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Molecular spectroscopy

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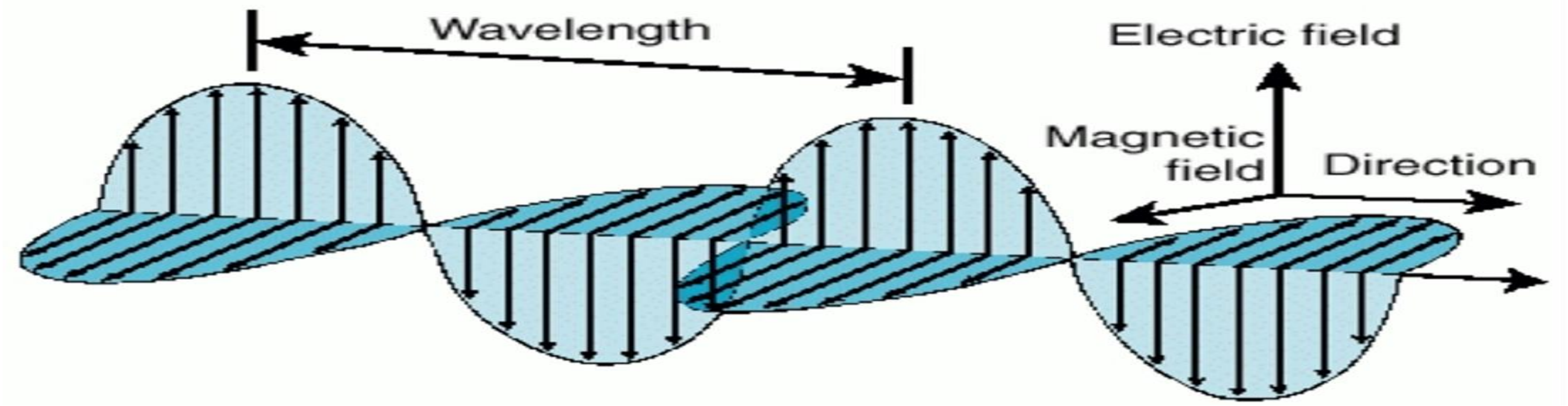
MOLECULAR SPECTROSCOPY

SPECTROSCOPY:

Is the branch of science which deals with the study of interaction of Electromagnetic Radiation 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 radiation are given below…
- They have dual character.
- These waves are associated with electric and magnetic fields.



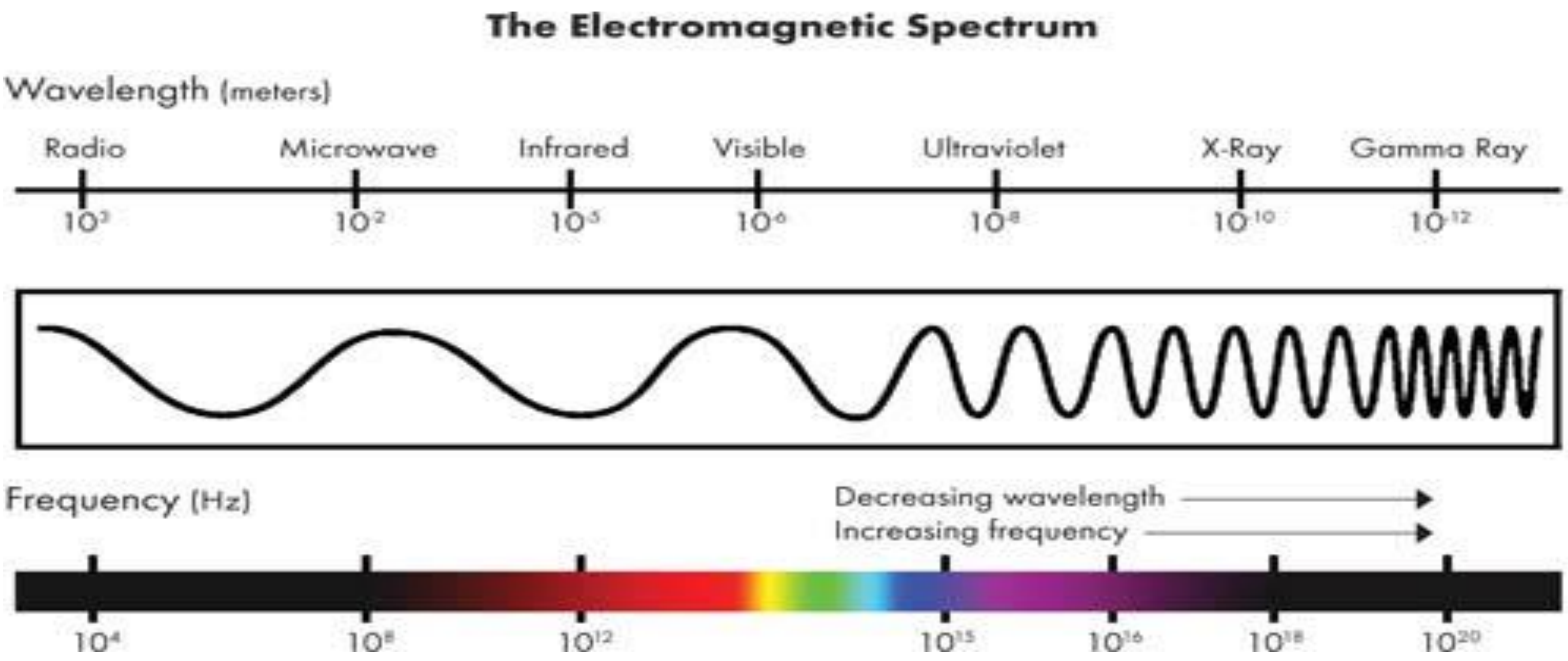
All electromagnetic radiations travel with the velocity of light

$$c=\nu\lambda.$$

Each photon is a packet of energy whose energy is given by Planck's equation **$E=h\nu$.** where h is Planck's constant

Electromagnetic Spectrum

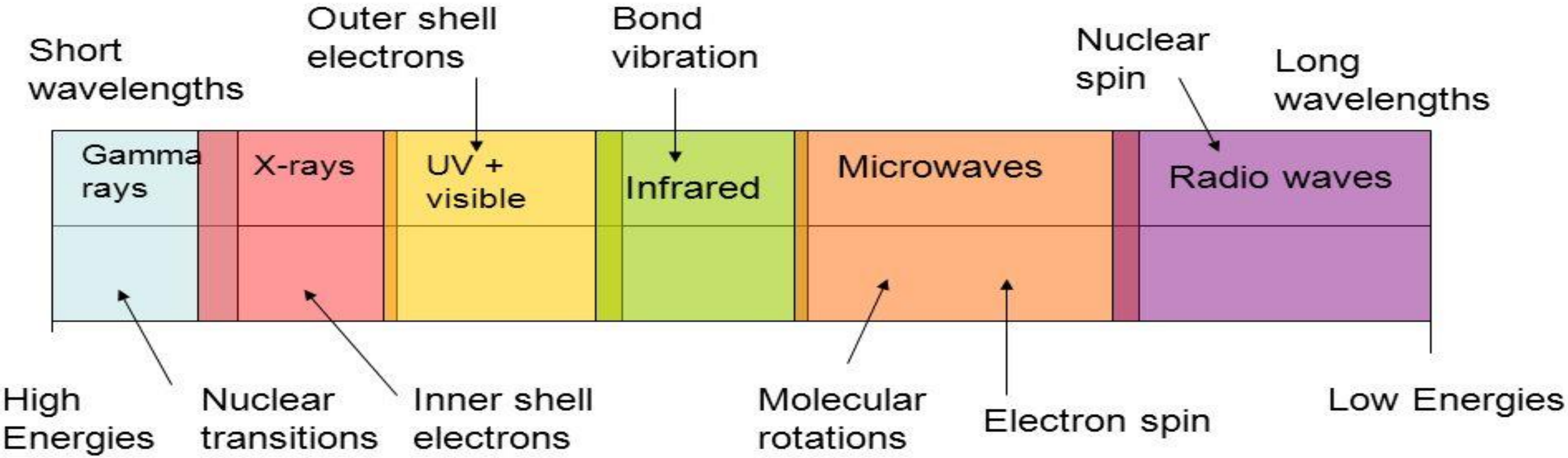
When the different types of electromagnetic radiations are arranged in order of their increasing wavelengths or decreasing frequencies, the complete arrangement is called electromagnetic spectrum.

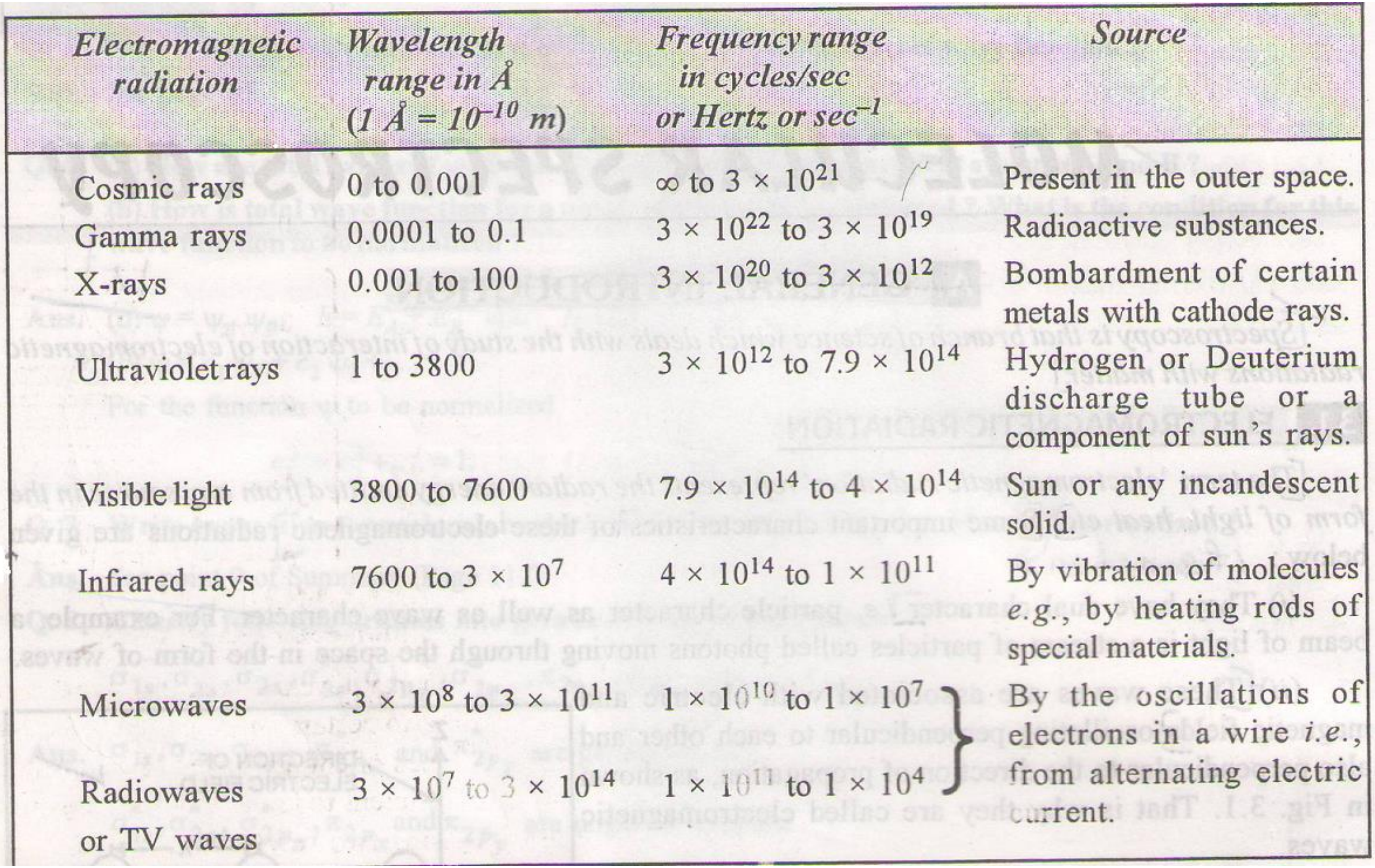


Spectroscopy

Regions of the Electromagnetic Spectrum

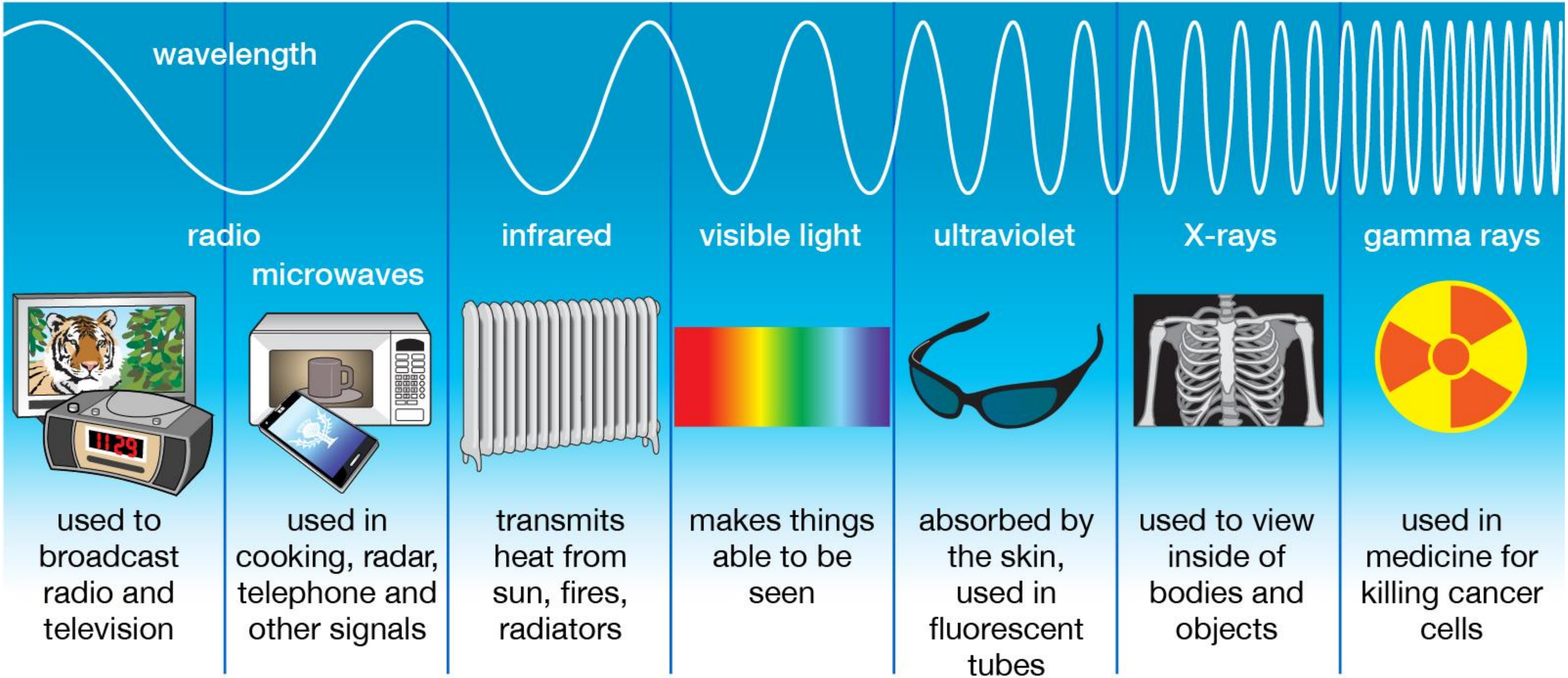
Many regions are defined as much by the types of transitions occurring (e.g. outer shell electron) as by the frequency or energy of the transitions





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

Types of Electromagnetic Radiation

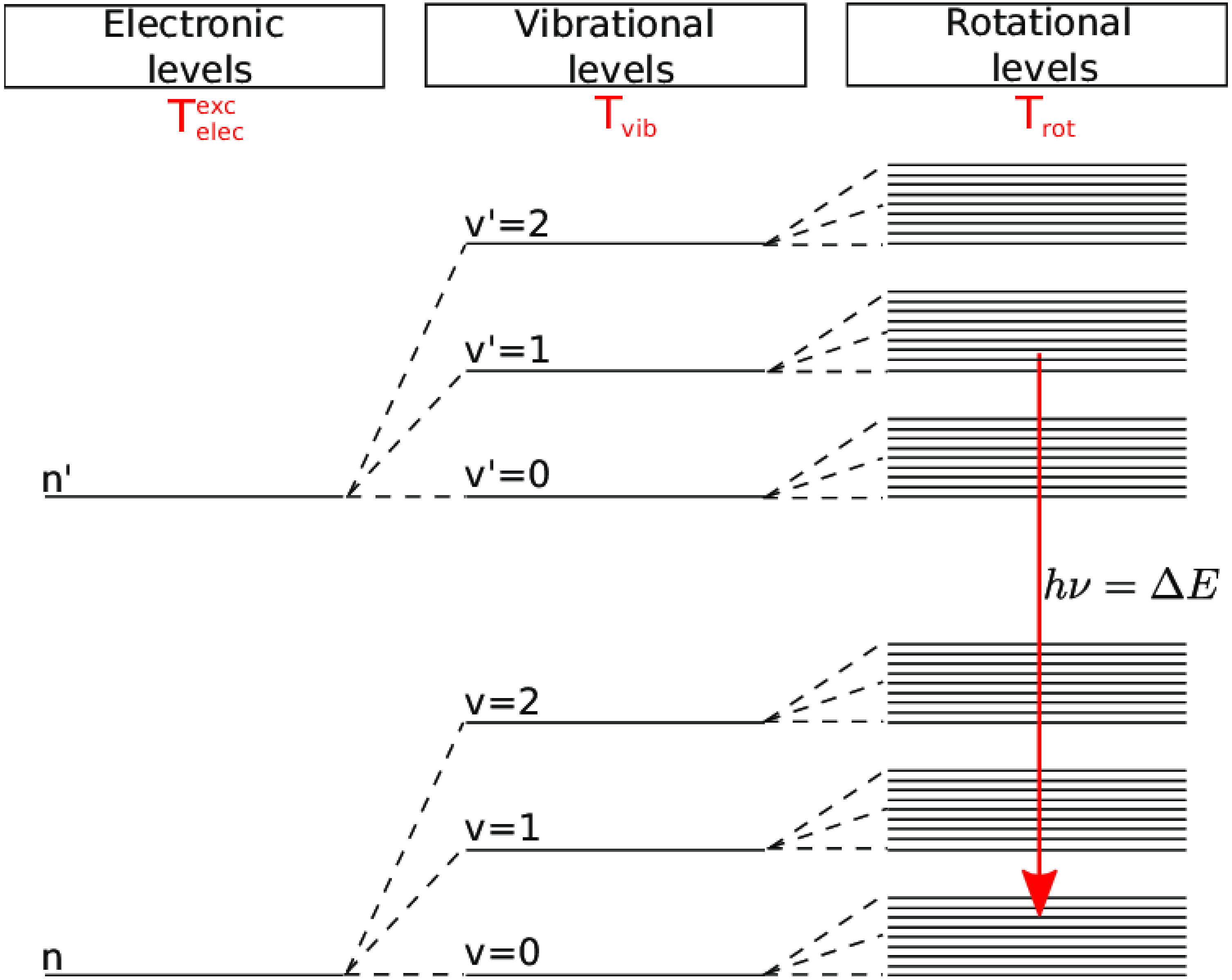


radio	microwaves	infrared	visible light	ultraviolet	X-rays	gamma rays
used to broadcast radio and television	used in cooking, radar, telephone and other signals	transmits heat from sun, fires, radiators	makes things able to be seen	absorbed by the skin, used in fluorescent tubes	used to view inside of bodies and objects	used in medicine for killing cancer cells

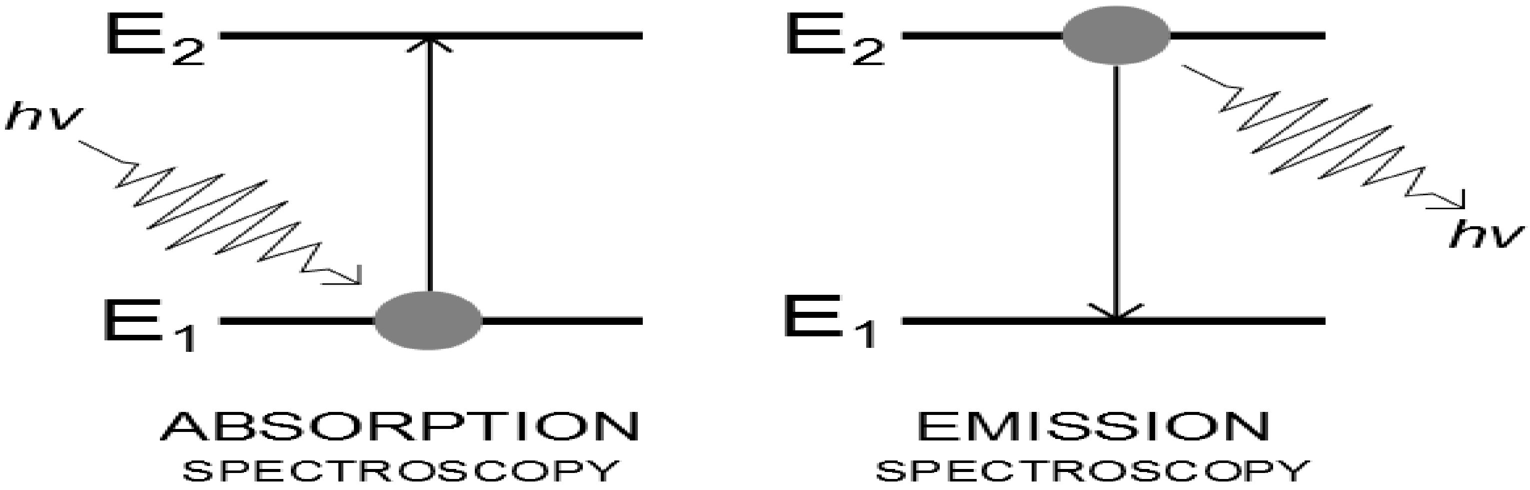
Introduction to Molecular Spectroscopy and its difference from Atomic Spectroscopy

- In case of Molecules, when the energy is absorbed, it may result into rotation, vibration or electronic transition. Just as electronic energy is quantized, the rotational and vibration energies are also quantized.

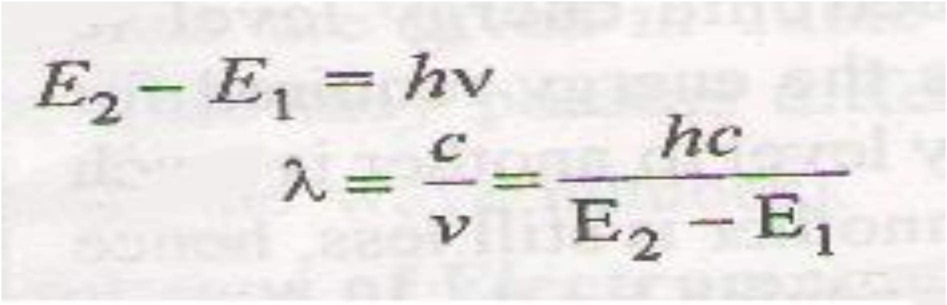
- The rotational, vibrational and electronic energy levels of a molecule are collectively called molecular energy levels. The transitions of energies can take place only between these levels. The result is a molecular spectrum.


Electronic levels
T_{elec}^{exc}
Vibrational levels
T_{vib}
Rotational levels
T_{rot}
v'=2
v'=1
v'=0
n'
$h\nu = \Delta E$
v=2
v=1
v=0
n

Absorption and Emission spectroscopy



The energy of photon hv emitted or absorbed is given by bohr's frequency formula …



$$E_2 - E_1 = h\nu$$

$$\lambda = \frac{c}{\nu} = \frac{hc}{E_2 - E_1}$$

- The transition may take place from lower energy level to higher energy level by absorbing energy. it is then called absorption spectroscopy and the result obtained as a result of a number of such transitions is called absorption spectrum.
- the transition may take place from higher energy level to a lower energy level thereby emitting the excess energy as a photon.it is then called emission spectroscopy and the result obtained as a result of no. of such transitions is called emission spectrum.

Types of molecular energies and born-oppenheimer approximation

A Molecule usually possesses four different types of energies. these are…
TRANSLATIONAL ENERGY
ROTATIONAL ENERGY
VIBRATIONAL ENERGY
ELECTRONIC ENERGY

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

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

It is found that the translational energy is negligibly small. so

$$E = E_v + E_r + E_e$$

The energy absorbed for any transition is equal to the difference in the energies of the two levels involved. It is found that these energies for transition are in order…

$$\mathbf{E_t \ll E_r \ll E_v \ll E_e}$$

Translational energy is considered as continuous and we do not observe any translational spectrum.

Types of molecular spectra

PURE ROTATIONAL (MICROWAVE) SPECTRA:

- These spectra occurs from transition between the rotational energy levels of gaseous molecules on the absorption of radiation falling in far infra-red region or in the Microwave region
- Spectral range of 1 to 100cm^{-1}
- Heteronuclear diatomic molecules exhibit rotational spectra which have permanent dipole moment Example: HCl, CO, NO, H_2O.
- Homonuclear diatomic molecules(H_2, Cl_2, N_2, O_2) and polyatomic molecules(CO_2) which do not possess dipole moment do not exhibit microwave spectra.

VIBRATIONAL ROTATIONAL SPECTRA:

- Here transition between vibrational levels within the same electronic level gives rise to vibrational and vibrational-rotational spectra in the near infra-red region.
- The energy range involved is 4000 to 667cm^{-1} for organic compounds.
- IR spectra are shown by molecules when vibrational motion is accompanied by a change in the dipole moment of the molecule.

ELECTRONIC BAND SPECTRA:

For a given electronic transition, a set of bands observed. This set of bands is called a band group or a band system. thus whereas atoms give line spectra, molecules give band spectra. These spectra are observed in the visible region and ultra violet region.

RAMAN SPECTRA: This is also a type of vibrational-rotational spectrum. It is based on scattering of radiation and not on the absorption of radiation by the sample. Raman spectra is observed in the visible region.

NUCLEAR MAGNETIC RESONANCE(NMR) SPECTRA: This type of spectra arises from the transition between the nuclear spin energy levels of the molecule when an external field is applied on it. The energies involved in these transitions are very high which lie in the radio frequency regions.

ELECTRON SPIN RESONANCE (ESR) SPECTRA: This type of spectrum arise from the transitions between the electron spin energy levels of the molecule when an external magnetic field is applied on it.

Region of electromagnetic spectrum and different types of molecular spectra

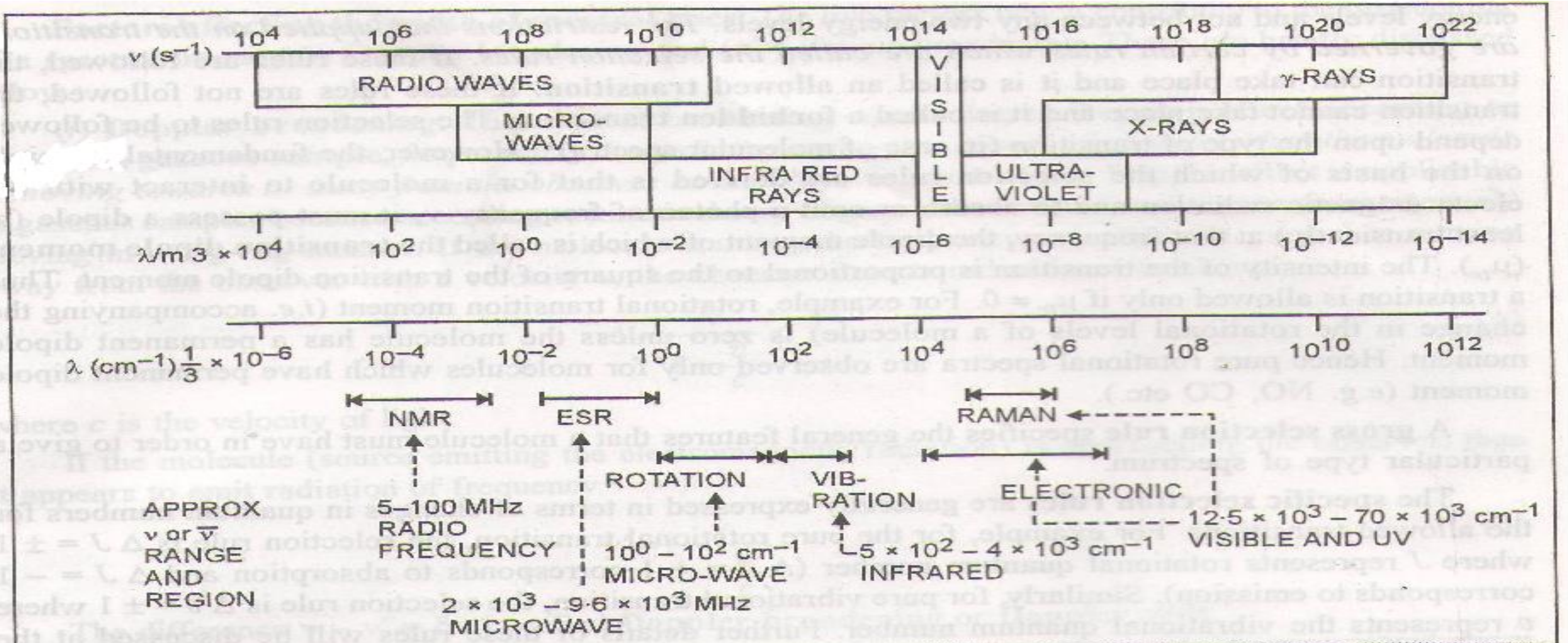


FIGURE 3.11

Regions of the electromagnetic spectrum and those of the different types of molecular spectra.

The theoretical treatment of rotation

Moment of inertia:

- It is a measure of an object's resistance to changes to its rotation.
- Also defined as the capacity of a cross-section to resist bending.
- It must be specified with respect to a chosen axis of rotation.
- It is usually quantified in m^4 or kgm^2

Theoretical treatment of rotation:

- Rotational spectrum is obtained by interaction of radiation with rotating molecule which causes transition between rotation energy levels.
- For microwave absorption, the molecule must possess a permanent dipole moment.
- A rotating Heteronuclear diatomic molecules such as HCl (or CO, NO, H_2O) will give rise to sinusoidally varying component of electric dipole moment vector interact with electrical field vector of the microwave radiation.

Rigid Rotor or Rotational spectrum of rigid diatomic molecules

Note : In some text books R is represented as r and r_0 as well

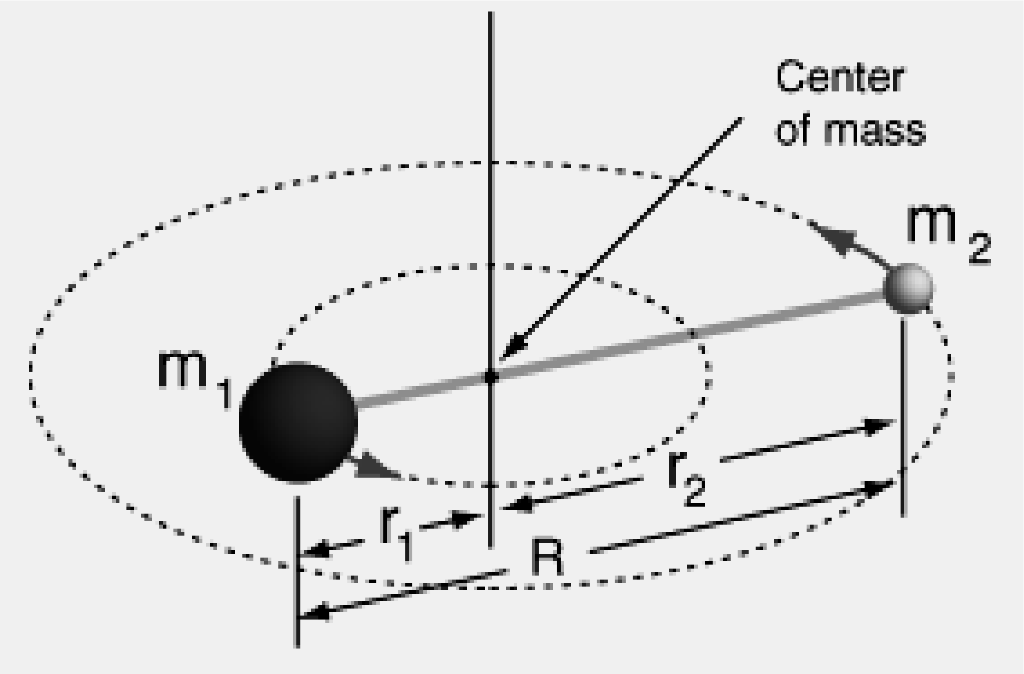


Fig: Rotation of a diatomic molecule about its centre of gravity

The centre of gravity is defined as the equality of the moments about it.

i.e., $m_1r_1 = m_2r_2$ --------------1

The moment of inertia I of a molecule (rotating as a rigid rotor, not subject to centrifugal forces that tend to distort the molecular geometry and change the moments of inertia) is defined as

$I = \Sigma\, m_i r^2_i$ ------------------2

Where r_i is the distance of the ith particle of mass m_i

Since a diatomic molecule has two atoms , we have

$I = m_1r_1^2 + m_2r_2^2$ ------------------3

$= m_2r_2r_1 + m_1r_1r_2$ (From Equation-1)

$= r_1\, r_2\, (m_1 + m_2)$ ------------------4

Also, as seen from fig. $r = r_1+r_2$ ------------------5

Therefore from equation 1 & 5

$$m_1r_1 = m_2r_2 = m(r-r_1)$$

$$= m_1r_1 = m_2r-m_2r_1$$

$$m_1r_1 + m_2r_1 = m_2r$$

$$(m_1 + m_2)r_1 = m_2r$$

Hence $r_1 = m_2r/(m_1+m_2)$ ----------------6

And $r_2 = m_1r/(m_1+m_2)$ ----------------7

substituting the above values of r_1 and r_2 in equation 3

$$\mathbf{I = m_1m_2^2/(m_1+m_2)^2\, r^2 + m^2{}_1m_2/(m_1+m_2)^2\, r^2}$$

After simplification we get $\mathbf{I = \mu r^2}$ --------8

Where $\mathbf{I = \dfrac{m_1m_2}{(m_1+m_2)}}$ called reduced mass of the molecule

Classically angular momentum L of a rotating molecule is given by $L=I\omega$ where ω is its angular velocity, however angular momentum is quantized

$L=\sqrt{J(J+1)}h/2\pi \quad J=0,1,2,\ldots..$

The energy of a rotating molecule is given by $\frac{1}{2} I\omega^2$.

Hence the quantized rotational energy of a rigid diatomic molecule are given by

$E_J = \frac{1}{2} I\omega^2 = (I\omega)^2 /2I = L^2 /2I$

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1)$$ **Joules. Where J= 0,1,2,….**

The rotational energy is quantized as

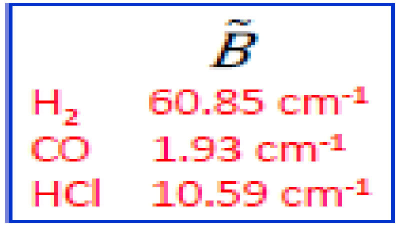
$\boxed{E_{rot} = \frac{h^2}{8\pi^2 I} J(J+1)}$ **Joules.----------------9**

$E_J = E_{J/hc} = E_J = \boxed{\frac{h}{8\pi^2 Ic} J(J+1)}$ **Cm^{-1}**.-----------------10

$\boxed{E_{rot} = BJ(J+1)\ Cm^{-1}}$ → the rotational energy of a molecule

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

→ *rotational constant* (in cm^{-1})

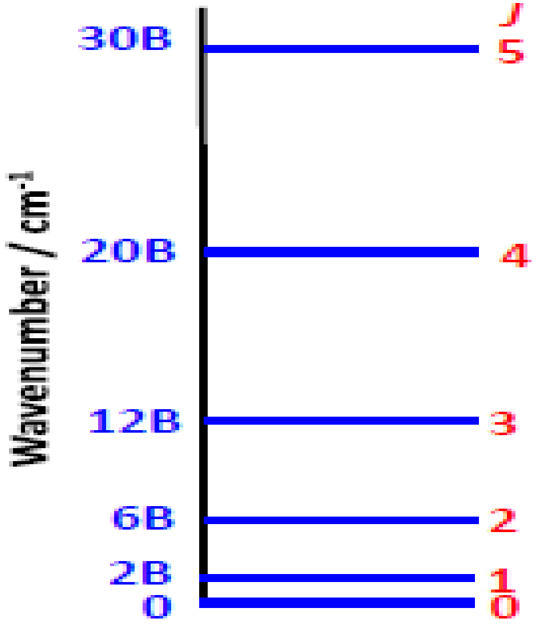


	$\tilde{B}$
H_2	60.85 cm^{-1}
CO	1.93 cm^{-1}
HCl	10.59 cm^{-1}

J= Rotational angular momentum

The rotational energy $E_J = BJ(J+1)$ Cm^{-1} for

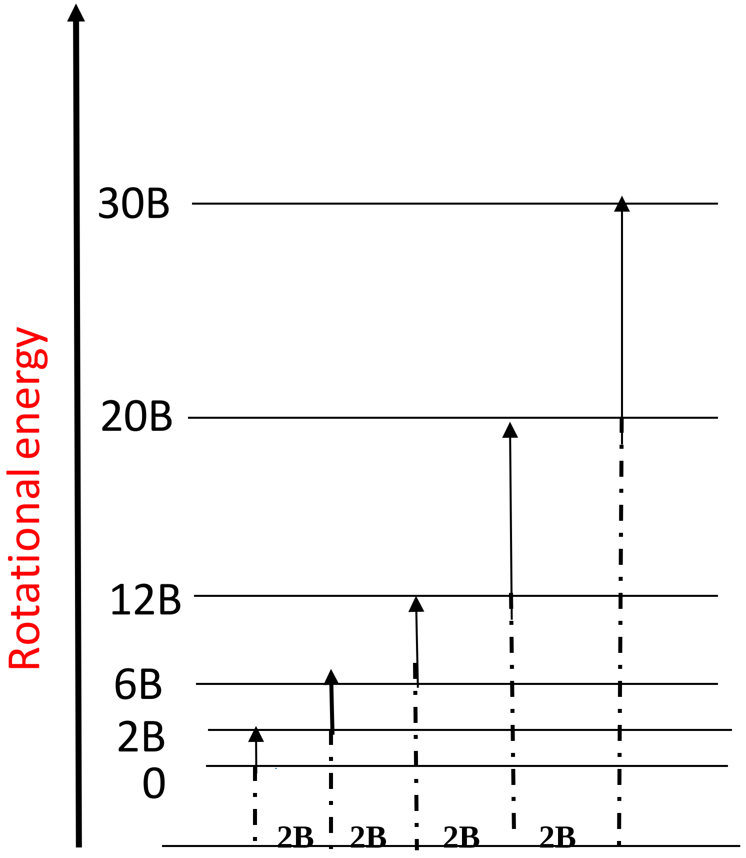
$$E_{rot5} = 30B$$
$$E_{rot4} = 20B$$
$$E_{rot3} = 12B$$
$$E_{rot2} = 6B$$
$$E_{rot1} = 2B$$
$$E_{rot0} = 0$$



For a transition taking place from J to J+1, the rotational frequency is given by

$$\nu_{(J \rightarrow J+1)} = B(J+1(J+2) - BJ(J+1)$$
$$= B(J^2+3J+2) - B(J^2+J)$$
$$= 2B(J+1) \text{ Cm}^{-1}$$

$\nu_{(0\rightarrow1)} = 2B$; $\nu_{(1\rightarrow2)} = 4B$, ; $\nu_{(2\rightarrow3)} = 6B$; $\nu_{(3\rightarrow4)} = 8B$ etc..



Rotational spectrum of a rigid diatomic molecule.

The rotational energy for J=0, E_J = BJ(J+1) = 0

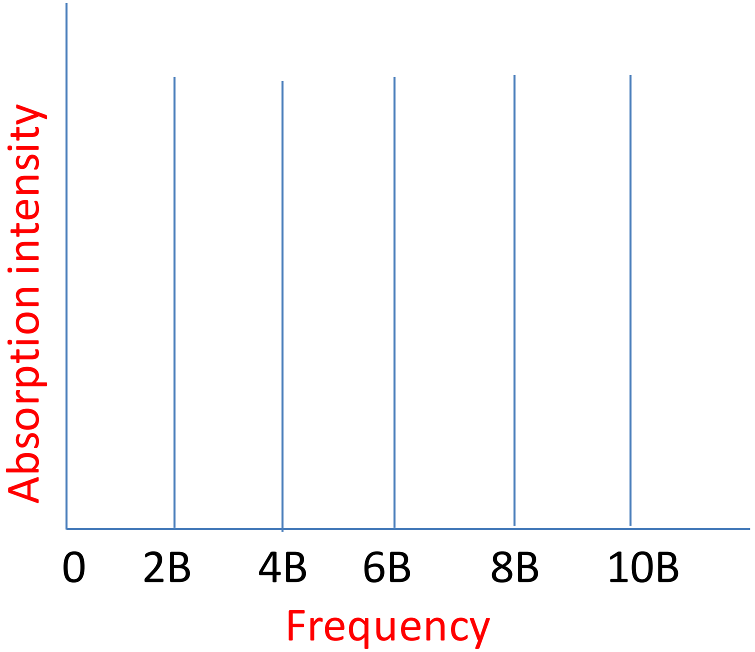
J=1, E_J =2B,

J=2, E_J =6B……. With increase in J value E_J also increases.

E_1-E_0 = 2B, E_2-E_1 = 6B-4B = 2B

Centrifugal force increases the rotating ability of molecules is greater than the strength of the bond and bond is broken.

Selection rules: the selection rules for a transition between any two rotational states **ΔJ = ±1** are allowed transition and all other transitions are forbidden.



Observations: $B = \frac{h}{8\pi^2 c \cdot I} = \frac{h}{8\pi^2 c \cdot \mu R^2}$

→ For large molecules (μ): - the moment of inertia (I) is high,
- the rotational constant (B) is small

For large molecules the rotational levels are closer than for small molecules.

→ From rotational spectra we can obtain some information about geometrical structure of molecule (r):

For diatomic molecule we can calculate the bond length

→ Diatomic molecules rotations can partial apply to linear polyatomic molecules.

→ An isotopic effect could be observed: **$B \sim 1/(\mu R^2)$**

$$\frac{\tilde{B}_{H^{35}Cl}}{\tilde{B}_{H^{37}Cl}} = \frac{\mu_{H^{37}Cl}}{\mu_{H^{35}Cl}} = \frac{37u.u}{38u} . \frac{36u}{35u.u} = 1.0015$$

Rotational spectrum in Non-rigid rotor

- In the pure rotational spectra of a diatomic molecule when the bond in it is considered as rigid the spacing between 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 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, moment of inertia increases with the rotational energy. This causes rotational levels to be as the **‘J’** values increases

Spectrum of a Non-rigid rotor

The Schrodinger equation may be employed for a non-rigid rotor. The energy levels of a non-rigid rotor are given by these equation as follows:

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

Or $E_J = E_J/hc = BJ(J+1) - DJ^2(J+1)^2 \ Cm^{-1}$

D is centrifugal distortion constant, $D = h^3/32\pi^4 I^2 c\, r^2 k \ Cm^{-1}$ ----------1

k is the bond stretching force constant

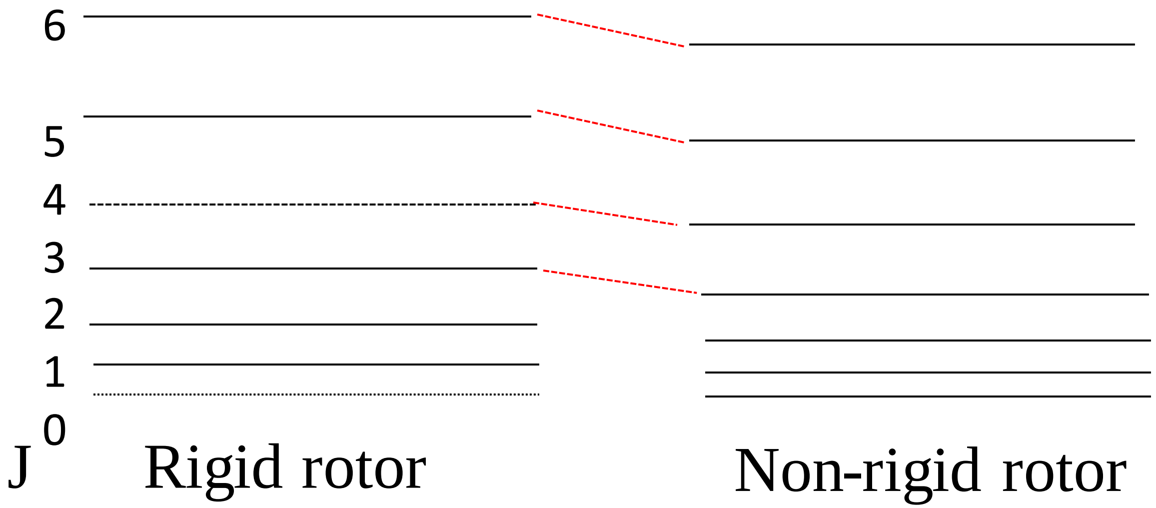
Equation 1 is applicable to a diatomic harmonic oscillator.

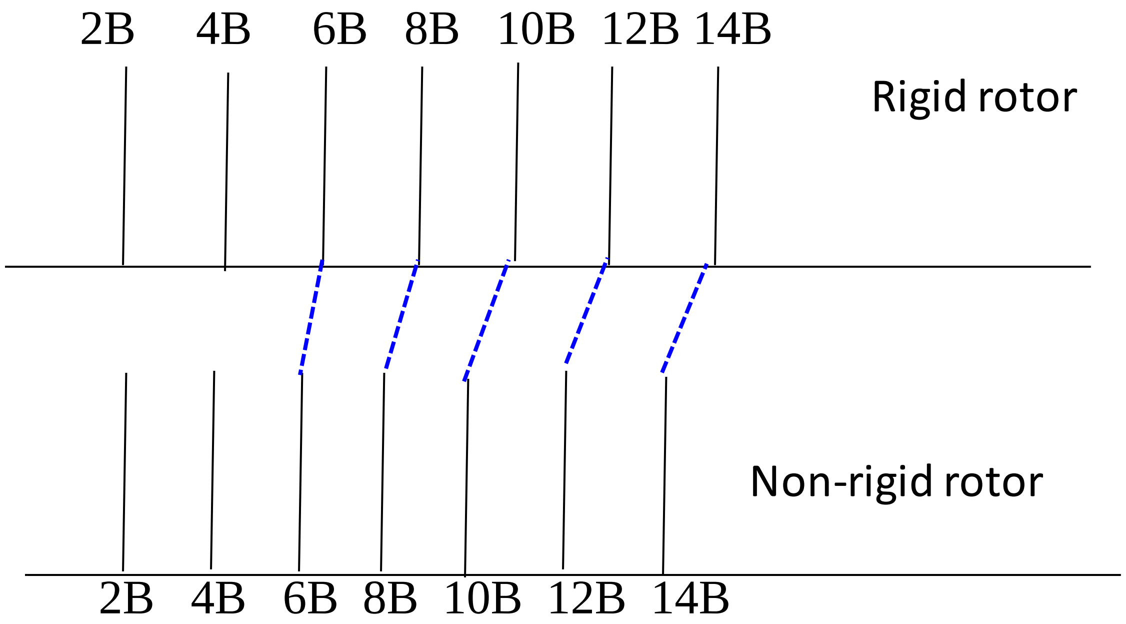
For the Anharmonic oscillator the expression should be modified as

$$E_J = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + KJ(J+1)^4 \ldots\ldots Cm^{-1}$$

$D = 4B^3 / W^2$

D is always positive


6
5
4
3
2
1
0
J
Rigid rotor
Non-rigid rotor


2B
4B
6B
8B
10B
12B
14B
Rigid rotor
Non-rigid rotor
2B
4B
6B
8B
10B
12B
14B

Linear polyatomic molecules

Linear polyatomic molecules can be treated like diatomic molecules.

The rotational energy E_J , in this case is given by $E_J = Bhc\ J(J+1)$

The transition from one rotational state to another in rotational spectra it needs

1. Bhor quantum condition, $\Delta E = h\gamma$ or hc/λ
2. Molecule must possess a permanent dipole moment.
3. $\Delta J = \pm 1$

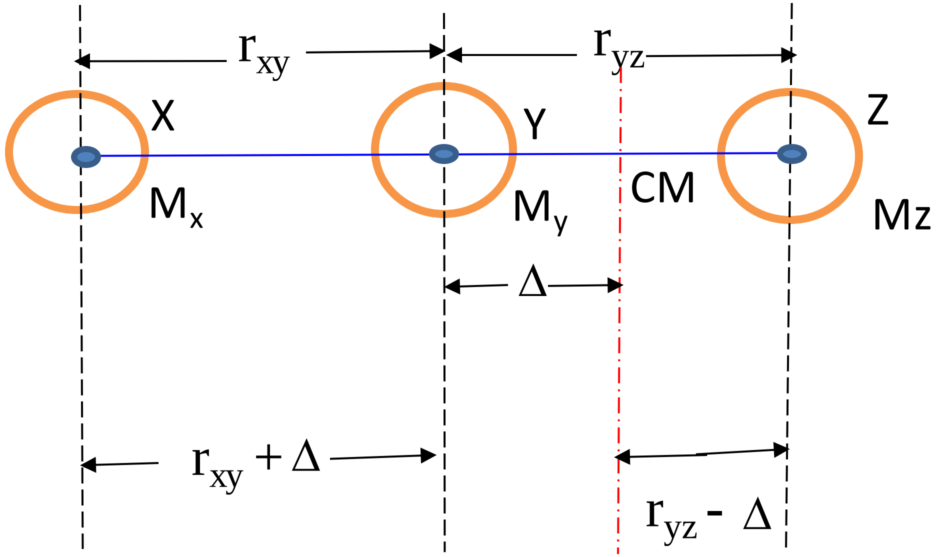
- Thus the rotational spectra of a linear polyatomic molecules will consists of a set of nearly equally spaced lines from which a rotational constant B can be determined.
- This B can be used to determine I and r.
- But only one moment of inertia for the end-over-end rotation can be obtained from the spectrum.
- It is impossible to obtain two unknowns from equation.
- If there is ‘**n**’ number of atoms in the molecule we have **(n-1)** different moment of inertia can be obtained.
- The internuclear distances for the isotopic molecules are assumed to be same.

Consider linear unsymmetrical triatomic molecule such as **OCS, HCN** as shown in figure

The conservation of moments in fig.

$$M_x(r_{xy} - \Delta) + M_y\Delta = M_z\ (r_{yz} - \Delta)$$

$$\Delta = \frac{M_z r_{yz} - M_x r_{xy}}{M_x + M_y + M_z}$$



The moment of inertia of the molecule about an axis passing through centre of mass will be

The moment of inertia of the molecule about an axis passing through centre of mass will be

$$I = M_x(r_{xy}+\Delta)^2 + M_y\Delta^2 + M_z\ (r_{yz} - \Delta)^2$$

$$I = \frac{M_x M_y r^2_{xy} + M_x M_z (r_{xy} + r_{yz})^2 + M_z M_y r^2_{yz}}{M_x + M_y + M_z}$$

This gives two moment of inertia are used to calculate two bond lengths.

Non – linear polyatomic molecules:

The rotational spectra of polyatomic molecules show features not found in the spectra of diatomic molecules. Whereas the diatomic have only one bond distance and hence one moment of inertia, polyatomic molecules have more than one bond distance and hence several moment of inertia.

Classification of polyatomic molecules:

Moment of inertia	**Type of rotor**	**examples**
$I_A = I_B = I_C = 0$	Linear	HX,O=C=S,HCN
$I_A = I_B = I_C$	Spherical top	CH_4,SF_6,UF_6
$I_A > I_B = I_C$ $I_A < I_B = I_C$	Prolate symmetric top Oblate symmetric top	NH_3,$CHCl_3$,CHCl BCl_3
$I_A \neq I_B \neq I_C$	Asymmetric top	H_2O, SO_2,Vinyl chloride

Effect of isotopic substitution on the transition frequencies:

- When a particular atom is replaced by its isotope, the resulting substance is identical chemically with original molecule changes in atomic mass.

- The **bond length does not change on isotopic substitution,** only changes in total mass, moment of inertia **‘ I ’** and rotation constant **“B”** of the molecule.

- The internuclear distance does not alter for equilibrium configuration. Since electronic energy depends only on the nuclear charges and not on the nuclear mass

- However, the molecule has Zero point and this changes the conditions since the vibrational level , that is the Zero point vibration

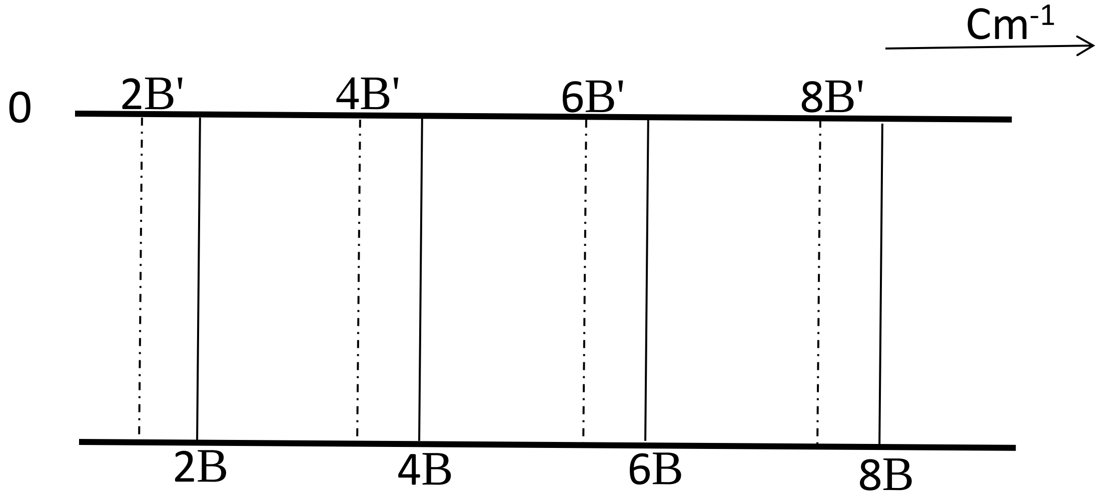
- Thus, the molecules having different isotopes of the same element exhibit different spectra. Hence reduced mass as well frequencies of vibration and rotation would be different

- Force constant which depends upon the extra nuclear electrons mainly are to remain constant.
- The vibrational frequency of lighter species will be larger than that of the heavier one.
- Assuming harmonic vibration of each species, the rotation constant would change because **‘I’** would be different.
- As a consequence, two species would give two superimposed bands with their origins slightly shifted from one another and the lines in the fine structure appear as doublet. Such doublets have been established and the isotope shift in the lines measured.

Rotational spectrum of CO to show the effect of isotopic substitution

From **$^{12}C^{16}O$ to $^{13}C^{16}O$** there is an increase in mass and hence a decrease in B value,
i.e., **B > B'**

❖This change is reflected in the rotational energy of CO molecule



$\mathbf{B} = h/8\pi^2 IC \quad B' = h/8\pi^2 IC$

$$\mathbf{B' / B} = \mu / \mu'$$

$$\mathbf{B} \propto \mathbf{1}/\mu$$

Reduced mass increases Rotational constant decreases

Determination of bond lengths

- A microwave spectrum can be provide upto three moments of inertia, **‘I’** for the molecule.
- Employing I’s and appropriate isotopic substitution, it is possible to calculate accurate bond lengths.
- Linear and symmetric molecules give only one moment of inertia and planar molecules yield two I’s , but their spectra indicate their symmetry.

Calculation of bond length:

- The spacing between spectral lines in case of diatomic molecules is **2B Cm^{-1}** where **$B = h / 8\pi^2 I^2 C \ Cm^{-1}$**
- Thus from rotational spectra, **B** is determined and from the value of **B**, moment of inertia ‘**I**’ and bond length ‘r’ can be determined.

Calculation of bond length:

Problems:

1. The pure rotational spectrum of gaseous HCl molecule consists of series of equally spaced lines separated by 23.80 cm^{-1} .Calculate the internuclear distance of the molecule. The atomic masses are: $^{1}H = 1.67x\ 10^{-27}$ kg : $^{35}Cl = 58x\ 10^{-27}$ kg.
2. In the rotational spectrum of gaseous CO molecule consists of series of equally spaced lines separated by 3.844cm^{-1}
3. First line in rotational spectrum of CO appears at 4 Cm^{-1} . Find its bond length.

Vibrational spectroscopy

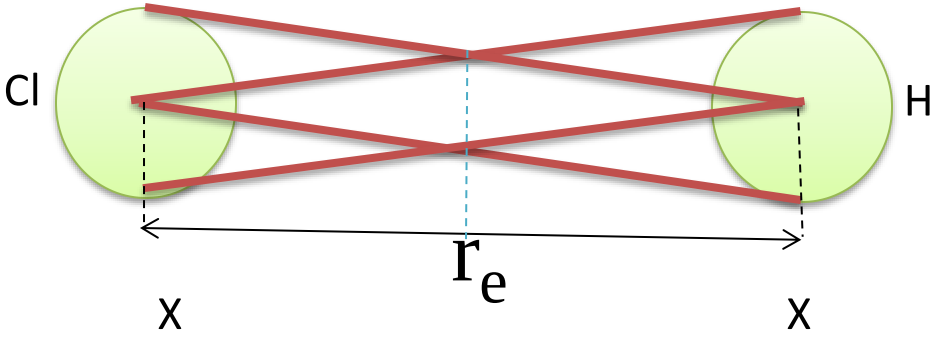
Vibrational (Infrared) spectra of diatomic molecules

A diatomic molecule **m_1** and **m_2** joined by a chemical vibrates as a one-dimension oscillator (S.H.O). Classically the vibrational frequency of a by a spring of force constant is given by

- Hook’s law relates the restoring force, F as

$$F = -kx.$$

where k is a force constant



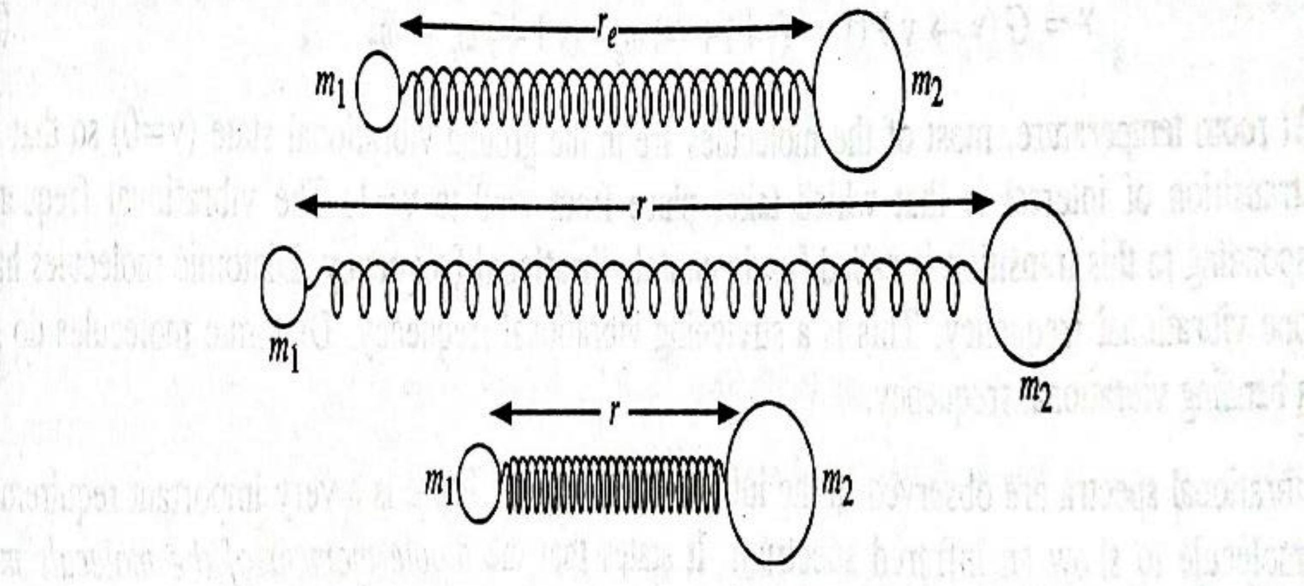


Fig. 12. Vibration of a diatomic molecule.

$$\boldsymbol{\nu} = \frac{1}{2\pi}\left[\frac{k}{\mu}\right]^{1/2} \text{Hz}$$

$\boldsymbol{\nu}$ is the vibrational frequency

To convert the vibrational frequency $\boldsymbol{\nu}$ from **S^{-1}** to Hertz to **Cm^{-1}**, we divide by C, the velocity of light.

$$\left[C = \nu\lambda = \frac{1}{\lambda} = \bar{\nu} = \nu/C\right]$$

$$\bar{\boldsymbol{\nu}} = \frac{1}{2\pi C}\left[\frac{k}{\mu}\right]^{1/2} \textbf{Cm}^{-1}$$

The units of the force constant are Nm^{-1}. the potential energy of the simple harmonic oscillator (S.H.O) as a function of displacement from the equilibrium configuration is given by the parabolic hook's law equation,

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

Where $x = (r - r_e)$ is the displacement, r_e being the equilibrium bond length.

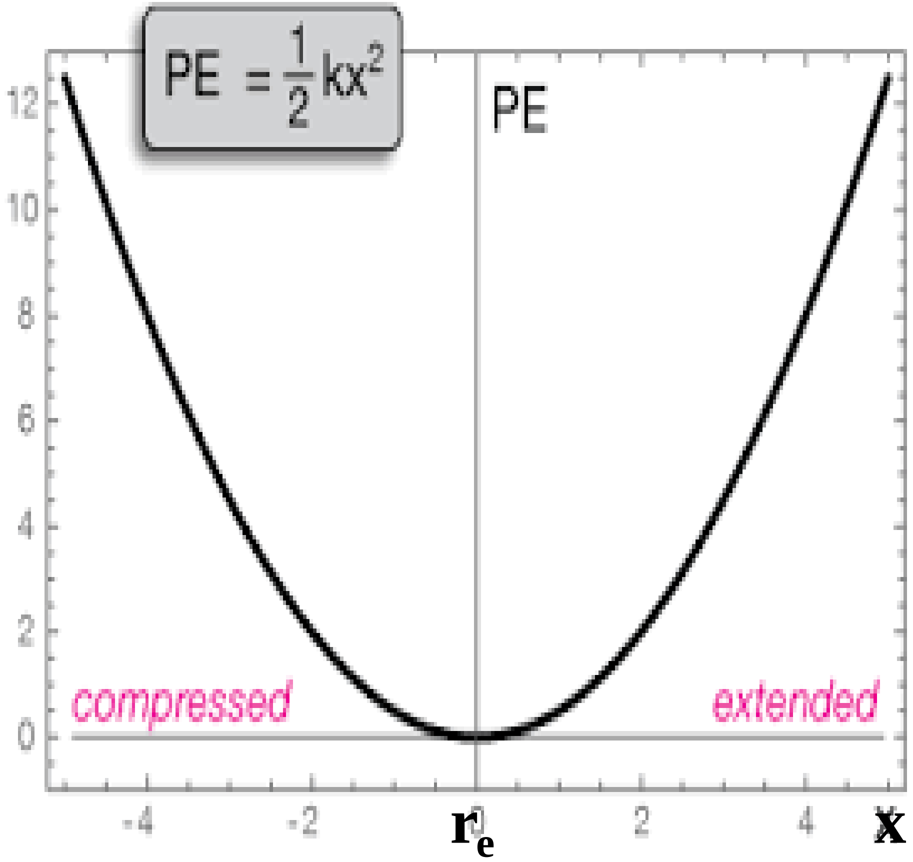
The hook’s law potential energy is shown in below fig.

The vibrational energy of diatomic molecule is given by

$\mathbf{E_v} = (v + \frac{1}{2})\, h_0 \nu_{osc}$; $v = 0,1,2,3,\ldots.$

v = Vibrational quantum number.

ν_{osc} = frequency of oscillation



Converting energy into spectroscopic units i,.e Cm^{-1}

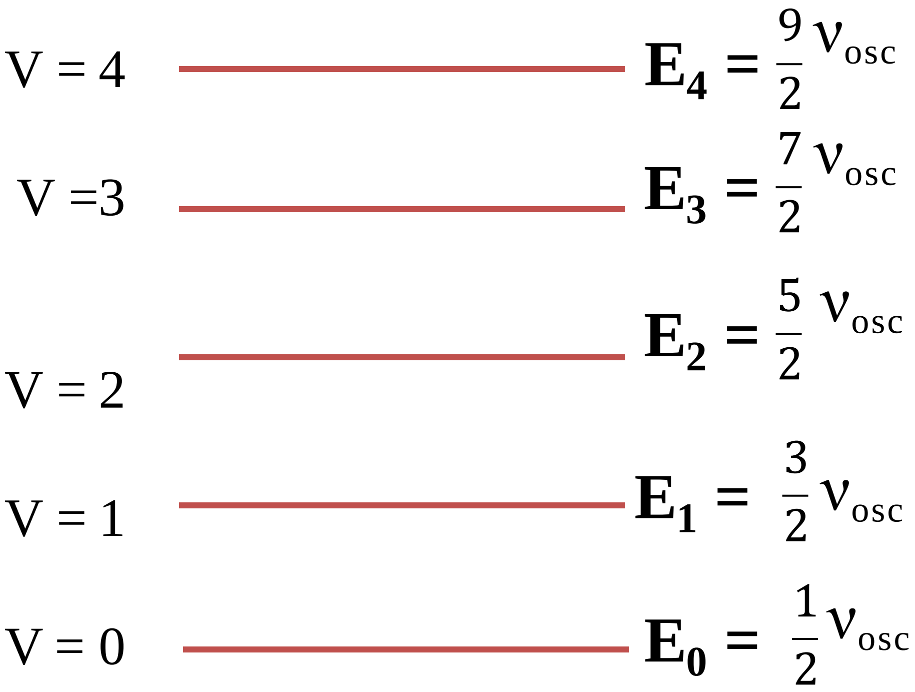
$\mathbf{Ev} = \frac{E_v}{hc} = (V + \frac{1}{2})\ \nu/c = (V + \frac{1}{2})\ w_e\ cm^{-1}$, V = 0,1,2,3,…. Where E_v is called the vibrational term, where $\nu/c = \nu_{osc} = w_e$

Selection rules: ΔV = ± 1

$\mathbf{E_0} = {}^{1}/_{2}\ \nu_{osc}$ $\mathbf{E_1} = {}^{3}/_{2}\ \nu_{osc}$ $\mathbf{E_2} = {}^{5}/_{2}\ \nu_{osc}$

$\mathbf{E_3} = {}^{7}/_{2}\ \nu_{osc}$ $\mathbf{E_4} = {}^{9}/_{2}\ \nu_{osc}$

$\Delta E = E_1 - E_0 = \nu_{osc}\ Cm^{-1}$ is constant for all the transition that follow selection rules



V = 4 $\mathbf{E_4} = \frac{9}{2}\nu_{osc}$

V =3 $\mathbf{E_3} = \frac{7}{2}\nu_{osc}$

V = 2 $\mathbf{E_2} = \frac{5}{2}\nu_{osc}$

V = 1 $\mathbf{E_1} = \frac{3}{2}\nu_{osc}$

Zero point energy → V = 0 $\mathbf{E_0} = \frac{1}{2}\nu_{osc}$

Vibrational transitions

Simple harmonic oscillator

- The vibrational motion resembles the motion observed for a ball attached to a string i.e., Harmonic oscillator which obeys hook’s law.

i.e., the force the spring excise on the particle is proportional to the displacement from the equilibrium position, x (x=0).

- Hook’s law relates the restoring force, F as F= - kx.

  where k is a force constant

∴ Potential energy of the particle

$$V(x) = Kdx \text{ or } V(x) = \int k(x).dx$$

$$\text{Thus, } V(x) = \frac{1}{2}kx^2$$

Application of newton’s second law gives the familiar equation of simple harmonic motion (S.H.O) $F = m\frac{d^2x}{dt^2}$

Hence, restoring force $m\frac{d^2x}{dt^2} = -kx$

The fundamental frequency of the oscillator is

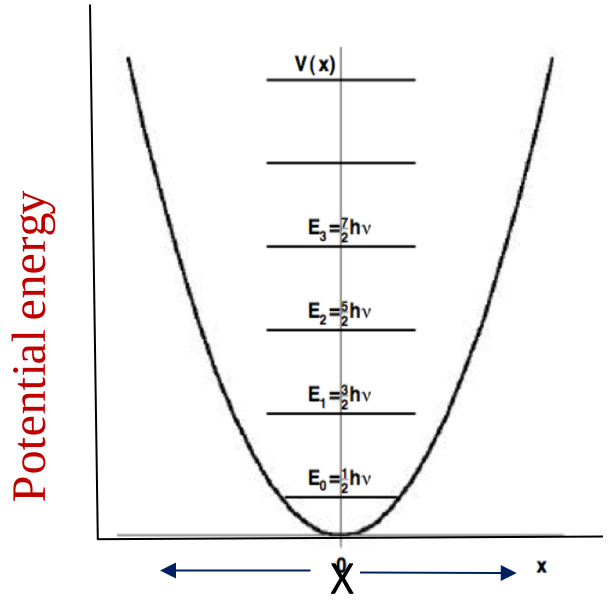
$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

The energy of S.H.O is quantized and is given by

$$E_v = \left(v + \frac{1}{2}\right) h\nu_{osc} \quad v = 0,1,2,3,\ldots.$$

$$E_v = \left(v + \frac{1}{2}\right) h\nu_{osc}\frac{c}{c} = E_v = \left(v + \frac{1}{2}\right)\bar{\nu}_{osc} \text{ Joules}$$

$$E_v = \left(v + \frac{1}{2}\right)\bar{\nu}_{osc} = \left(v + \frac{1}{2}\right) w_0 \text{ cm}^{-1}$$



The Hook's law potential energy for a diatomic vibrator

Thus a series of equally spaced and never ending vibrational levels are predicted and the molecule cannot dissociate.

Thus, the energy difference between successive vibrational levels is $\bar{\nu}$ Cm^{-1}. These levels are equally spaced(in figure)

Zero point energy:

- The lowest energy of a quantum mechanical harmonic oscillator is not zero but it is equal to ½ hν is called Zero point energy.
- The energy of each energy level arise from two sources, these are Kinetic energy and potential energy.
- The vibrational motion of an harmonic oscillator is that the difference between the energy levels is same for all the values of V. i,.e $\Delta E = E_{v+1} - E_v = \nu_{osc}$ Cm^{-1}
- For V = 0 Zero point energy ½ hν. It cannot be removed fro the molecule even by cooling it to 0K.
- Molecules has oscillator should always have some energy in the lowest energy state.
- Particles are fluctuating around its equilibrium position and close to zero displacement with zero point energy, ½ hν.
- For water molecule, the zero point energy taking the symmetric stretching, bending and asymmetric stretching vibrations at 3650, 1595 and 3750cm^{-1}

Force constant and bond strengths

- In a harmonic oscillator, the restoring force per unit displacement is known as force constant f and given by
- $f = 4\pi^2\nu^2 \dfrac{m_1\, m_2}{m_1 + m_2}$

- Force constant is increased approximately in proportion to the multiplicity of the bond.
- It's unit is dynes Cm^{-1} .
- Force constant increases as the bond energy increases and bond length decreases.

Ex: H—H $\longrightarrow$ 514 Nm^{-1} , F—F $\longrightarrow$ 445 Nm^{-1}, Cl—Cl $\longrightarrow$ 329Nm^{-1},
H — Cl $\longrightarrow$ 480 Nm^{-1} , H — Br $\longrightarrow$ 420 Nm^{-1} , H — F $\longrightarrow$ 970 Nm^{-1}

$\mathbf{Ev} = \frac{E_v}{hc} = (V + \frac{1}{2})\, \nu/c = (V + \frac{1}{2})\, w_e\ \mathrm{cm}^{-1}$,

$v = 0,1,2,3,\ldots$. Where $\mathbf{E_v}$ is called the vibrational term,

where $\nu/c = \nu_{osc} = w_e$

The selection rule for vibrational transition in the simple harmonic oscillator

$$\Delta \mathbf{V} = \pm \mathbf{1}$$

The operative part of the selection rule for the absorption spectrum is $\Delta V = +1$, i.e., the vibrational quantum number changes by unity. Using the selection rule, the frequency of the vibrational transition is given by

$$\bar{\mathbf{v}} = \mathbf{E(v \longrightarrow v+1) = (v+1 + \tfrac{1}{2})w_e - (v+1)\, w_e}$$

At room temperature, most of the molecules are in ground vibrational state (v = 0) so that the only the transition of interest is that which takes place from v = 0 to v = 1.The vibrational frequency corresponding to this transition is called fundamental vibrational frequency . Diatomic molecule have only one vibrational frequency. This is stretching vibrational frequency. Diatomic molecule do not have a bending vibrational frequency.

Vibrational spectra are observed in the infrared (IR) region. There is a very important requirement for a molecule to show an infrared spectrum.it states that the dipole moment of the molecule must change during the vibration. Homonuclear diatomic molecule such as H_2, O_2, N_2 , etc., do not have the permanent dipole moment nor does the stretching of the bond between the two atoms change the dipole moment from Zero. Hence , Homonuclear diatomic do not show IR spectra. On the other hand, heteronuclear diatomic molecules such as CO, NO, CN, HCl, do posses a dipole moment which changes when the bond length changes. Hence, they show IR spectra. Thus, Homonuclear diatomics are IR inactive while heteronuclear diatomics are IR active.

In practice, the molecule does not always vibrate as a simple harmonic oscillator; there is presence of what is called **anharmonicity.** In 1929 P. M. Morse suggested an empirical expression for the potential energy of an harmonic oscillator, given by

$$V(r) = D_e\,[1- \exp\{a(r-r_e)\}]^2$$

Here **a** is a constant and D_e is the dissociation energy of the molecule.

The Morse potential energy is as shown in below figure

Morse potential

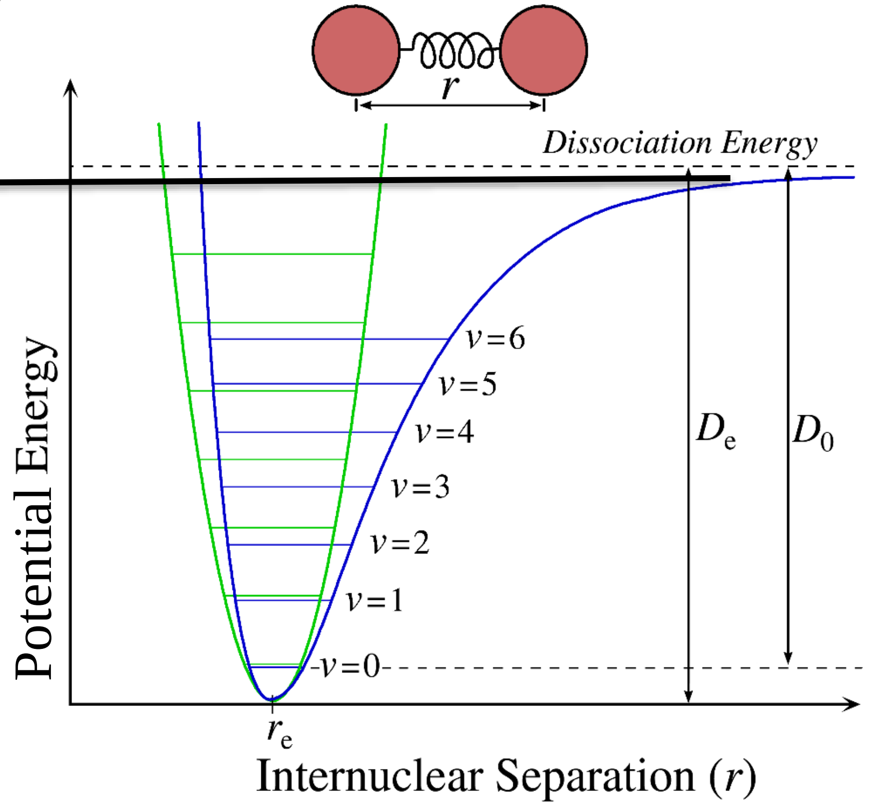


Fig: Morse potential energy for an anharmonic diatomic oscillator

It may be pointed out that the dissociation energy D_e in the Morse potential energy curve is measured from the bottom of the potential well. The experimentally measured dissociation energy D_0 is measured from the ground level (v = 0) to the top. Thus, $D_e = D_0 + {}^{h\nu}/_{2}$

When the Schrodinger equation for an anharmonic oscillator is solved using the Morse potential energy, the energy levels are given by

$$E(v) = = (V + \frac{1}{2}) w_e - (V + \frac{1}{2})^2 w_e x_e \;\; ; (v = 0,1,2,3,\ldots.)$$

Where $\mathbf{w_e x_e}$ is called the **anharmonicity constant.**

As expected, $w_e x_e \ll w_e$ .The consequence of anharmonicity is that the vibrational energy levels of the S.H.O. are slightly lowered and the spacing between them is no longer constant but goes on steadily decreasing with increase vibrational quantum number. Also, because of anharmonicity, the rule for vibrational transition is no longer **ΔV=±1**. Instead transitions corresponding to **ΔV= ±2**, **±3**, etc., are also observed in the IR spectra. These are called the first overtone, the second overtone, etc., respectively

The intensity of an overtone is dependent on the anharmonicity of the vibration. Compared with the highly intense fundamental vibrational frequency, the overtone are very weak, i. e., of considerably low intensity.

Overtones: Transition from ground state (v = 0) to the second excited state (v = 2) called 1st overtone. The transition from (v = o) to (v = 3) called 2nd overtone.

Hot bands: Transition from (v = 1) to (v = 2) or (v = 3)… are called Hot bands.

ROTATION – VIBRATION (IR) SPECTRA OF DIATOMIC MOLECULES

Pure vibrational spectra can be observed only in liquids where interaction between molecules inhibit rotation. Since rotational energies are considerably smaller than vibrational energies, the freely moving molecules in the gaseous state are almost always rotating regardless of their vibration state. Hence , molecules in gaseous state show rotation-vibration spectra. The rotation and vibration are, to a first approximation, independent of each other. Ignoring the effect of centrifugal distortion and taking into account the anharmonicity, the **rotation vibration** term, $S(\nu\ J)$, for vibrating rotator is given by

$$S(\nu\ J) = F(J) + G(\nu)$$

$$BJ(J + 1) + (\nu + \tfrac{1}{2})\, w_e - (\nu + \tfrac{1}{2})^2\, w_e x_e \ \ Cm^{-1} \text{ ---------1}$$

The selection rules for combined vibrational and rotational transitions are

$\boldsymbol{\Delta V = \pm 1}$ **and** $\boldsymbol{\Delta J = \pm 1}$ ----------2

It is customary to designate the lower energy state by double prime and upper energy state by a single prime. Using the energy level expression (1) and the selection rule (2), we have

$$\boldsymbol{\Delta S(}\nu, J\boldsymbol{)} = BJ'(J' + 1) \left[\frac{3}{2} w_e - \frac{9}{2}\ wexe\right] – \left[BJ''(J''+ 1) + \left(\frac{1}{2} w_e - \frac{1}{4} w_e x_e\right)\right]$$

$$= w_0 + B(J' - J'')(J' + J'' + 1)\ \mathrm{cm}^{-1}$$

where $w_0 = w_e(1-2x_e)$

Here we have assumed that the rotational constant B is the same in the upper and lower vibrational states, an assumption that is just justified by the fact that rotation and vibration are, to a first approximation, independent. Since most of the molecules are in the round vibrational state at room temperature, only the **V = 0 to V = 1 transition is of interest.**

i) For the **ΔJ = +1** transition $J' = J'' + 1$,

i.e., $J' - J'' = +1$ so that

$\boldsymbol{\Delta S}(\nu, J) = w_0 + 2B(J'' + 1)\ \mathrm{cm}^{-1}$; $J'' = 0,1,2,3,\ldots\ldots$ --------3

ii) For the **ΔJ = -1** transition, $J'' = J' + 1$,

i.e., $J' - J'' = -1$ so that

$\boldsymbol{\Delta S}(\nu, J) = w_0 + 2B(J' + 1)\ \mathrm{cm}^{-1}$ $J' = 0,1,2,3,\ldots\ldots$--------4

Combining the expressions 3 & 4

$\mathbf{\Delta S}$ **(**ν, J**)** = ν_{spec} = w_0 + 2B m cm^{-1} m = ±0, ±1,±2, ±3, ±4, ……----------5

Notice that m = J′′+ 1in equation 3 and J′ + 1 in equation 4 ;

it is positive for ΔJ = +1 and negative for ΔJ = -1

The frequency $w_{0,}$ is called the band centre, doesnot appear in the rotation-vibration spectrum which consists of equally spaced lines with spacing equal to 2B on each side of the band centre (in fig).

The lines corresponding to **ΔJ=-1** are called **P branch** while those corresponding to **ΔJ=+1** are called the **R branch.**

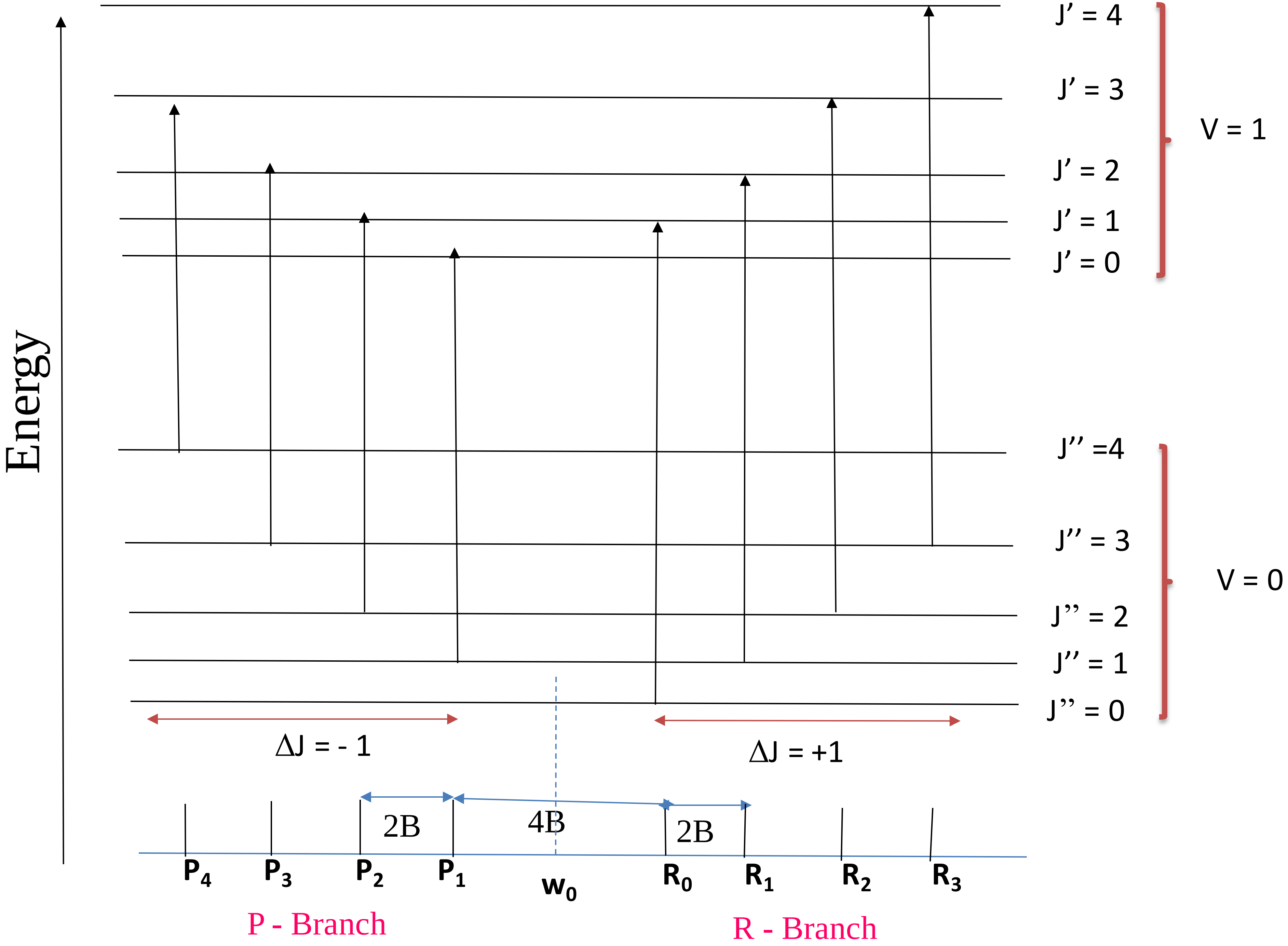


Fig. The Rotation – Vibration spectrum of a diatomic molecule.