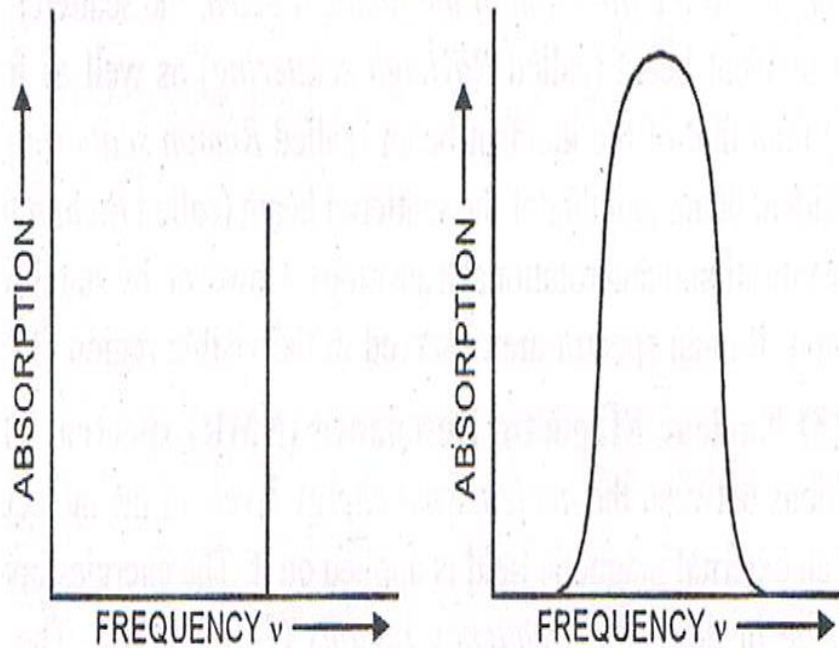
$$E = E_t + E_r + E_v + E_e$$

It is found that the translational energy is negligibly small. Hence Born-Oppenheimer approximation can be written as

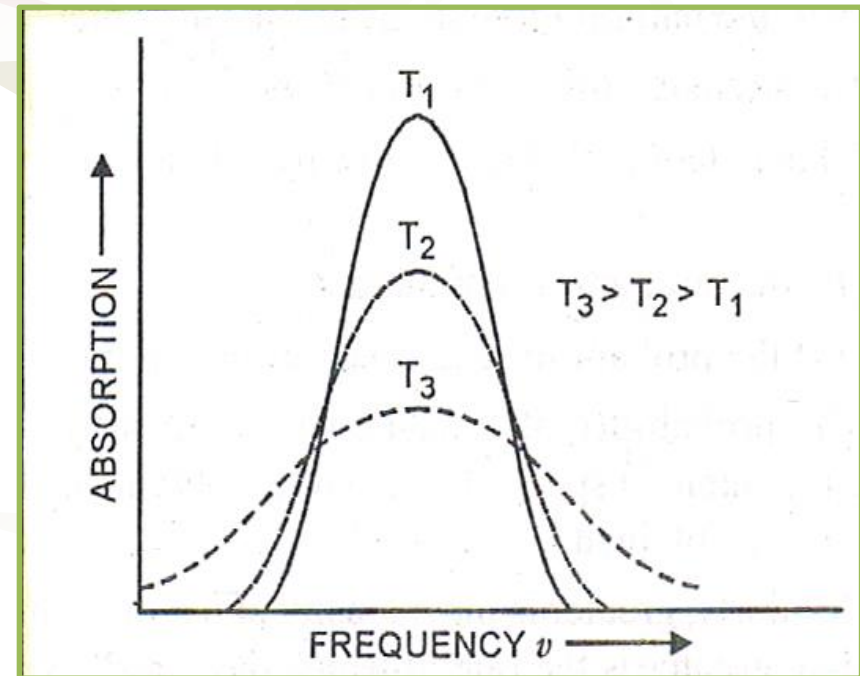
$$E = E_r + E_v + E_e$$

# WIDTHS AND INTENSITIES OF THE SPECTRAL LINES

Factors affecting the width of spectral lines. The two factors which contribute to the broadening of a spectral line are (i) Doppler Broadening and (ii) Lifetime broadening



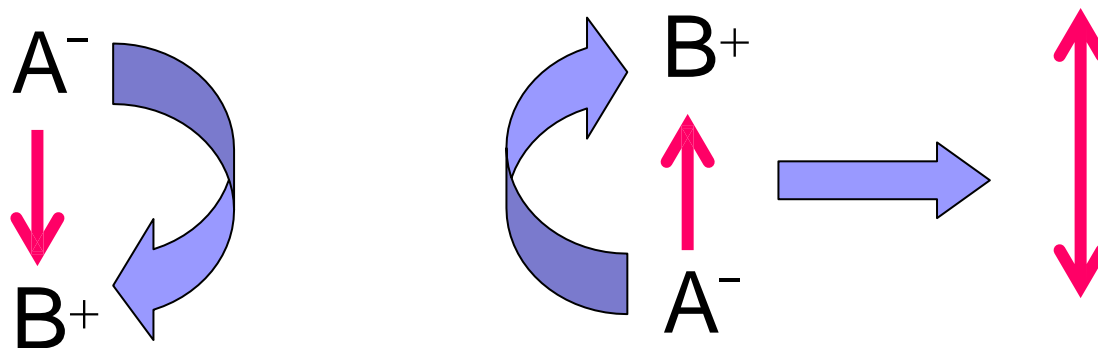
- (a) A sharp spectral line  
(b) A spectral line having a width.



The line broadens as the temperature is increased.

# Microwave Spectroscopy

It is concerned with transitions between rotational energy levels in the molecules, the molecule gives a rotational spectrum only if it has a permanent dipole moment:



## Rotating molecule

- H-Cl, and C=O give rotational spectrum (microwave active).
- H-H and Cl-Cl don't give rotational spectrum (microwave inactive).

Rotational spectroscopy is only really practical in the gas phase where the rotational motion is quantized. In solids or liquids the rotational motion is usually quenched due to collisions between their molecules.

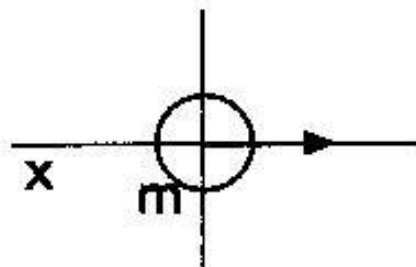


# General features of rotating system:

## 1- Rotational motion in classical mechanics

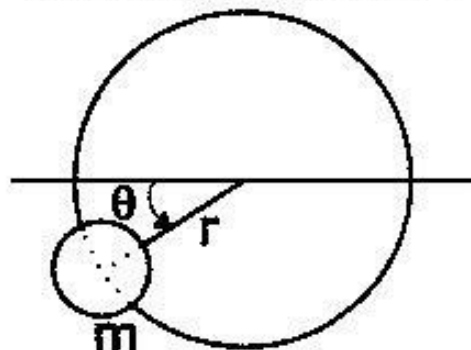
Rigid Rotors: molecules in which bonds don't distort under the stress of rotation.

Linear Motion



$$\text{Linear velocity (v)} = \frac{\text{Distance}}{\text{Time}}$$

Angular Motion



$$\text{Angular velocity (\omega)} = \frac{\text{Radians}}{\text{Time}}$$

**Linear momentum (P) = m . v**

**Angular momentum (J) = I .  $\omega$**

**Then; I = m . r<sub>2</sub>**

**Where; the moment of inertia for a molecule (I) =  
=  $\Sigma m r^2$**

Where: r is the perpendicular distance of the atom from the axis of rotation (bond length).

**Moment of inertia (I)**, also called mass moment of inertia which is a measure of an object's resistance to changes in its rotation rate. It is the rotational analog of mass.

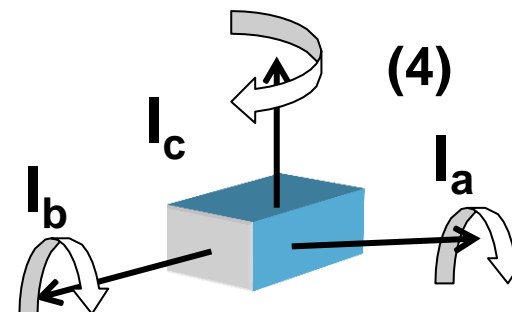
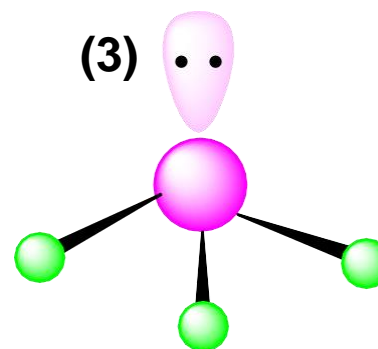
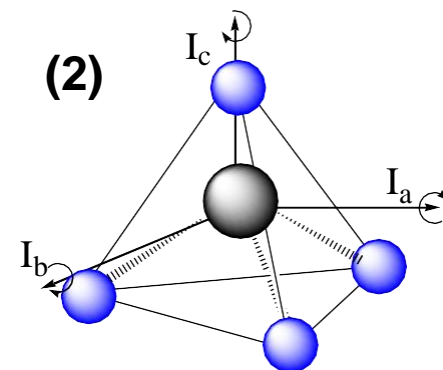
# Rigid rotors are classified into four groups:

1- Linear rotors: such as diatomic or linear molecules, as H-Cl, O=C=S, acetylene and O=C=O, have;  $I_a=0$  and  $I_b=I_c$ .

2- Spherical tops rotors: e.g.  $\text{CH}_4$ ,  $\text{SiH}_4$  and  $\text{SF}_6$  have three equal moments of inertia..  $I_a=I_b=I_c$ .

3- Symmetric tops rotors: e.g.  $\text{NH}_3$ ,  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{Cl}$ , have two equal moments of inertia. ,  $I_a=I_b \neq I_c$ .

4- Asymmetric tops rotors: e.g.  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ , vinyl chloride  $\text{CH}_2=\text{CHCl}$  and formaldehyde, have three different moments of inertia.  $I_a \neq I_b \neq I_c$ .



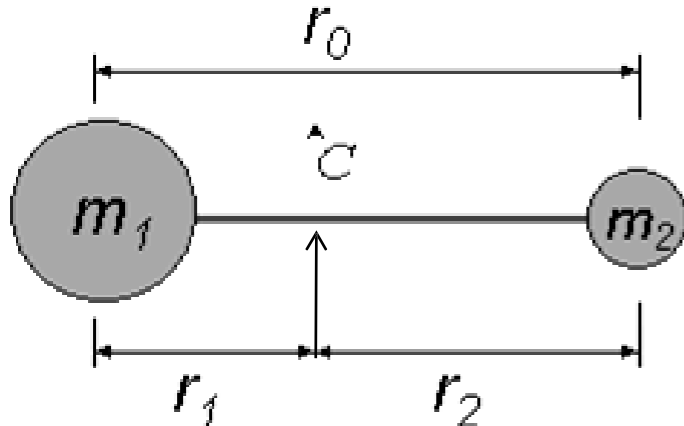
# Classes of Rotating Molecules

- Molecules can be classified into five main groups depending on their moments of inertia.

1.	$I_C = I_B, I_A = 0$	Linear molecules
2.	$I_C = I_B = I_A$	Spherical top
3.	$I_C = I_B > I_A$	Symmetric top
5.	$I_C > I_B > I_A$	Asymmetric top

- ❖ **Homonuclear diatomic molecules (such as H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, Cl<sub>2</sub>) – have zero dipole (non polar) - have zero change of dipole during the rotation, hence NO interaction with radiation - hence homonuclear diatomic molecules are microwave inactive**
- ❖ **Heteronuclear diatomic molecules (such as HCl, HF, CO) – have permanent dipole moment (polar compound) - change of dipole occurs during the rotation – hence interaction with radiation takes place – Therefore, heteronuclear diatomic molecules are microwave active.**

For linear diatomic molecules, the moment of inertia can be calculated as follows;



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

$C$  – centre of gravity

express  $I$  via  $m_1$ ,  $m_2$  and  $r_0$

$$m_1 r_1 = m_2 r_2 \quad (1)$$

from  $r_1 + r_2 = r_0 \quad (2)$

$$I = m_1 r_1^2 + m_2 r_2^2 \quad (3)$$



$$I = \frac{m_1 \cdot m_2}{m_1 + m_2} \cdot r_0^2 = \mu \cdot r_0^2$$

$\mu$  - reduced or effective mass

units:  $\text{kg} \cdot \text{m}^2 = \text{kg} \cdot \text{m}^2$

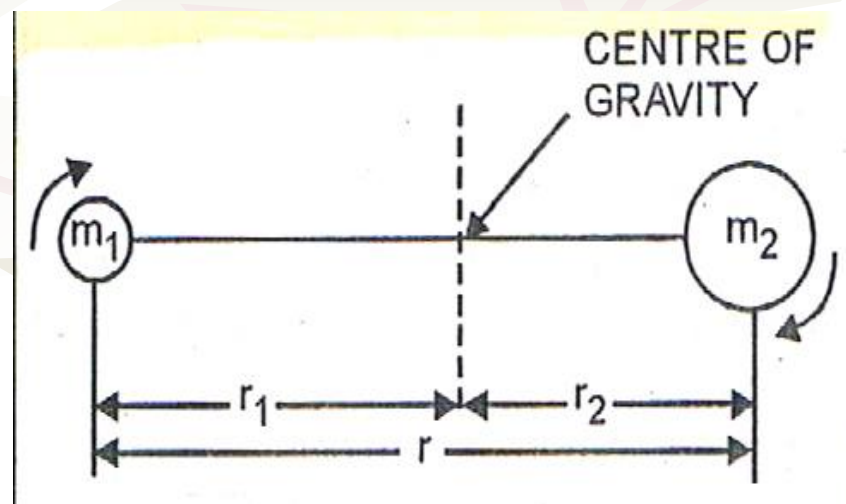
From the moment of inertia one can calculate the bond length as well as the atomic masses

# ROTATIONAL (MICROWAVE) SPECTRA OF DIATOMIC MOLECULES

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

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2$$

Where  $m_1$  and  $m_2$  are the atomic masses of the two atoms of the diatomic molecule and

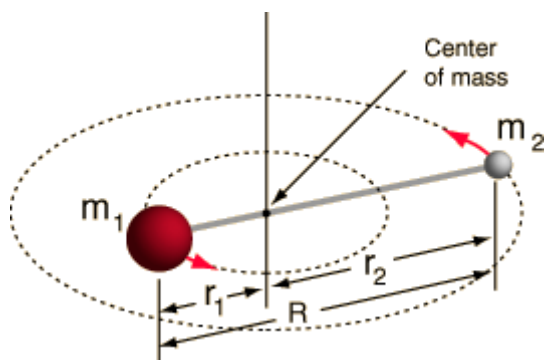


$$\frac{m_1 m_2}{m_1 + m_2} = \mu$$

# Rotational Spectra of Linear Rigid Rotators

**Simplest Case:** Diatomic or Linear Polyatomic molecules

**Rigid Rotor Model:** Two nuclei are joined by a weightless rod



From solution of Schrodinger equation;  $E_J = \frac{h^2}{8\pi^2 I} J(J + 1)$

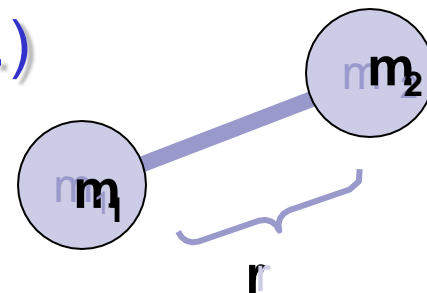
$E_J$  = Rotational energy of rigid rotator (in Joules)

$J$  = Rotational quantum number ( $J = 0, 1, 2, \dots$ )

$I$  = Moment of inertia =  $\mu r^2$

$\mu$  = reduced mass =  $m_1 m_2 / (m_1 + m_2)$

$r$  = internuclear distance (bond length)



$$I = \mu r^2$$

$$L = I \omega$$

$$L = \sqrt{J(J+1)} \frac{h}{2\pi}$$

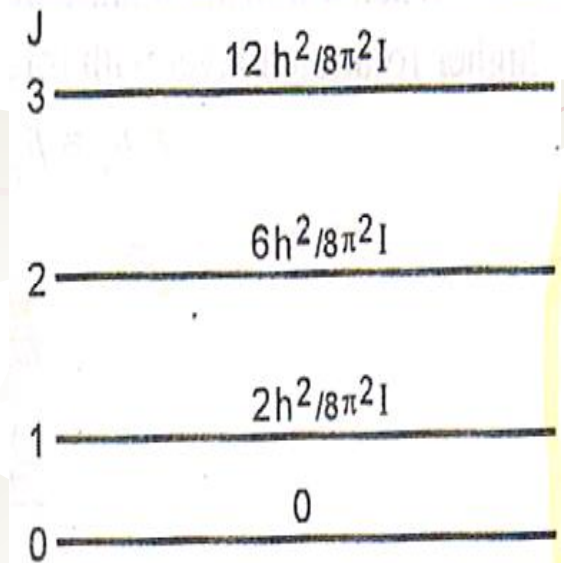
Where  $J = 0, 1, 2, 3, \dots$ , called the rotational quantum numbers

$$E = I \omega^2$$

$$E_r = \frac{1}{2} I \omega^2 = \frac{I \omega^2}{2} = \frac{L^2}{2I}$$

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

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



**FIGURE 3.18**

**Rotational energy levels of a diatomic molecule treating it as a rigid rotator.**



# Energy levels of a rigid diatomic rotor

1. Rotational energy for a rigid diatomic rotor  $E_J$  is quantized:

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \quad \text{units: } \underline{\text{Joules}}$$

$J = 0; 1; 2; \dots$  - rotational quantum number

2. Rotational energy is normally expressed in  $\text{cm}^{-1}$

recall:  $E = h \cdot \nu = h \cdot c \cdot \tilde{\nu}$  therefore:  $\tilde{\nu} \equiv \varepsilon = \frac{E}{h \cdot c}$

$$\varepsilon_J = \frac{E_J}{hc} = \frac{h^2 J(J+1)}{4\pi^2 \cdot 2I \cdot hc} = \frac{h}{8\pi^2 I \cdot c} J(J+1)$$

$B$  - rotational constant, units =  $\text{cm}^{-1}$

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

$$B = \frac{h}{8\pi^2 I \cdot c}$$

Note: units for  $c$ !

$B$  can be determined from spectroscopic experiments

# Rotational transitions in rigid diatomic molecule.

## Selection rules:

1. molecule gives a rotational spectrum only if it has a permanent dipole moment

2.  $\Delta J = \pm 1$

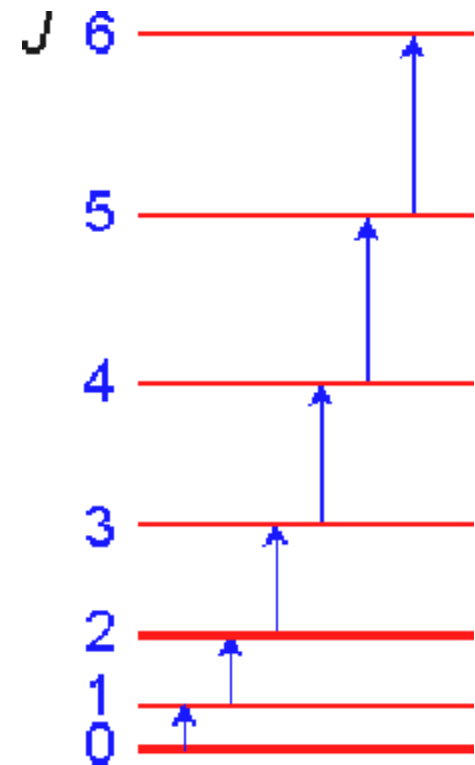
+1 absorption.

-1 emission.

Separation between adjacent levels:

$$\Delta E_J = E(J) - E(J-1) = 2BJ$$

and  $B$  can be obtained from the spacing between rotational lines in the spectra of molecules.



Allowed transitions

## Transitions observed in the rotational spectrum

\* For the transition;  $J = 0 \rightarrow J = 1$     **Since;**  $E_J = \frac{h}{8\pi^2 I_c} J(J + 1)$

**and;**                     $B = h/8 \pi^2 I_c$

**Then;**  $\Delta E_j = E_{j=1} - E_{j=0} = 2B - 0 = 2B \text{ cm}^{-1}$   
*= position of the first line in the spectrum =  $\bar{\nu}_{j=0 \rightarrow j=1}$*

\* For the transition;  $J = 1 \rightarrow J = 2$

$\Delta E_j = E_{j=2} - E_{j=1} = 6B - 2B = 4B \text{ cm}^{-1}$   
*= position of the second line in the spectrum =  $\bar{\nu}_{j=1 \rightarrow j=2}$*

\* For the transition;  $J = 2 \rightarrow J = 3$

$\Delta E_j = E_{j=3} - E_{j=2} = 12B - 6B = 6B \text{ cm}^{-1}$   
*= position of the third line in the spectrum =  $\bar{\nu}_{j=2 \rightarrow j=3}$*

Since, The allowed rotational energies are given by;

$$\begin{aligned}\bar{\nu} &= \frac{h}{8\pi^2 I_c} J(J+1) \\ &= BJ(J+1)\end{aligned}$$

The wave numbers of the different rotational levels will be; **0, 2B, 6B, 12B, 20B, 30B (cm<sup>-1</sup>),...** and so on

And for two adjacent rotational states, the energy difference is given by;

$$\Delta E_j = E_{j+1} - E_j = 2B(j+1) \text{ cm}^{-1}$$

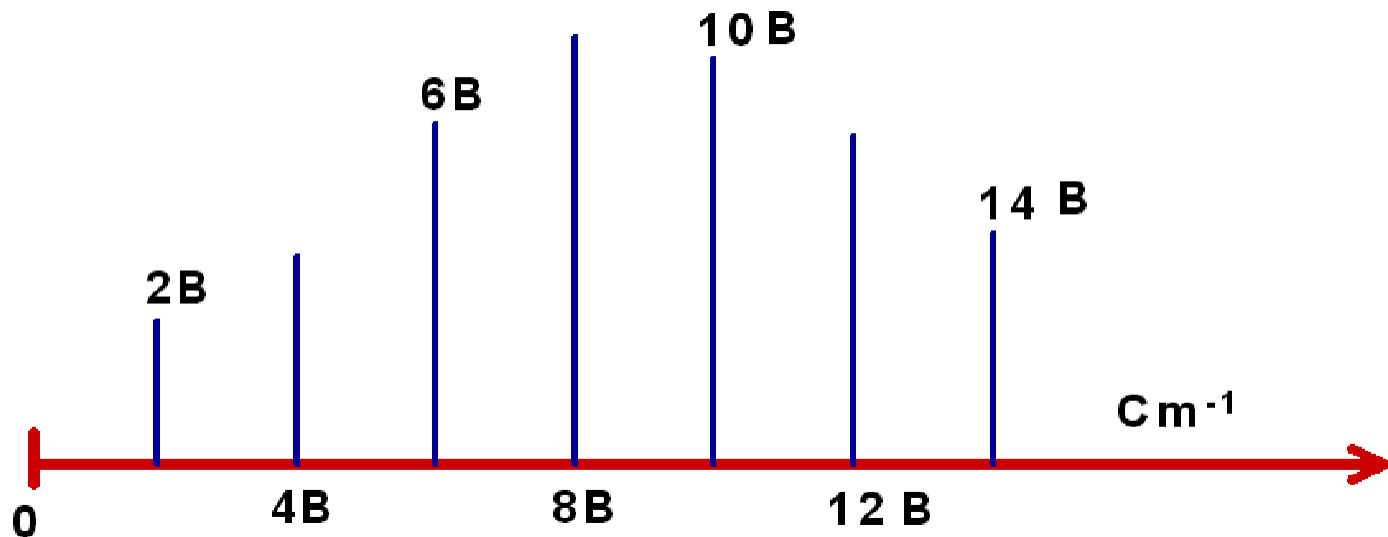
Hence, the wave number of the lines observed in the rotational spectrum will be; **2B, 4B, 6B, 8B (cm<sup>-1</sup>), .....** and so on.

**And the various lines in the rotational spectra will be equally spaced (separation between lines = 2B)..**

## Energy levels of a rigid diatomic rotor

$$\varepsilon_J = B \cdot J(J + 1) \quad J=0; 1; 2; \dots$$

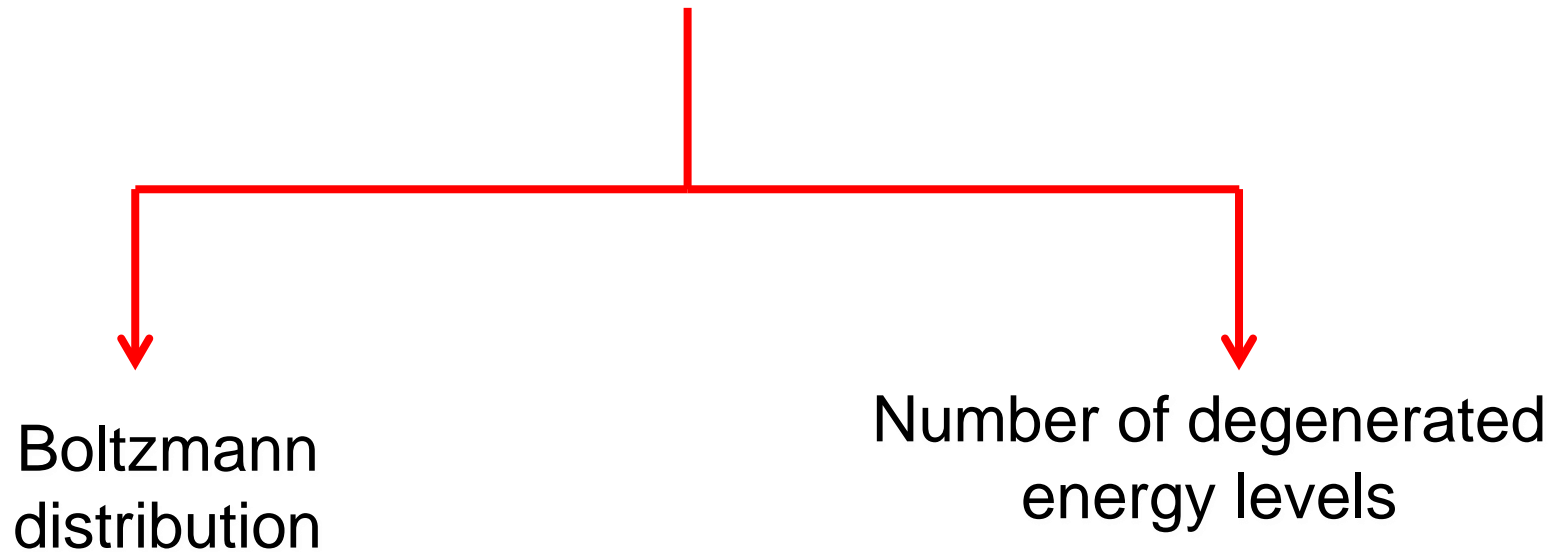
$J$	6	_____	42B	$\varepsilon_J$
	5	_____	30B	
	4	_____	20B	
	3	_____	12B	
	2	_____	6B	
	1	_____	2B	
	0	_____	0	



## Microwave spectrum of rigid rotator

**Separation between adjacent lines =  $2B$**   
**So,  $B$  can be obtained from the spacing between rotational lines.**

# Intensity of rotational spectral lines (Population of energy levels)



**Population of energy levels is affected by;**

- 1- Boltzmann distribution**
- 2- Number of degenerated energy levels (levels which have the same energies)**

# 1-Boltzmann distribution

*The number of molecules in the first state =  $N_o$*

*The number of molecules in any higher state =  $N_j$*

$$\frac{N_j}{N_o} = e^{-E_J/kT} = e^{-(h\nu/kT)} = e^{-(hc\bar{\nu}/kT)}$$

$$\varepsilon_j = \bar{\nu} = B J (J+1) \quad \text{So,}$$

$$\frac{N_j}{N_o} = e^{-[BhcJ(J+1)]/kT} = e^{-BJ(J+1)hc/kT}$$

The population of the state decreases as the J –value increases.



## 2-Degeneracy

The existence of more than two energy states having the same energy.

Kinetic energy (K.E) in rotational motion =  $\frac{1}{2} I \omega^2$   
and since, angular momentum (P) =  $I \omega$  then;

$$E = \frac{I \times I \omega^2}{2I} = \frac{I^2 \omega^2}{2I} = \frac{P^2}{2I} \quad \rightarrow \quad P = \sqrt{2 E I}$$

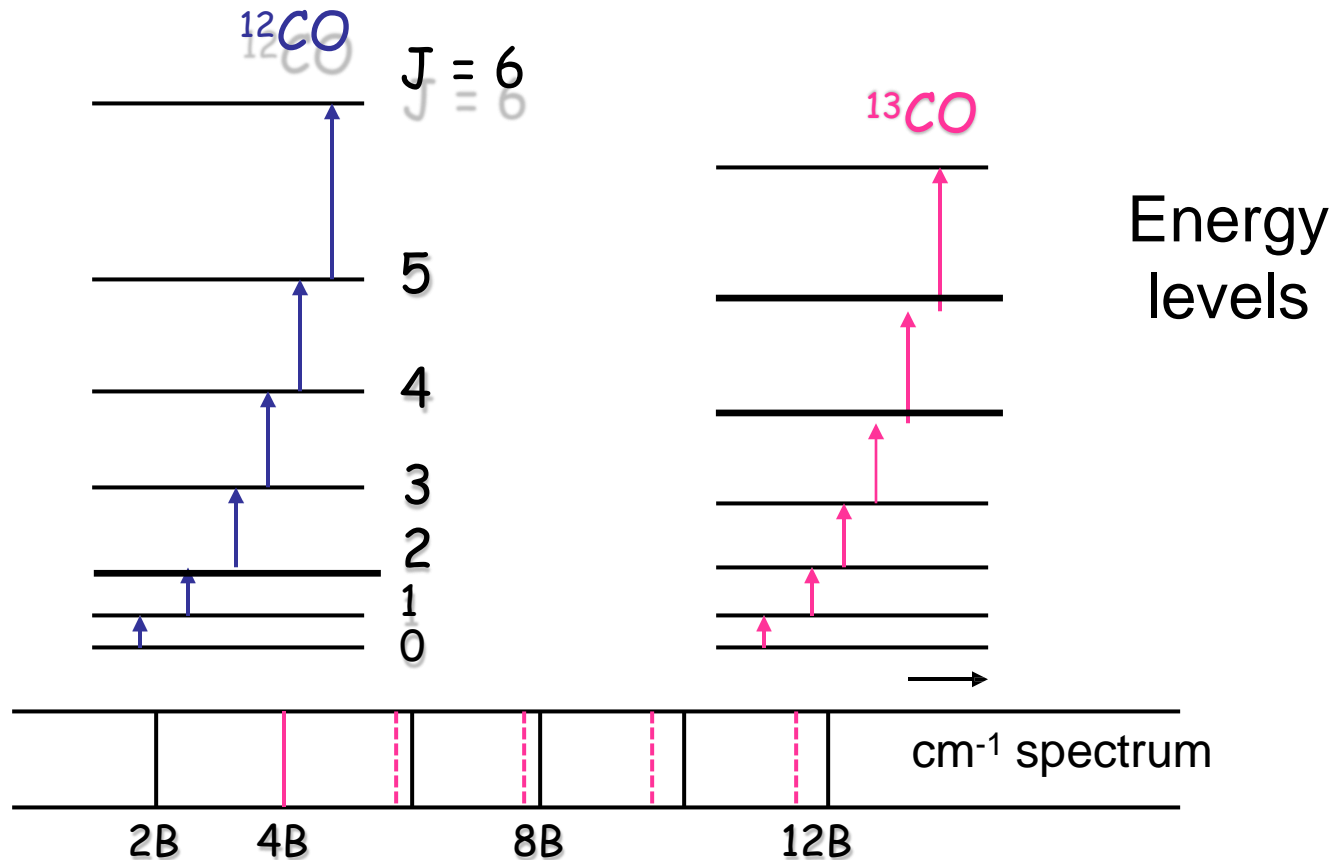
$$E = \frac{h^2}{4\pi^2} \frac{J(J+1)}{2I} \quad \rightarrow \quad 2 E I = \frac{h^2}{4\pi^2} J(J+1) = P^2$$

$$P = \sqrt{J(J+1)} \times \frac{h}{2\pi} = \sqrt{J(J+1)} \text{ unit.}$$

$\frac{h}{2\pi}$  is the fundamental angular momentum unit.

# Effect of isotopic substitution

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



# From comparison of rotational energy levels of $^{12}\text{CO}$ and $^{13}\text{CO}$

We can determine:

- (i) isotopic masses accurately, to within 0.02% of other methods for atoms in gaseous molecules;
- (ii) isotopic abundances from the absorption relative intensities.

## Example:

for  $^{12}\text{CO}$  the transition  $J=0 \rightarrow J=1$  appears at  $3.84235 \text{ cm}^{-1}$

for  $^{13}\text{CO}$  the transition  $J=0 \rightarrow J=1$  appears at  $3.67337 \text{ cm}^{-1}$

Given :  $^{12}\text{C} = 12.0000$  ;                       $\text{O} = 15.9994$       amu

# Non-rigid Rotor

For a non-rigid rotor, the bond length increases as the angular velocity increases

$$B = \frac{h}{8\pi^2 I \cdot c}$$



$$B \propto \frac{1}{r^2}$$



$B$  decreases with  $J$

Rotational transitions of HF

Transition	$E_{calc}$ $cm^{-1}$	$E_{exp}$ $cm^{-1}$	$r$ , Å
0→1	20.56	20.55	0.929
1→2	20.56	20.48	0.931
2→3	20.56	20.43	0.932
3→4	20.56	20.31	0.935
4→5	20.56	20.16	0.938
5→6	20.56	20.04	0.941
6→7	20.56	19.82	0.946
7→8	20.56	19.64	0.951
8→9	20.56	19.45	0.955
9→10	20.56	19.16	0.963
10→11	20.56	18.91	0.969

for a non-rigid rotor

$$E_J = B \cdot J(J+1) - D \cdot J^2(J+1)^2$$

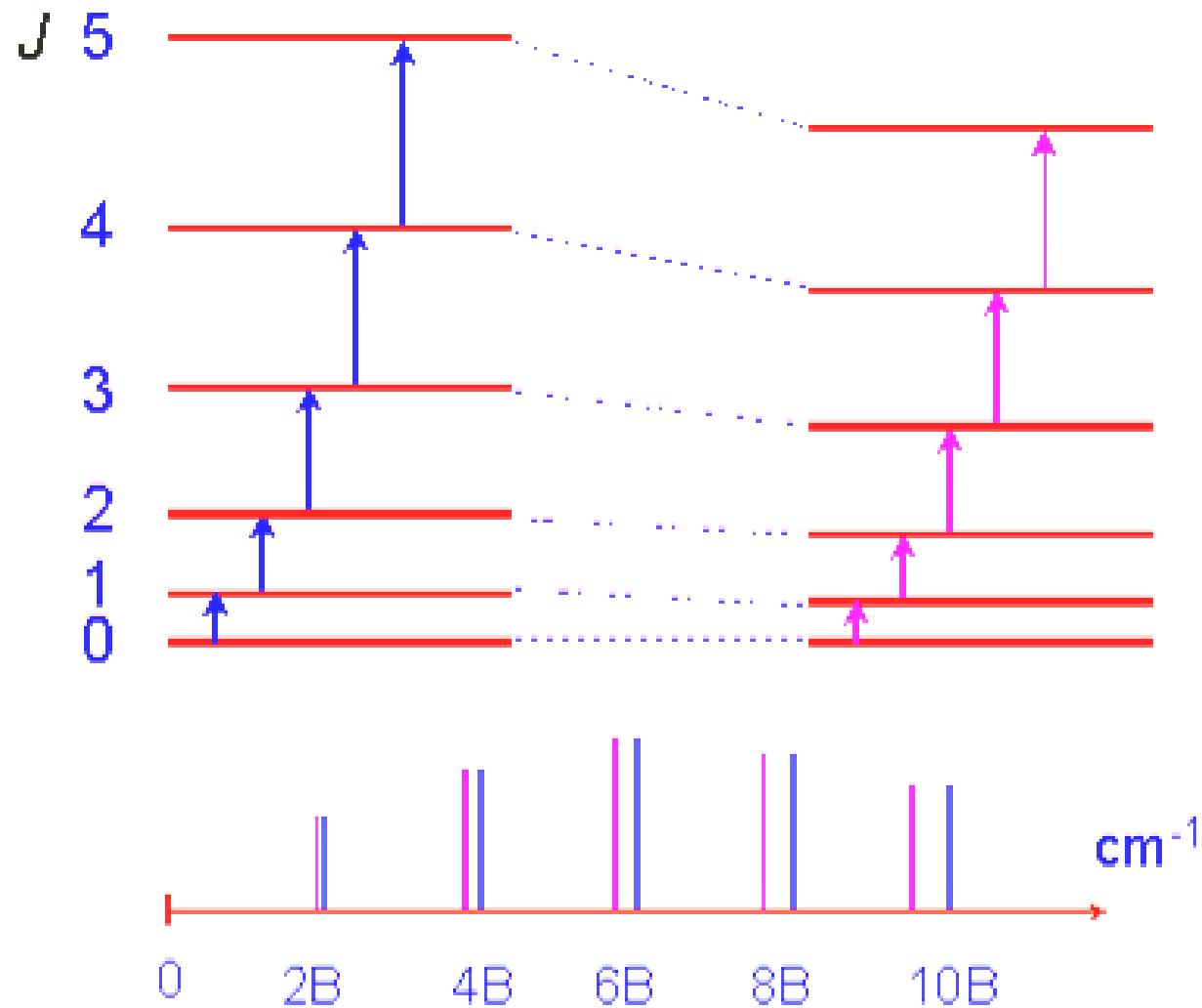
$D$  – centrifugal distortion constant  
(‘stiffness’ constant)  
units:  $cm^{-1}$

## rigid rotor

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

## non-rigid rotor


$$\varepsilon_J = B \cdot J(J+1) - D \cdot J^2 (J+1)^2$$



# Applications of microwave spectroscopy

Microwave spectroscopy has been used in monitoring and control of industrial processes. It is an ideal process analyzer as it is:

1. non-invasive: the measurement can be made outside of the reaction chamber, eliminates the need for sampling or physical removal of sample.
2. non-destructive.
3. can be used for solids, liquids, gases and suspensions .
4. can be used for dark coloured samples.
5. analyses large sample volumes, as microwaves diffuse out from the transmitter though the entire sample becomes lower.



Microwave spectroscopy has been used in monitoring and control of industrial processes, such as;

1. materials with low dielectric constants, such as plastics, glass, ceramics and composite materials.
2. determination of moisture in various tobacco types.
3. Monitoring of a batch esterification reaction as in the esterification of butanol by acetic acid.
4. Monitoring of the drying process in industry as it is one that is hard to monitor. For example, huge cakes of wet material when dried in big vessels.
5. Astrophysical applications, radioastronomy: probe of the molecular universe (molecular clouds) using Telescope.