SPECTROSCOPY

Spectroscopy is the study of interaction of electromagnetic radiation with matter. It is used as an analytical tool to determine the composition of matter.

Advantages of spectroscopy

1. Accurate result
2. Fast and easy .
3. Only trace amount of substance is required
4. Sample recovery is possible

Expression for energy of a photon of radiation

$E = h\nu = hc/\lambda = hc\bar{\nu}$

$h = 6.626 \times 10^{-34}$ Js (Planck's constant) ν = frequency, c = velocity of light = 3×10^8 ms-1 , λ is wavelength. $\bar{\nu}$ is the wavenumber.

Electromagnetic spectrum

Electromagnetic radiations can be arranged in increasing order of wavelength as given below.

Gamma rays < x rays < UV < Visible < IR < microwaves < radiowaves.

Since energy and wavelength are inversely related, the above order is decreasing order of energy of radiations.

Types of spectra

1.Based on nature of interaction

a. Absorption spectra
When an atom or molecule undergoes transition from ground state to excited state by absorption of a photon, the resulting spectra is an absorption spectra.
Ex: UV-Visible spectra, IR spectra etc

b. Emission spectra
When an atom or molecule undergoes transition from excited state to ground state by emission of a photon, the resulting spectra is called emission spectra.
Ex: Hydrogen spectra, fluorescence spectra etc

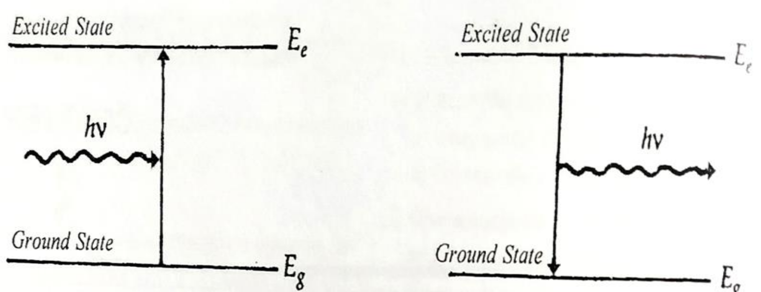


Fig. 3.1 Absorption Spectrum
Fig. 3.2 Emission Spectrum

2. Based on interacting species

a. Atomic spectra

Here atoms interact with electromagnetic radiation. Since atoms have only limited number of energy levels, resulting atomic spectra appears as line spectra.

b. Molecular spectra

Here molecules interact with electromagnetic radiation. Since molecules have large number of energy levels, large number of transitions are possible. So resulting molecular spectra will consist of broad peaks .

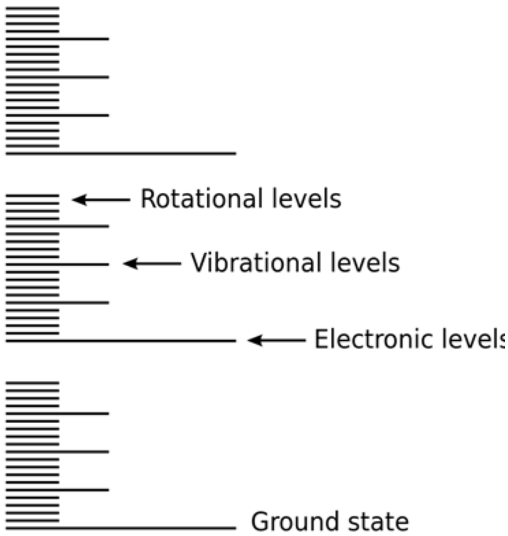
Energy of a molecule

A molecule possess translational, rotational, vibrational and electronic energies. Since translational energy is negligible, total energy can be written as the sum of rotational, vibrational and electronic energies. This is known as Born- oppenheimer approximation.

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

$E_{elec} > E_{vib} > E_{rot}$

Electronic transitions require greater amount of energy. Electronic transitions will be always accompanied by vibrational and rotational transitions. Means, large number of transitions occur simultaneously. So electronic spectrum consist of broad peaks , rather than sharp lines.



Beer-Lambert Law

When a beam of monochromatic radiation is passed through a solution, the rate of decrease in intensity of radiation with thickness of solution, is directly proportional to concentration of solution and the intensity of incident radiation.

$\frac{-dI}{dx} \alpha \, cI$

$\log I_0/I = \varepsilon cx$

where I_0 is the intensity of incident radiation, I is the intensity after passing through the solution, ε is the molar absorption coefficient and x is the thickness of solution. The quantity $\log I_0/I$ is called the absorbance A of the solution.

$A = \varepsilon c x$

Plot of A vs c will be a straight line with slope εx.

Transmittance T is given as,

$T = I/I_o$

$A = -\log T$

[problems in class note]

<u>Application of Beer Lambert law</u>

<u>Determination of unknown concentration</u>

From Beer Lambert law, it follows that absorbance is directly proportional to concentration. A plot of absorbance vs concentration will be a straight line.

To determine concentration of a solution, first we make a set of known concentrations of that compound and find absorbance of each of them. Then absorbance vs concentration graph is plotted. Absorbance of solution of unknown concentration is noted and marked in graph. Concentration of unknown can be now obtained from the graph by interpolation.

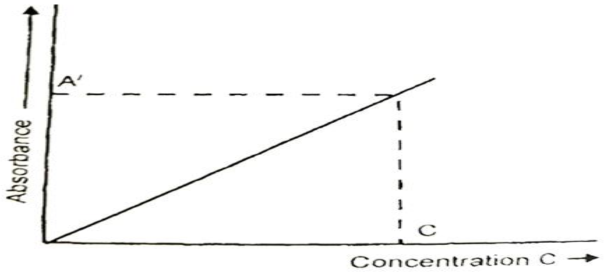


Fig. 3.9 Absorbance vs Concentration