Methods for structure determination

There are two important methods for structure determination

Chemical method

This involves estimation of functional groups, elements detection, preparation of derivatives and degradation of molecule.

Disadvantages of chemical method

1) Large number of chemicals are required.
2) Wastage of sample.
3) Require long time period for analysis.

Methods for structure determination

Physical method

This includes determination of M.P/B.P., dipole moment, refractive index etc. Physical method also includes crystallography and spectroscopy.

Advantages of physical method

Amount of sample required is very small.

Sample can be recovered.

These methods are very quick.

These methods give lot of information about structure.

Disadvantages of physical method

Method requires costly instruments.

Trained person (expert) is required for analysis.

Types of Spectroscopic Techniques

U.V. Spectroscopy

I.R. Spectroscopy

NMR Spectroscopy: PMR/CMR

Mass Spectroscopy

Spectroscopy

Spectroscopy

Spectroscopy is the branch of chemistry which studies, the responses of the molecule when it is exposed to certain kind of radiation.

Responses given by molecule are recorded in the form of graph called as spectrum.

Spectroscopy

Absorption and emission spectroscopy

When molecule is exposed to radiation, it absorbs part of it and goes to excited state.

Amount and type of radiation absorb (U.V., Visible, I.R., Microwave, Radio wave) give information about the structure of molecule.

Absorption spectroscopy

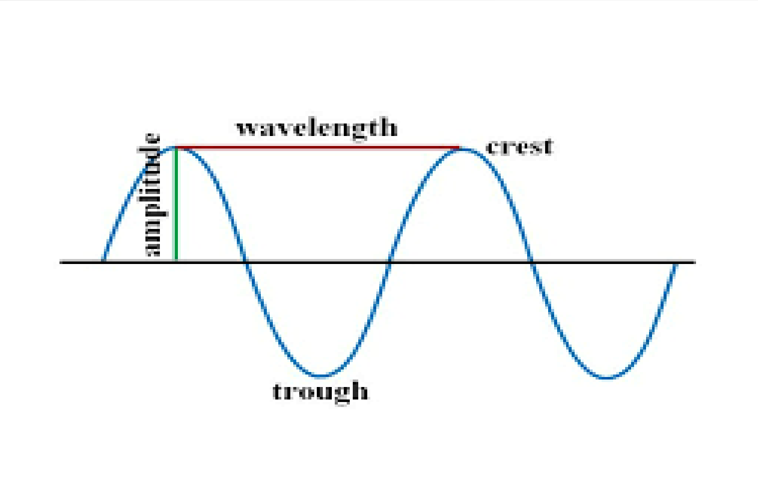
The spectroscopy in which the nature of the radiation absorbed is studied is called as absorption spectroscopy.

Spectroscopy

Emission spectroscopy

In emission spectroscopy absorbed energy is given out in the form of heat and other radiation. Thus, radiation emitted by molecule is studied to reveal the structure of molecule is called as emission spectroscopy.

Wave Parameters



Wave length (λ): - The distance between two consecutive crests or troughs is known as wavelength.

Amplitude (a): - Maximum displacement of the wave from the ‘x’ axis is called as amplitude of radiation.

Frequency (υ): - Number of wavelengths produced (or number of oscillations completed) per unit time is called frequency.

Wave Parameters

Energy of radiation (E): -

$$E = h\,\upsilon \quad \rightarrow \text{Eq.1}$$

Where 'h' is plank's constant, 'υ' is frequency

As we know,

$$C = \upsilon\,\lambda$$

$$\upsilon = C / \lambda$$

Putting value of 'υ' in eq. 1, we get

$$E = h \times C / \lambda$$

$$E = h \times C \times 1 / \lambda \text{ (as h and C are constant)}$$

$$E \propto 1 / \lambda$$

Thus, energy of radiation is inversely proportional to its wavelength and directly proportional to its frequency.

Units of measurements

Wavelength: - Angstrom, Nanometer, Micron are the basic unit of wavelength measurement.

$1\ A^0 = 10^{-8}$ c.m. $=10^{-10}$ m

1 nm $= 10^{-7}$ c.m. $=10^{-9}$ m

$1\ \mu = 10^{-4}$ c.m. $=10^{-6}$ m

for U.V. and visible A^0 and nm are good units, for I.R. μ is convenient.

Frequency: - It is measured in Hertz.

1 Hertz = one cycle per second

1 kilohertz = 1000 hertz

1 megahertz = 10^{6} hertz

:

Units of measurements:-

Wave number: -

Number of waves / cm   i.e.(cm^{-1}) or kayser (K)

4) Energy: -Measured in Erg or Joule

$1J = 10^{7}$ erg

Types of electromagnetic radiation

Sr. No.	Radiation	Wavelength (λ)
1	Cosmic rays	10^{-5} nm to 10^{-3} nm
2	Gamma rays	10^{-3} nm to 0.1 nm
3	X rays	0.1 nm to 100 nm
4	U.V.	100 nm to 400 nm
5	Visible	400 nm to 800 nm
6	I.R.	800 nm to 10^{5} nm
7	Microwave	10^{5} nm to 10^{7} nm
8	Radar	10^{7} nm to 10^{9} nm
9	TV	10^{9} nm to 10^{10} nm
10	Radio (NMR)	10^{10} nm to 10^{11} nm

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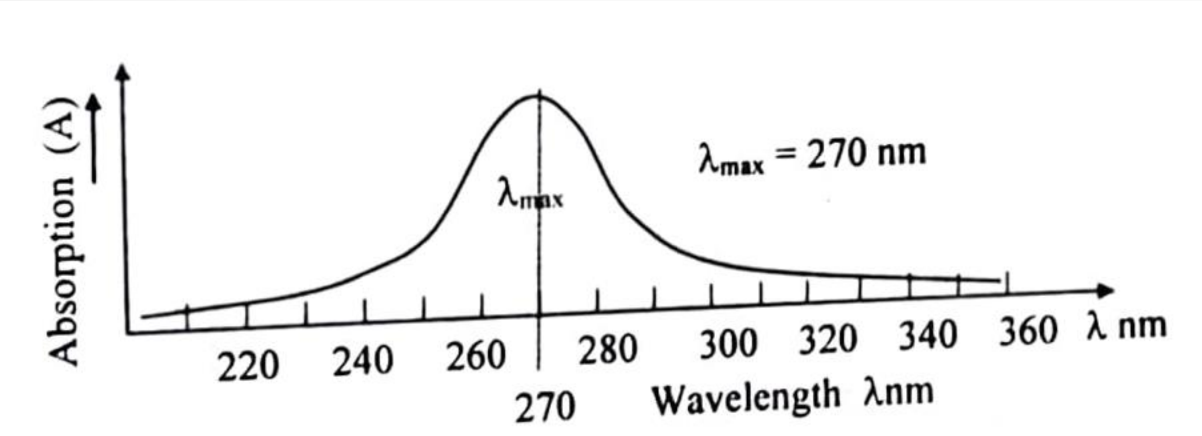
Absorption Spectroscopy

When Molecule is exposed to radiation . Wavelength of radiation slowly changes from minimum to maximum in given region and absorbance of the molecule at every wave length is recorded.

A graph of Absorbance vs Wavelength is plotted

The wavelength at which there is maximum absorption is called wavelength of maximum absorption.



Types of Spectroscopic method

Type of Spectroscopy	Radiations used	Nature of excitations
1. U.V. and Visible spectroscopy	U.V and visible (100 Kcal / mole)	Electronic excitation accompanied by vibrational and rotaional
2. I.R. spectroscopy	I.R. (10 Kcal / mole)	Vibrational excitation accompanied by rotational excitation
3. Microwave spectroscopy	Microwaves	Rotational excitations
4. N. M. R. spectroscopy	Radio waves	Nuclear excitations

Interaction of radiation with matter

A) Molecular Excitation:

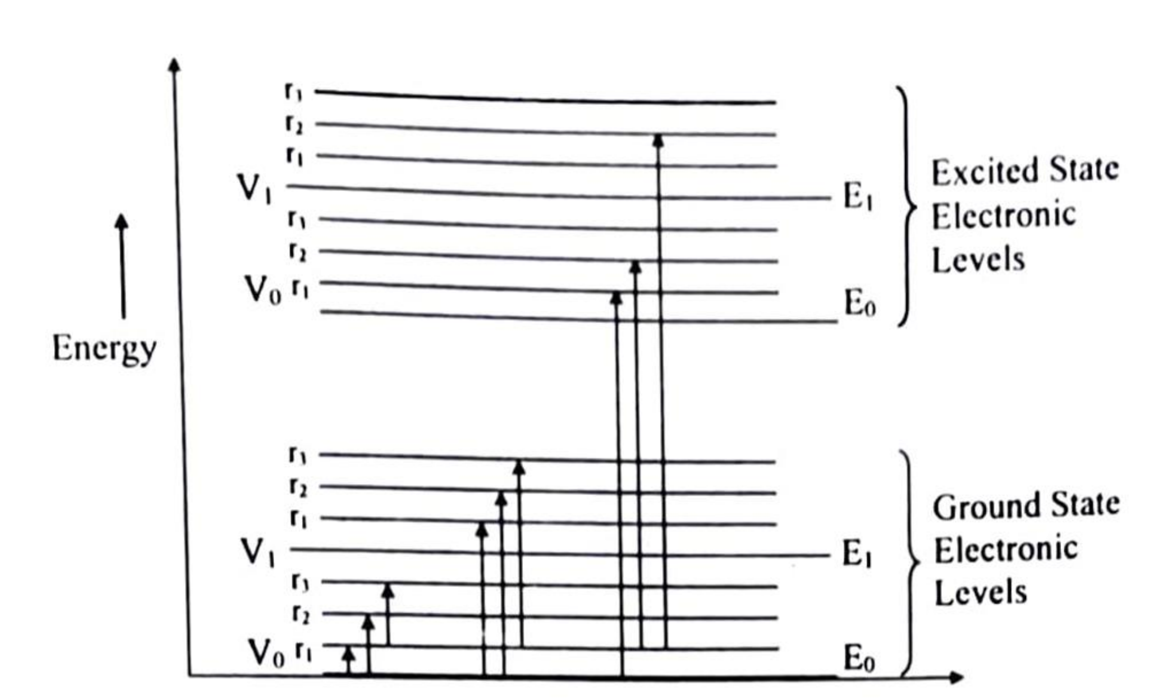
Rotational Excitation (Wavelength 10^5 to 10^7 nm)

Vibration excitation, (wavelength 800 nm to 10^5)

Electronic excitation (wavelength 100 to 800 nm)

Microwave	Rotational excitation
IR	Rotational and vibrational
Visible and UV	Rotational, Vibrational and Electronic excitation

Interaction of radiation with matter



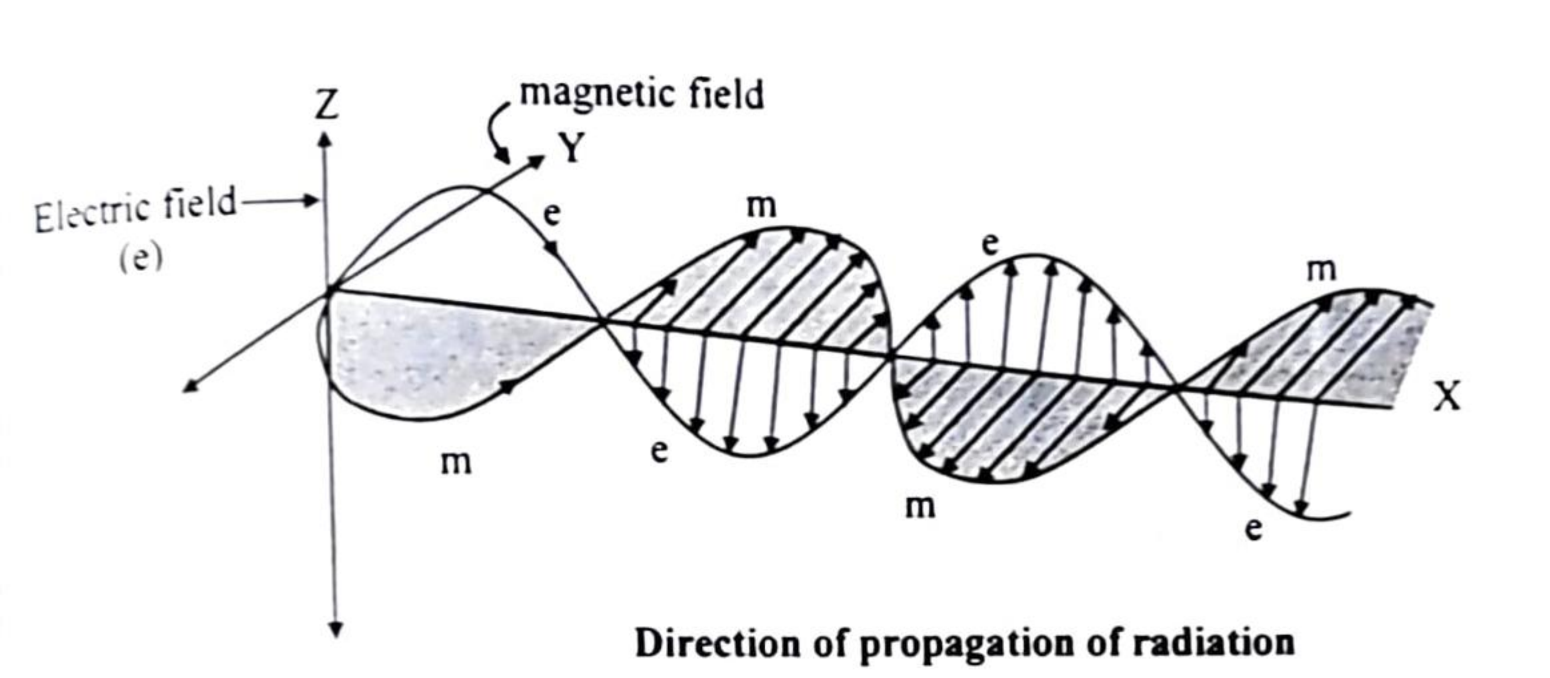
B) Molecular Energy level

E0, E1 and E2 electronic level

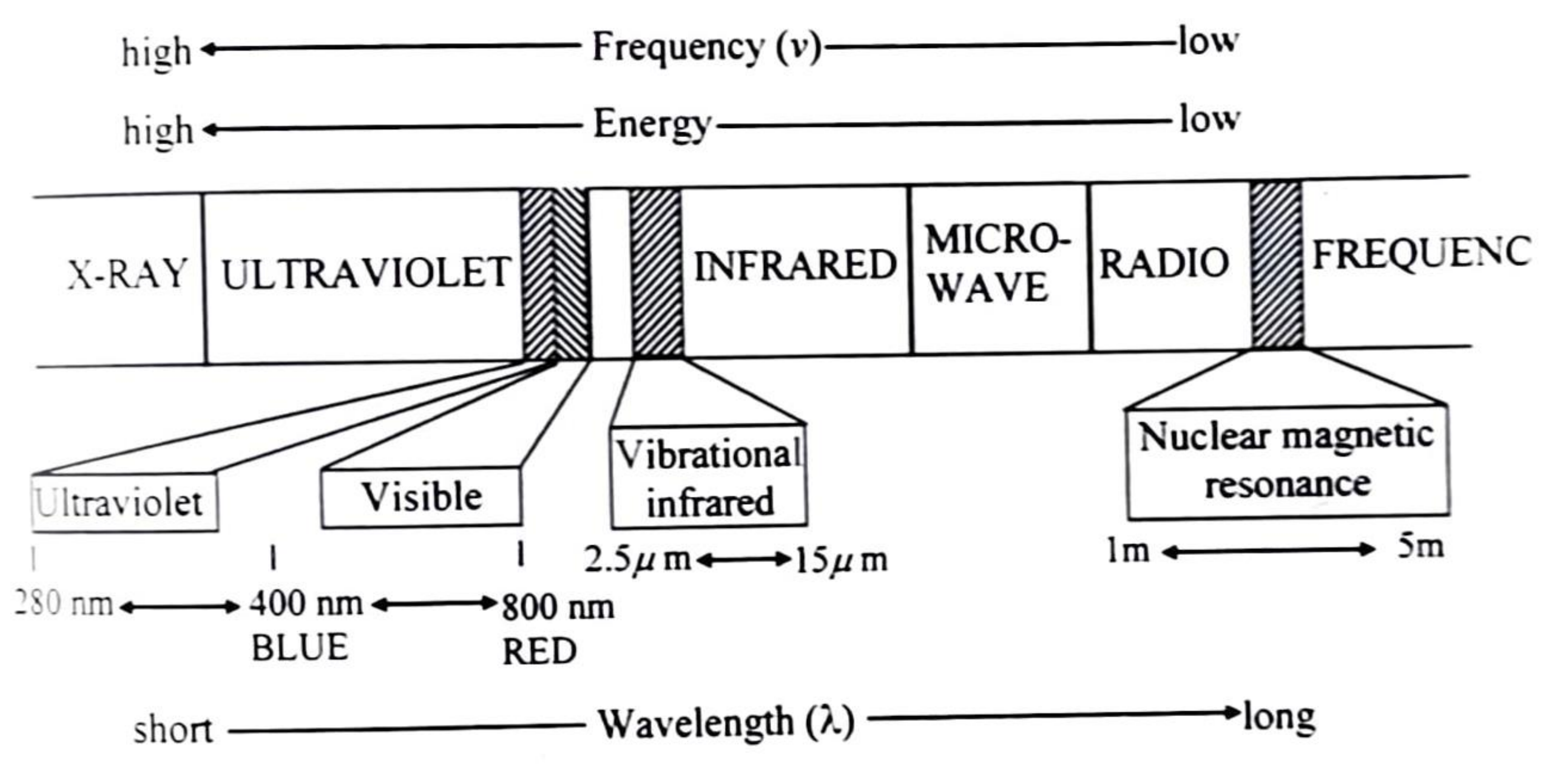
V0, V1, V2 Vibrational Level

R0,r1,r2 rotational level

Types of electromagnetic radiation



Types of electromagnetic radiation



Types of radiations according to wavelength

Types of electromagnetic radiation

(1) Wavelength of radiation is 2μ. Express this in terms of cm^{-1}; wave numbers and frequency.

Solution : Wavelength (λ) in terms of cm^{-1}

$$\because 1\mu = 1000\ nm = 10{,}000\ A^{o} = 10^{-4} cm$$

$$\therefore 2\mu = 2 \times 10^{-4} cm.$$

(B) Wavelength in terms of wavenumber $(\bar{\upsilon})$.

$$\bar{\upsilon} = \frac{1}{\lambda} = \frac{1}{2 \times 10^{-4}\ cm} = 5{,}000\ cm^{-1}$$

(C) Wavelength in terms of frequency (ν).

$$\upsilon = \frac{C}{\lambda} \quad \text{where } C = \text{velocity of light} = 3 \times 10^{10}\ cm/sec$$

$$= \frac{3 \times 10^{10}}{2 \times 10^{-4}} = 1.5 \times 10^{14}\ Hz.\ (Hertz).$$

Types of electromagnetic radiation

(2) Two radiations having wavelengths 3,000 A^0 and 20,000 A^0. Calculate their energies in terms of ergs. Which has higher energy ?

Solution : a) Calculate the frequency of the first radiation.

$$\text{Frequency } (\upsilon) = \frac{C}{\lambda} \quad \text{where, } C = 3 \times 10^{10} \text{ cm /sec.}$$

$$= \frac{3 \times 10^{10}}{3 \times 10^{-5}} \quad [\lambda = 3000\ A^o = 3000 \times 10^{-8} \text{ cm} = 3 \times 10^{-5} \text{ cm.}]$$

$$= 1 \times 10^{15} \text{ Hz.}$$

Types of electromagnetic radiation

Energy is given by –

$E_1 = h \cdot \upsilon$ where, h = Plank's constant = 6.62×10^{-27} ergs / sec.

and υ = Frequency in hertz.

$\therefore \; E_1 = (6.62 \times 10^{-27})(1 \times 10^{15}) = 6.62 \times 10^{-12}$ Ergs.

Similarly calculate the energy of the second radiation :

Energy $E_2 = h \cdot \upsilon_2$ But $\upsilon_2 = \dfrac{C}{\lambda}$

$$= h \cdot \frac{C}{\lambda} \qquad = \frac{(6.62 \times 10^{-27})(3 \times 10^{10})}{20{,}000 \times 10^{-8}\ \text{cm}}$$

$E_2 = 9.73 \times 10^{-13}$ Ergs. $= 0.973 \times 10^{-12}$ Ergs.

Thus the energy of the first radiation (λ = 3000 A°) is greater than the energy of the second radiation (λ = 20,000 A°).

Thank You so Much