

Spectroscopy (uses, definition); Diff. b/w atomic, molecular spectrum; Quantisation of energy; Electromagnetic Spectrum; Scattering; Born - Oppenheimer Approximation

07 September 2023 09:31



NMR (Nuclear Magnetic Resonance)

Identification of "H" atoms

C¹³

Identification of "C" atoms

IR

Identification of functional groups

Mass spectroscopy

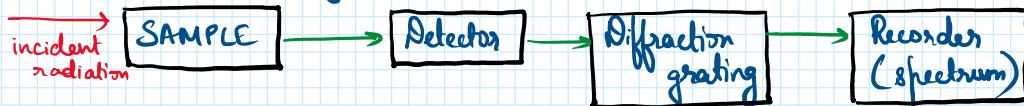
Identification of molecular weights

USES OF SPECTROSCOPY

- Identification of structures
- Identification of C, H, functional groups etc.
- Identification of bond angle, bond length
- Keto-enol tautomerism

SPECTROSCOPY: DEFINITION

- The interaction of electromagnetic radiation with matter.
- Branch of science that investigates the spectra emitted by matter when it interacts with electromagnetic radiation



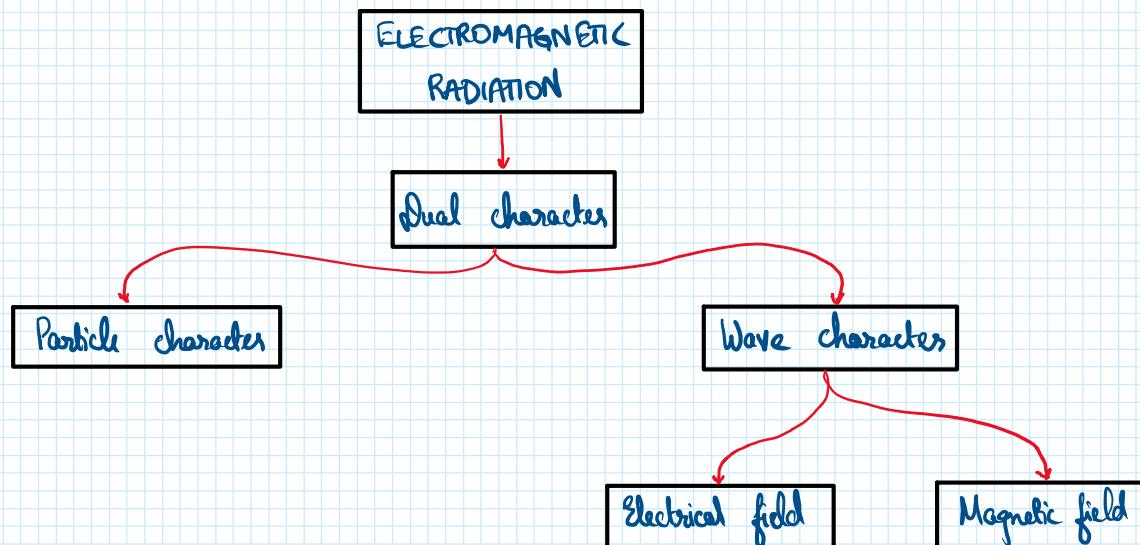
NOTE: Keto-enol tautomerism

Tautomers → readily interconverted isomers that differ in terms of the location of a particular group.

Keto → Having a carbonyl group

Enol → Having double bond and hydroxyl group

ELECTROMAGNETIC RADIATION



WAVE CHARACTERISTICS

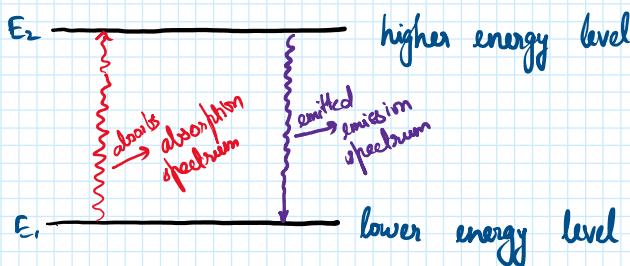
- Wavelength (λ) - $\text{Å}^\circ, \text{nm}, \text{m}$
- Frequency (ν) - $\text{Hz}, \text{sec}^{-1}$
- Wave number ($\bar{\nu}$) - cm^{-1}
- Energy ($E = h\nu$) - $\text{J} (\text{or}) \text{ erg}$

DIFFERENCE B/W ATOMIC & MOLECULAR SPECTRUM

Atom	Molecule
<ul style="list-style-type: none"> • line spectrum <p style="text-align: center;"><u>III</u></p> <p>Spectral lines are produced by transitions of electrons within atoms or ions. As the electrons move closer to or farther from the nucleus of an atom (or of an ion), energy in the form of light (or other radiation) is emitted or absorbed.</p> <ul style="list-style-type: none"> • electronic transition from one atomic orbital to another atomic orbital 	<ul style="list-style-type: none"> • Band spectrum <p style="text-align: center;"><u>IIII II</u></p> <p>Band spectra is the name given to groups of lines so closely spaced that each group appears to be a band—e.g., nitrogen spectrum. Band spectra, or molecular spectra, are produced by molecules radiating their rotational or vibrational energies, or both simultaneously.</p> <ul style="list-style-type: none"> • Electronic transition from HOMO (Highest Occupied Molecular Orbital) \downarrow LOMO (Lowest Occupied Molecular Orbital)

QUANTIZATION OF ENERGY

a quantized quantity only takes certain discrete (fixed) values



$$\text{When } \bar{\nu} = 1 \text{ cm}^{-1}$$

$$E = 1.99 \times 10^{-23} \text{ J}$$

$$E_2 - E_1 = h\nu$$

$$\Delta E = h\nu$$

$$\Delta E = h\left(\frac{c}{\lambda}\right) \quad \left[\because \nu = \frac{c}{\lambda}\right]$$

$$\therefore \frac{1}{\lambda} = \bar{\nu},$$

$$E = hc\bar{\nu}$$

$$\bar{\nu} = \frac{E}{hc} \text{ m}^{-1}$$

REASONING

- Energy levels of molecule are quantized (discrete).
- Hence when there is a transition in energy levels, frequency of light absorbed is the difference in energy b/w them

- ① An absorption spectrum wave no. is 1 cm^{-1} . Calculate the energy.

$$(h = 6.6 \times 10^{-34} \text{ /sec}, c = 3 \times 10^8 \text{ m/sec})$$

$$\bar{\nu} = 1 \text{ cm}^{-1}$$

$$\bar{\nu} = \frac{E}{hc}$$

$$\Rightarrow E = hc\bar{\nu}$$

$$= 6.6 \times 10^{-34} \times 3 \times 10^8 \times 0.01 \text{ m}^{-1}$$

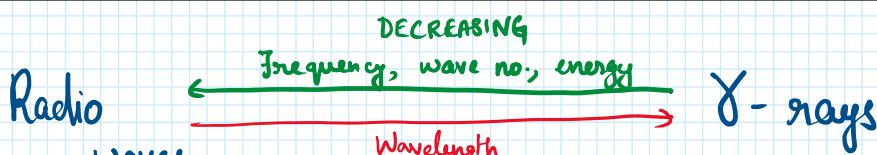
$$= 1.98 \times 10^{-23} \text{ J}$$

ELECTROMAGNETIC SPECTRUM

→ included in syllabus

	Radio waves NMR	Microwaves rotational transition	IR rays vibrational transition	UV-visible rays inner electronic transition	X-rays Electronic transition	γ -rays Nuclear rearrangement
Frequency (ν) (Hz)	3×10^6	3×10^8	3×10^{10}	3×10^{12}	3×10^{14}	3×10^{16}
Wave no. (cm^{-1}) (\bar{v})	10^{-4}	10^{-2}	1	10^2	10^4	10^6
Energy (ϵ)	10^{-3}	10^{-1}	10	10^3	10^5	10^7
Wavelength	10 m	100 cm	1 cm	100 nm	1 nm	100 pm

? Motion of the molecules that release the wave



Rotational transition < Vibrational transition < Electronic transition

$$\text{Rotational} \times 10^6 \approx \text{Vibrational} \times 10^3 \approx \text{Electronic}$$

RALEIGH SCATTERING

$$\text{wavelength} \propto \frac{1}{\text{energy}}$$

- Raleigh scattering → elastic scattering
- When monochromatic light passes through a transparent medium, wavelength of incident radiation is equal to wavelength of scattered radiation.

$$\lambda_{\text{IR}} = \lambda_{\text{SR}}$$

RAMAN

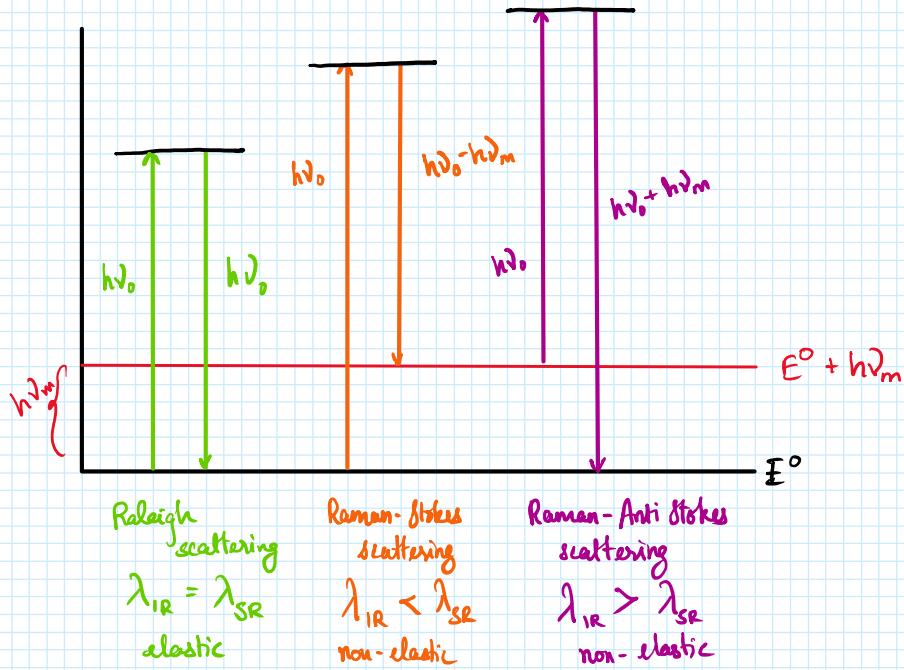
Raman - Stokes scattering

$$\lambda_{\text{IR}} < \lambda_{\text{SR}}$$

non-elastic scattering

Raman - Anti Stoke scattering

$$\lambda_{\text{IR}} > \lambda_{\text{SR}}$$



BORN - OPPENHEIMER APPROXIMATION

$$E_{\text{total}} = E_{\text{translational energy}} + E_{\text{rotational energy}} + E_{\text{vibrational energy}} + E_{\text{electronic energy}}$$

negligible; ignore

$$E_{\text{total}} = E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}}$$

} Total energy of a molecule

From above, we can say that electronic, vibrational and rotational energies are completely independent of each other.

Thus we have,

$$\Delta E_{\text{total}} = (\Delta E_{\text{rot}} + \Delta E_{\text{vib}} + \Delta E_{\text{elec}}) \text{J}$$

} Energy

$$\Delta E_{\text{total}} = (\Delta \varepsilon_{\text{rot}} + \Delta \varepsilon_{\text{vib}} + \Delta \varepsilon_{\text{elec}}) \text{cm}^{-1}$$

} Wave number

$$\Delta \varepsilon_{\text{elec}} \approx 10^3 \Delta \varepsilon_{\text{vib}} \approx 10^6 \Delta \varepsilon_{\text{rot}}$$

Energy Level Diagram for Diatomic Molecule

