Fundamentals of Spectroscopy

Mod2 S7

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Spectroscopy

Spectroscopy is the branch of science which deals with the study of interaction of light with matter.

Spectrum: A range of colours representing light of continuous freque

Light

Matter

Interaction

Light: Electromagnetic radiation

Matter: Any substance which has certain mass m and occupies space

The **molecular structure** can be derived indirectly from the technique, known as **spectroscopy**.

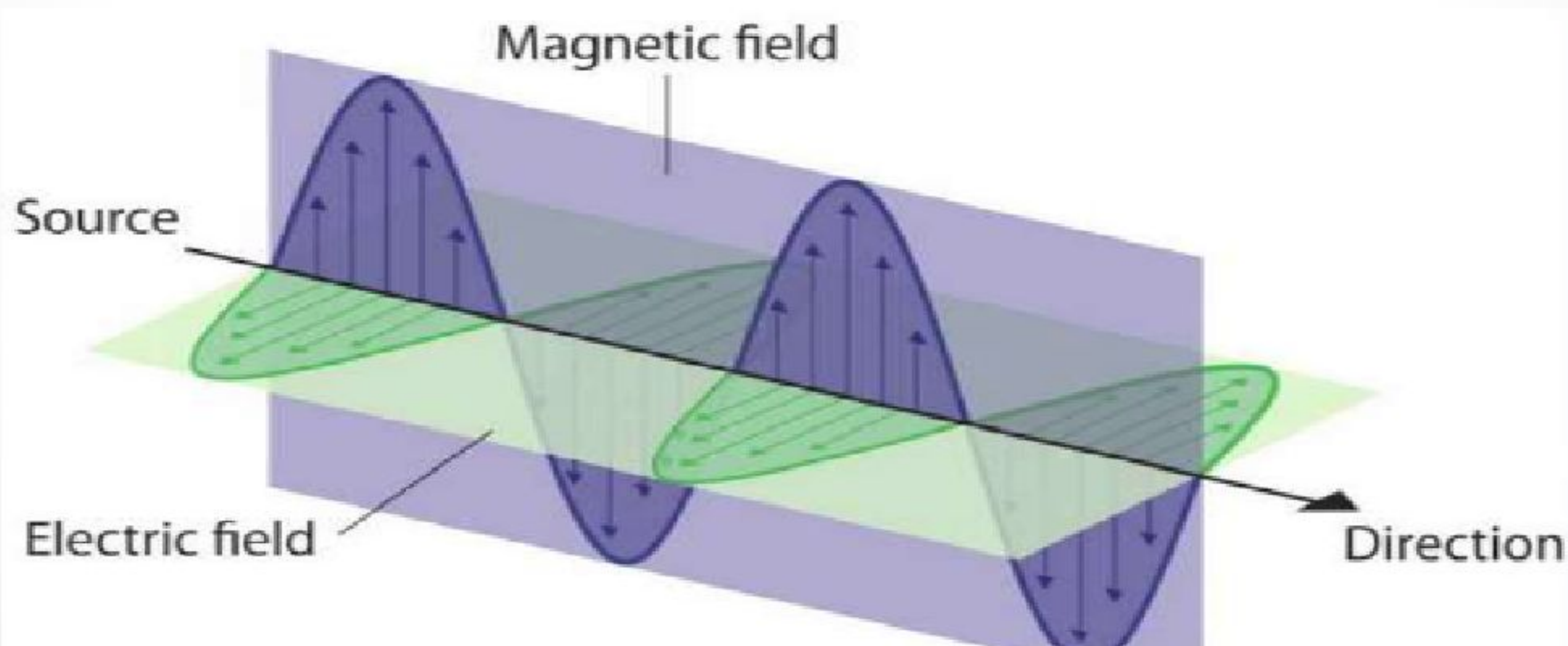
From **quantum chemistry**, we know that

- the **energy levels** of molecular systems are quantized
- designated by appropriate quantum numbers

Electromagnetic Radiation

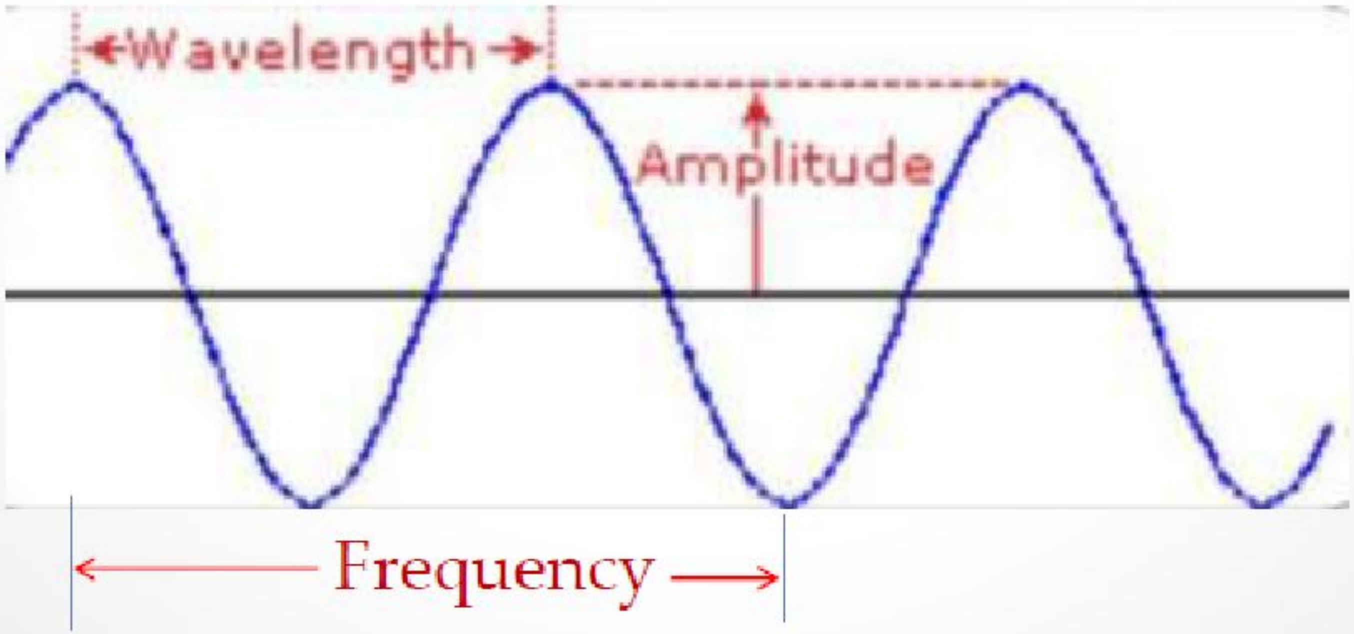
Electromagnetic Radiation:

- Wave produced by motion of electrically charged particles (Photon)
- Consists of two components – Electric and Magnetic



Properties of Waves

- Wavelength (λ) – Distance between two nearest crest or troughs
- Frequency – Number of wave cycle in a given time, measured in Hertz (Hz)
- Amplitude – Wave's height or length

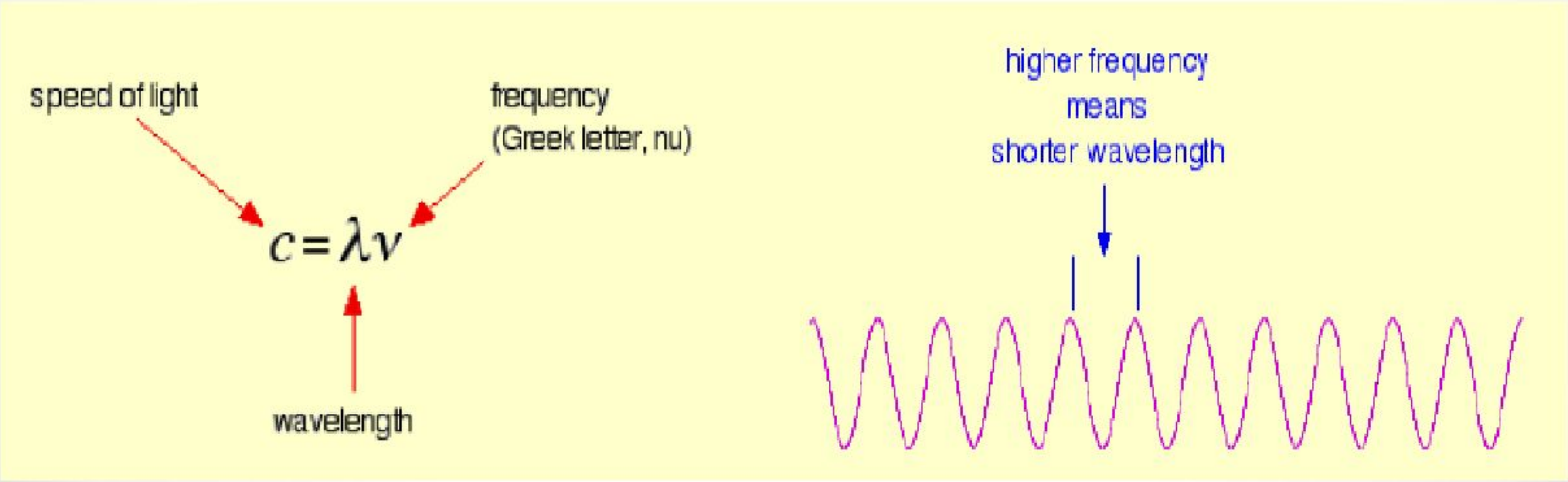


- Relation between frequency and wavelength – velocity (speed) of propagation

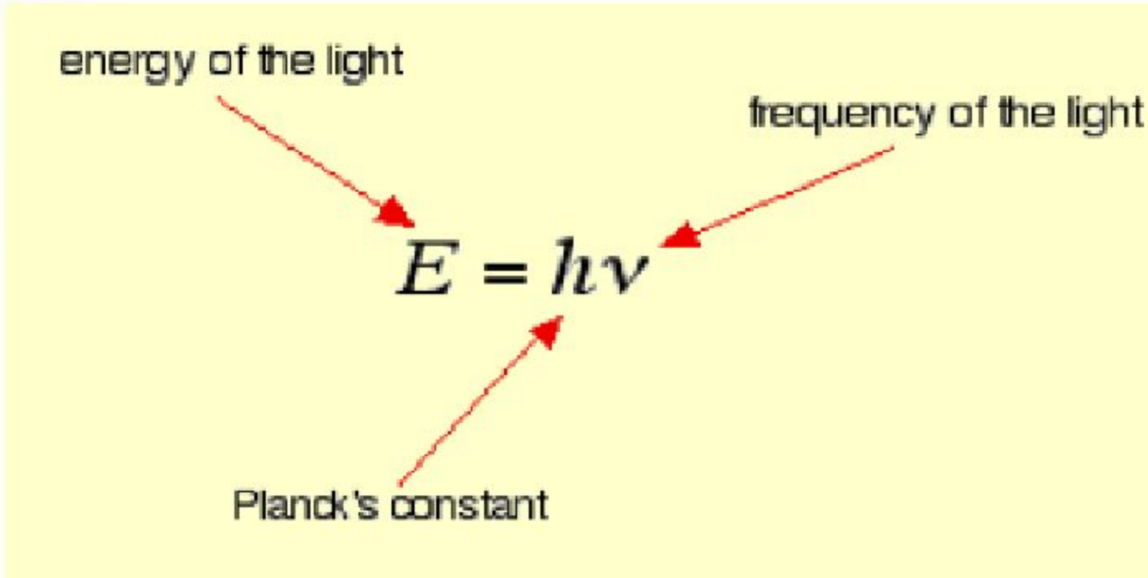
$$C = \upsilon \lambda$$

Where,

$$C = 2.99792 \times 10^8 \text{ m/s}$$



- Relation between frequency of light and energy

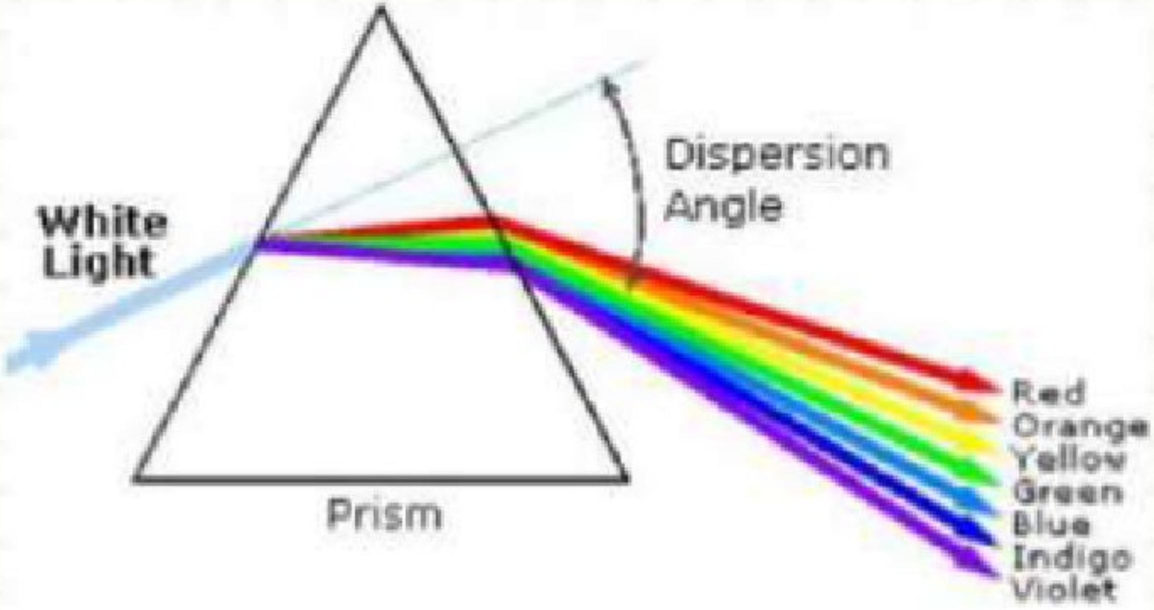


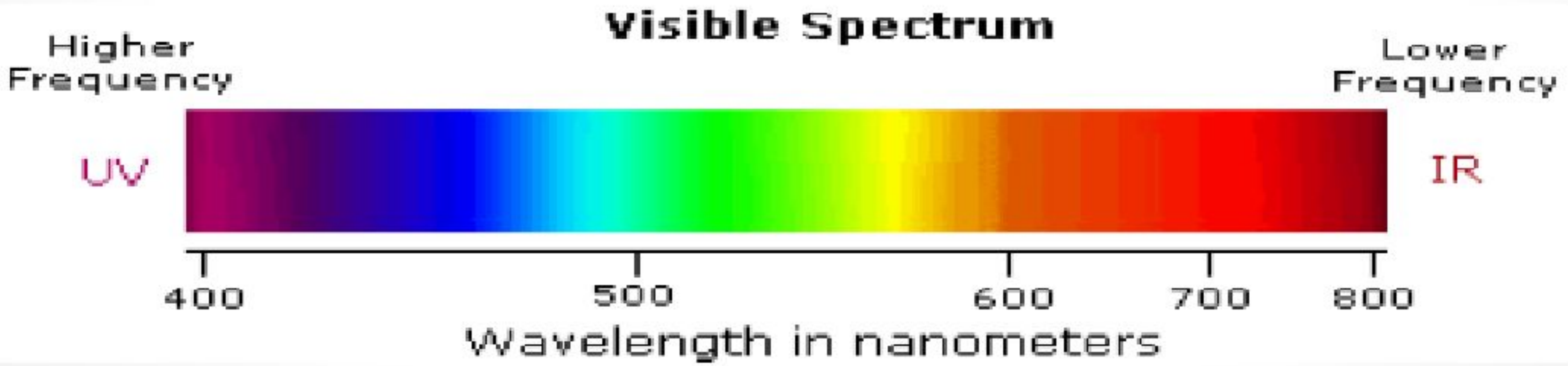
$$E = h\,C / \lambda \qquad\qquad (C = \upsilon\,\lambda)$$

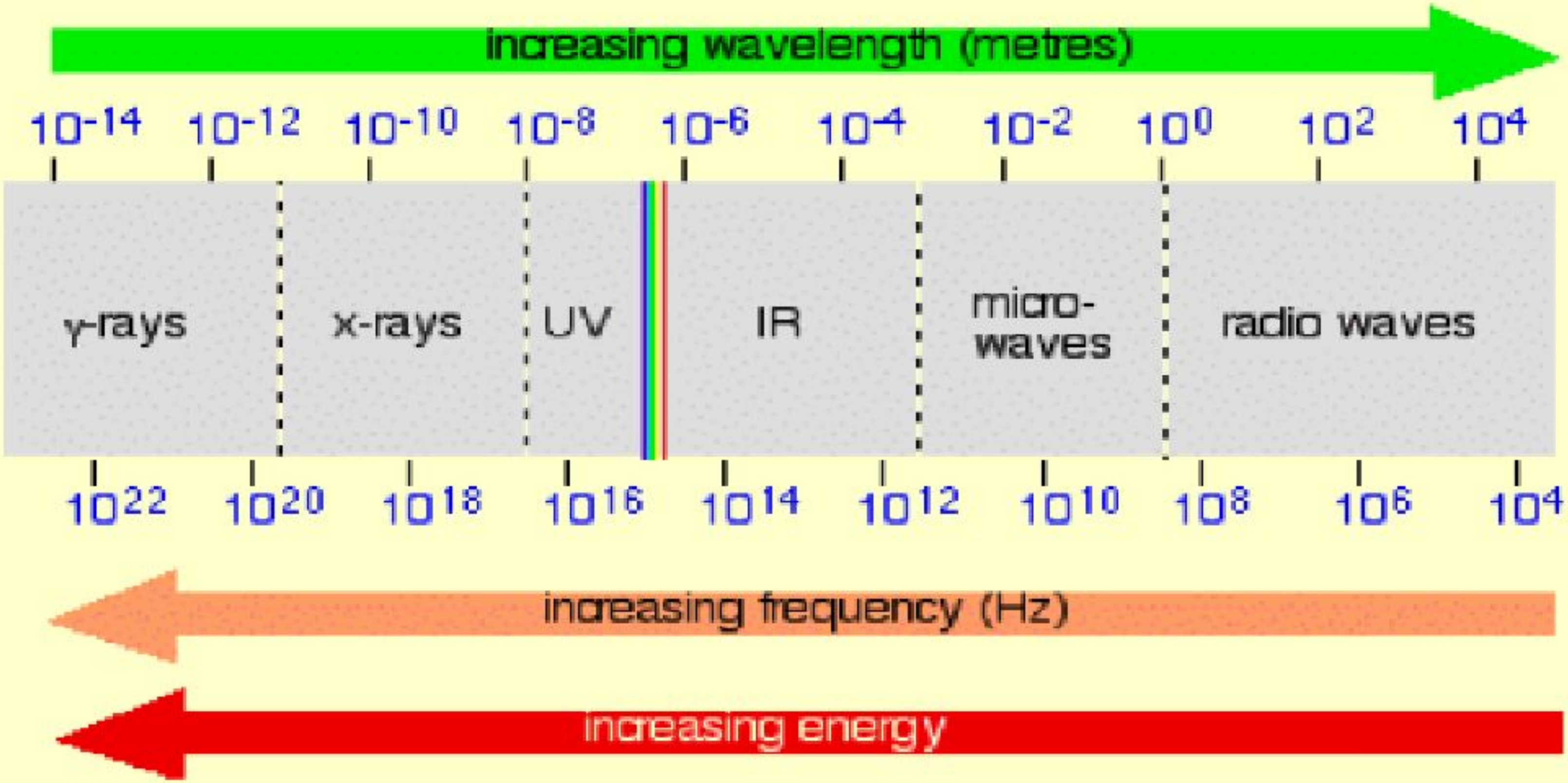
Where,

h = Planck's constant = 6.6261 x 10-34 J.s

Electromagnetic Radiation

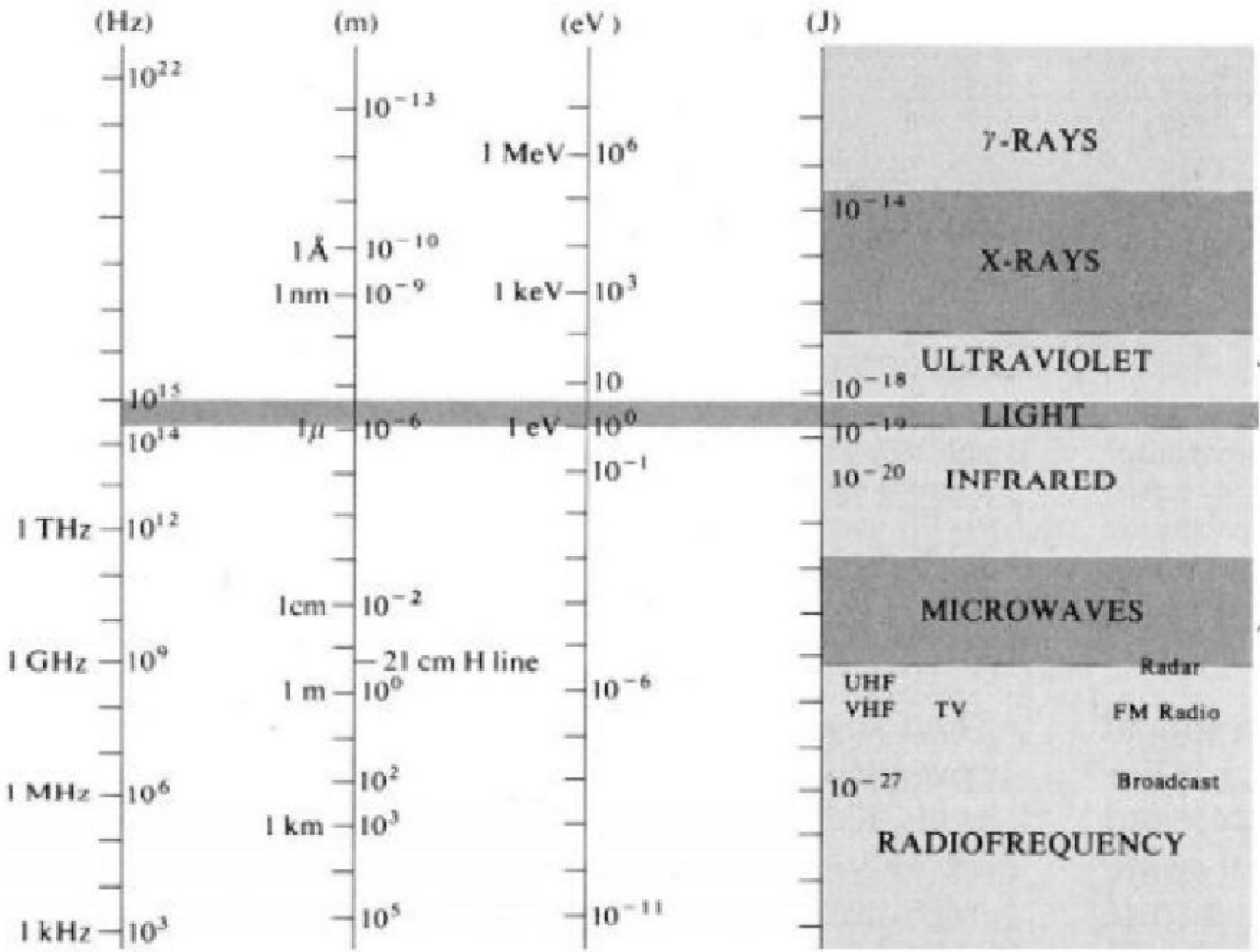






Violet	400 - 420 nm	Yellow	570 - 585 nm
Indigo	420 - 440 nm	Orange	585 - 620 nm
Blue	440 - 490 nm	Red	620 - 780 nm
Green	490 - 570 nm		

Electromagnetic Spectrum

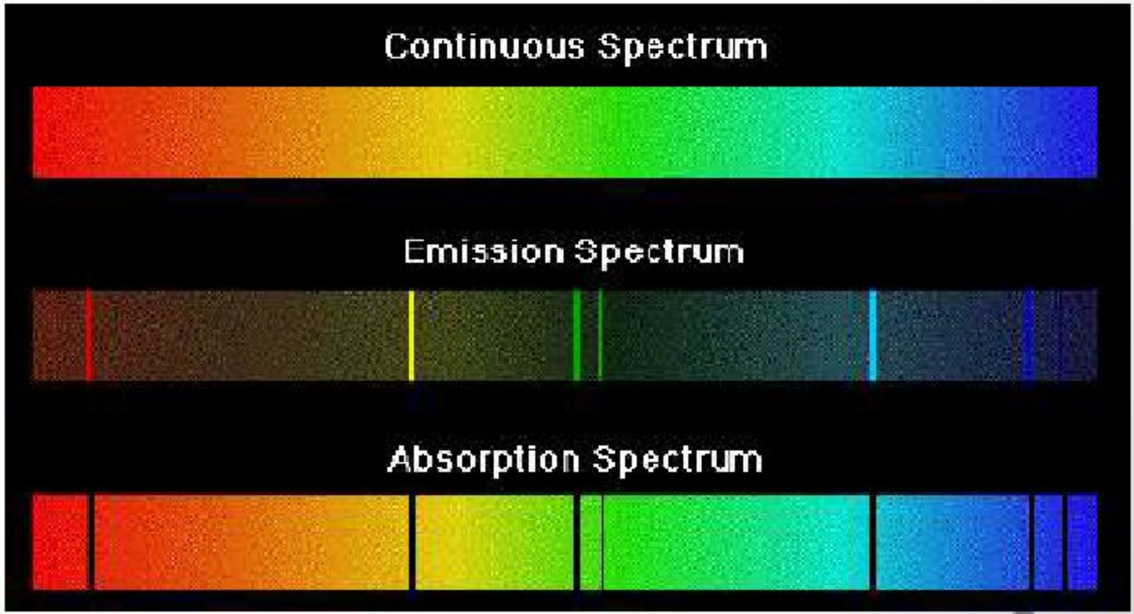


Spectral region for atomic and molecular spectroscopy

Principles of Spectroscopy

- **Principle** – based on measurement of spectrum
- **Spectrum** – graph or plot of intensity of absorbed emitted radiation by sample verses frequency or wavelength
- **Spectrometer** – Instrument design to measure the spectrum of a sample
- **Types of Spectra** –
  - Absorption Spectra
  - Emission Spectra
  - Continuous Spectra

- Continuous Spectra – Spectra obtained when white light passed through a prism
- Absorption Spectra – Spectra obtained by absorption of electromagnetic radiation to the atoms, ions or molecules of sample (UV/Visible, IR)
- Emission Spectra – Spectra obtained by emission of electromagnetic radiation to the atoms, ions or molecules of sample (Mass)



Interaction of EMR with matter

- Absorption : Light is absorbed
- Emission: Light is emitted or released
- Transmission: light is allowed to pass through
- Reflection: light is reflected or bounced away
- Diffraction: shows wave nature
- Refraction: shows particle nature
- Interference: light is disturbed
- Scattering: light is dispersed
- Polarization: light vibration is restricted to one direction

Interaction of EMR with matter

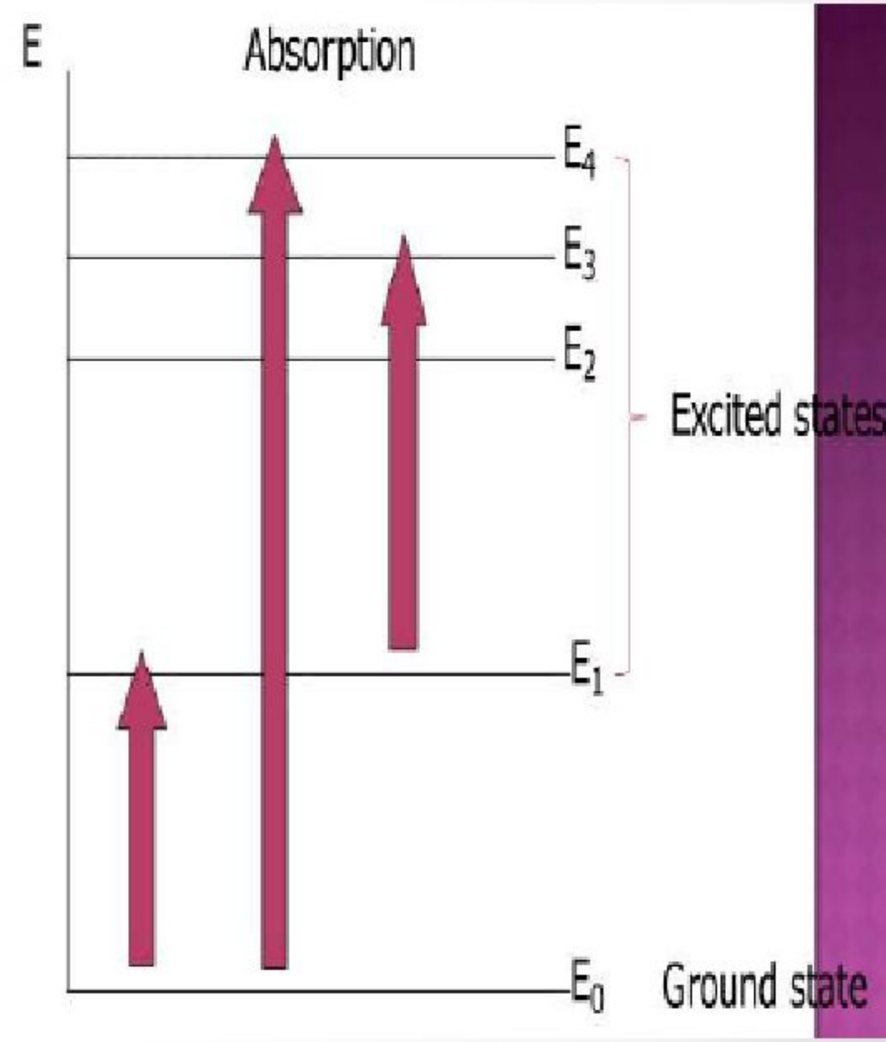
Absorption of Radiation:

1. Electronic energy level

- Molecules at RT – lowest energy level E_0
- Molecules absorbs energy (UV/ Visible) – promoted to higher energy level E_1, E_2……..E_4
- Difference in Energy

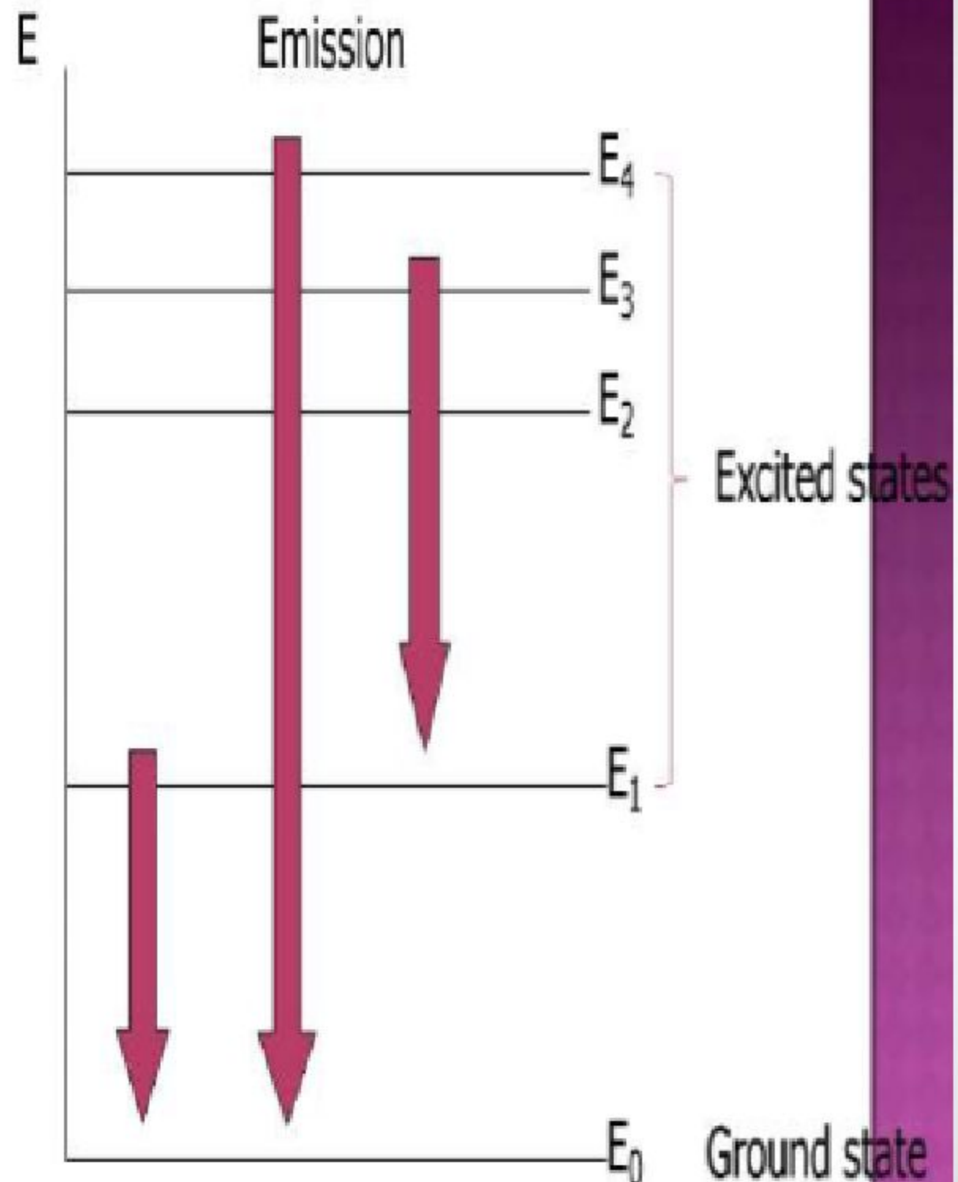
$$\Delta E = E_n - E_0$$

$$\Delta E = 35 \text{ to } 71 \text{ kcl/mol}$$



Emission of Radiation:

- EMR is produced when excited particles (ions, atoms, molecules) relax to lower energy levels by giving up their excess energy as photons.



2. Vibrational energy level:

- Molecules absorbs energy (IR) – promoted from one vibrational level to another vibrational level or vibrate with higher amplitude
- Difference in Energy

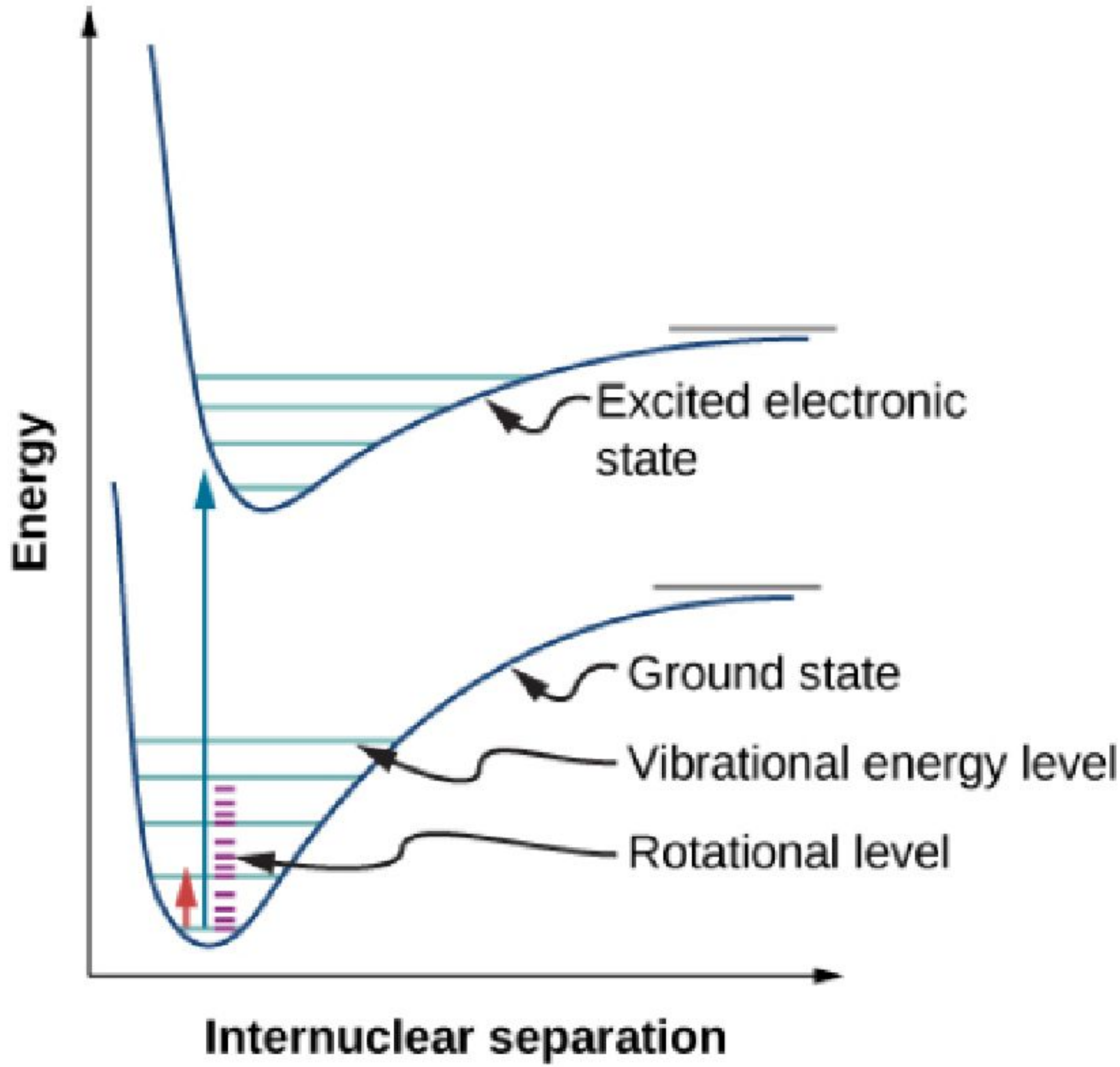
  $\Delta E = 0.01$ to 10 kcl/mol
- Less energy require than electronic energy level

3. Rotational energy level:

- Energy required is smaller than vibrational energy level

$$\Delta E_{rotational} < \Delta E_{vibrational} < \Delta E_{electronic}$$

Molecular Spectroscopy: Big Picture



Atomic emission:

- Atomic particles – gaseous states – emits radiation containing only few wavelengths – **discontinuous spectrum or line spectrum**
- Atomic particles – closely packed particles or molecules – produce continuous radiation – Continuous spectrum
- Solid particles – heated to incandescence - Thermal radiation – produce continuous spectra

Molecular spectra

The molecular spectra arise from three types of transitions.

1. Rotational
2. Vibrational
3. Electronic transitions

The total energy of a molecule is given by,

$$E = E_{tr} + E_{rot} + E_{vib} + E_{el}$$

As the translational energy is negligibly small, we can write

$$E = E_{rot} + E_{vib} + E_{el}$$

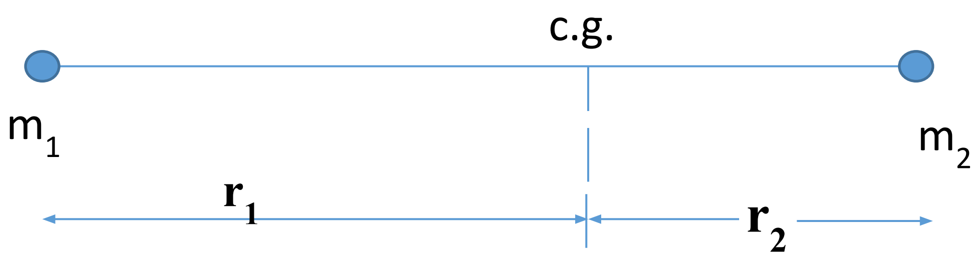
1. **Translational Energy**: A molecule possesses translational energy wh
as a result of motion, its centre of gravity changes

2. **Rotational energy:** It arises when the molecule rotates about an axis perpendicular to the internuclear axis and passing through the centre of gravity of molecule

3. **Vibrational energy:** It arises due to the to and fro motion of the nuclei the molecule such that the centre of gravity does not change

4. **Electronic energy** is associated with the transition of an electron from the ground state energy level to an excited state energy level of the molecule due to the absorption of a photon of suitable frequency

Rotational spectra of diatomic molecules



The centre of gravity is defined by the equality of moments about it,

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

The moment of inertia of a diatomic molecule can be given by,

$$\begin{aligned} I &= m_1 r_1^{\,2} + m_2\, r_2^{\,2} \\ &= m_2\, r_2\, r_1 + m_1 r_1 r_2 \\ &= \ r_1 r_2\, (m_1 + m_2) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2) \end{aligned}$$

As $r = r_1 + r_2$ or, $r_2 = r-r_1$

Thus, $m_1r_1=m_2r_2 = m_2(r-r1)$

or, $m_1r_1+m_2r_1 = m_2r$

Or, $r_1 = m_2r/m_1+m_2$

Similarly, $r_2 = m_1r/m_1+m_2$

Substituting the values of r_1 and r_2 in Eq. 2, we get

$I = (m_1m_2/m_1+m_2)\ r^2$

$\quad = \mu r^2$

The energy of a rotating molecule is given by,

$E_J = ½\ I\omega^2 \ = (I\omega)^2/2I$

The angular momentum of a rotating molecule is given by,

$L = I\omega$ where ω is angular velocity

Thus, $E_J = L^2/2I$ ………………………………………..(3)

The angular momentum L is given by,

$L = (J(J+1))^{1/2}\, h/2\pi$,   J=0, 1,2,3,………

Substituting the value of L in Eq. 3, we get

$E_J = J(J+1)h^2 /2I\text{x}4\pi^2$

$= (h^2/8\pi^2 I)\, J(J+1)$,   J=0, 1,2,3,………

$E_J\ (cm^{-1}) = E_J\ /hc$ (As $E = hc/\lambda = hc\bar{\upsilon}$, hence $\bar{\upsilon} = E/hc$)

$= (h/8\pi^2 Ic)\ J\ (J+1)$

$= B\ J(J+1)$

The rotational transitions for a rigid diatomic molecule are governed by the **selection rule**

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

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

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

$= 2\ B\ (J+1)$

Thus, $\nu\ 0 \rightarrow 1 = 2B$, $\nu 1 \rightarrow 2 = 4B$ and $\nu 2 \rightarrow 3 = 6B$

Thus, the rotational lines are equally spaced by an amount of **2B**

Question: 1

The internuclear distance of CO is 1.13 Å. Calculate the energy and angular velocity of CO in the 1^{st} excited rotational level?
Given: The atomic masses are: C: 1.99×10^{-26} kg, O: 2.66×10^{-26} kg