

INTRODUCTION TO SPECTROSCOPY

SEM-4, CC-8

PART-1

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Lecture material prepared by Dr. Kalyan Kumar Mandal, SPCMC, Kolkata

Dr. Kalyan Kumar Mandal
Associate Professor
St. Paul's C. M. College
Kolkata

Introduction to Spectroscopy (PART-1)

Spectroscopy is the study of interaction between matter (**matter** is any substance that has mass and takes up space by having volume) and electromagnetic radiation as a function of the wavelength or frequency of the radiation. **Radiation** is the emission or transmission of energy in the form of waves or particles through space or through a material medium. It includes electromagnetic radiation, such as *radio waves*, *microwaves*, *infrared*, *visible light*, *ultraviolet*, *X-rays*, and *gamma radiation*, etc. In simpler terms, **spectroscopy** is the precise study of colour as generalized from *visible light* to all bands of the electromagnetic spectrum (**Figure 1**).

The Electromagnetic Spectrum

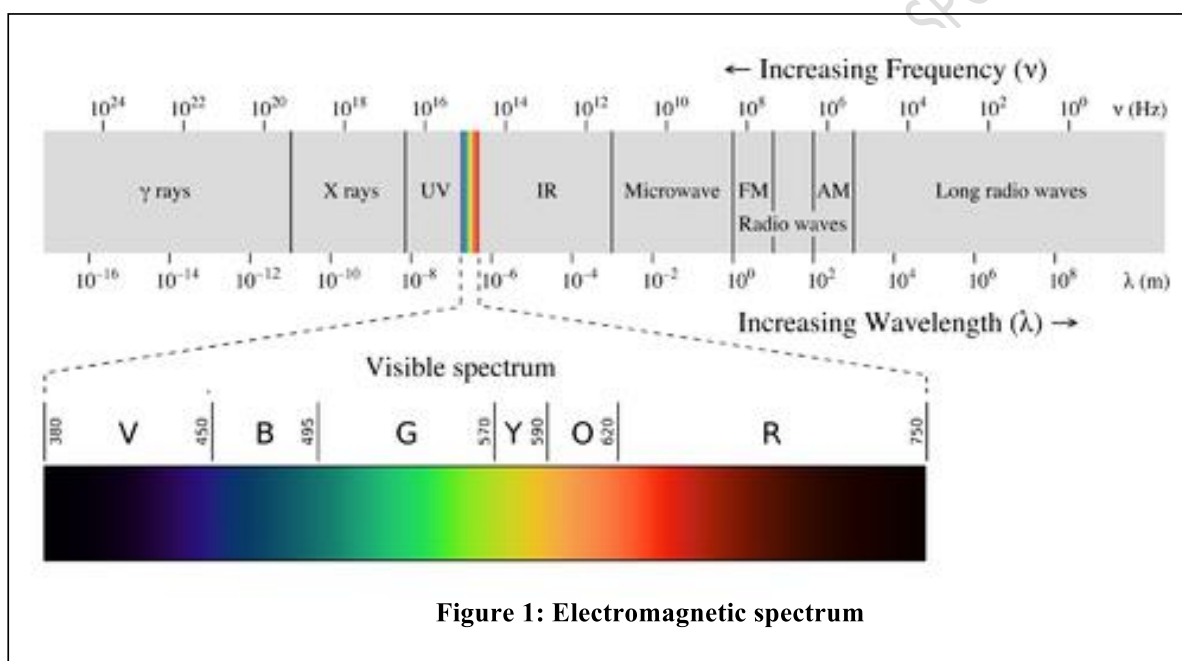


Figure 1: Electromagnetic spectrum

Electromagnetic radiation refers to the waves (or their quanta, photons) of the electromagnetic field, propagating (radiating) through space, carrying electromagnetic radiant energy.

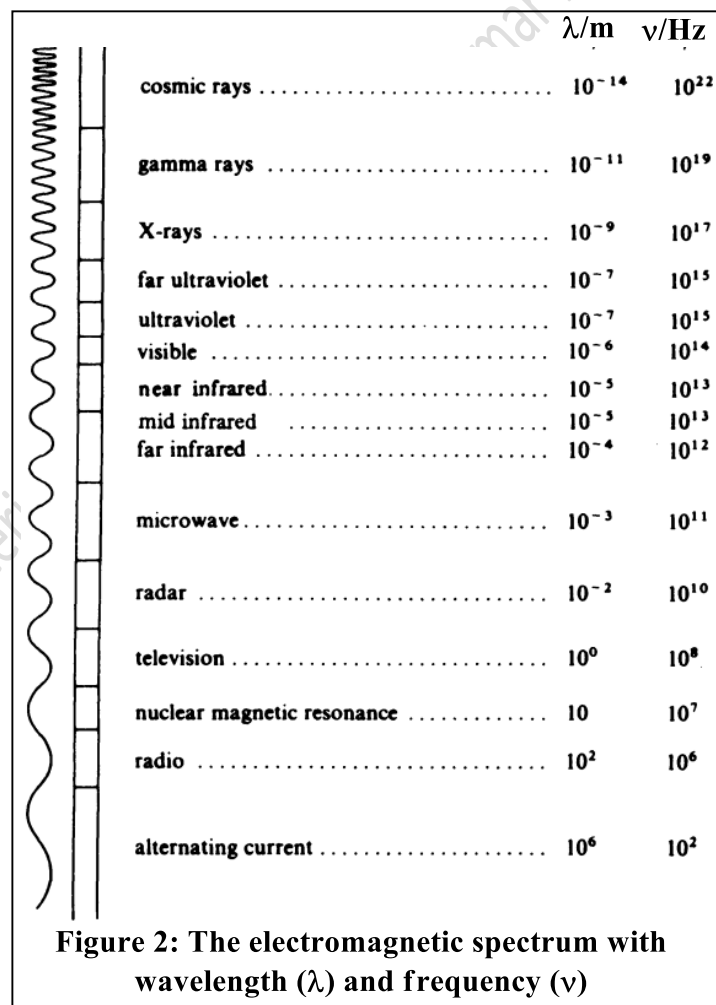
The **electromagnetic spectrum** is the range of frequencies of electromagnetic radiation and their respective wavelengths and photon energies. It covers electromagnetic waves with frequencies ranging from below one hertz to above 10^{25} hertz, corresponding to wavelengths from thousands of kilometers down to a fraction of the size of an atomic nucleus.

This frequency range is divided into separate bands, and the electromagnetic waves within each frequency band are called by different names; beginning at the low frequency (long wavelength) end of the spectrum includes *radio waves*, *microwave*, *infrared*, *visible light*, *ultraviolet*, *X-rays*, and *gamma rays* at the high-frequency (short wavelength) end. The

electromagnetic waves in each of these bands have different characteristics, such as how they are produced, how they interact with matter, and their practical applications.

The types of spectroscopy are distinguished by the type of radiative energy involved in the interaction. In many applications, the spectrum is determined by measuring changes in the intensity or frequency of this energy. The types of radiative energy studied include electromagnetic radiation. Techniques that employ electromagnetic radiation are typically classified by the wavelength region of the spectrum and include microwave, infrared, ultraviolet, x-ray spectroscopy.

The sensitivity limits of the human eye extend from violet light ($\lambda = 400 \text{ nm}$, $4 \times 10^{-7} \text{ m}$) through the rainbow colours to red light ($\lambda = 800 \text{ nm}$, $8 \times 10^{-7} \text{ m}$). Wavelengths shorter than 400 nm and longer than 800 nm exist, but they cannot be detected by the human eye. **Ultraviolet light** ($\lambda < 400 \text{ nm}$) can be detected on photographic film or in a photoelectric cell, and **infrared light** ($\lambda > 800 \text{ nm}$) can be detected either photographically or using a heat detector such as a thermopile. Beyond these limits lies a continuum of radiation as shown in **Figure 2**. Although all of the different divisions have certain properties in common (all possess units of λ , ν , $\bar{\nu}$, etc.).



Energy of Radiation

$$E = h\nu = \frac{hc}{\lambda}$$

where E = energy of the radiation in joules/J,

h = Planck's constant/ 6.626×10^{-34} J s,

ν = frequency of the radiation/Hz,

c = velocity of light/ 2.998×10^8 m s⁻¹,

λ = wavelength/m

The higher is the frequency, the higher is the energy of radiation. The longer is the wavelength, the lower is the energy. Cosmic radiation is of very high energy and ultraviolet light is of higher energy than infrared light, etc. To express energy in terms of J mol⁻¹, the expressions $E = h\nu$; etc., must be multiplied by the Avogadro constant, N ($= 6.023 \times 10^{23}$ mol⁻¹).

$$\begin{aligned} E &= Nh\nu = \frac{Nhc}{\lambda} \\ E &= \frac{6.023 \times 10^{23} \times 6.625 \times 10^{-34} \text{ (J s)} \times 3 \times 10^8 \text{ (m s}^{-1}\text{)}}{\lambda} \\ &= \frac{119.71 \times 10^{-3}}{\lambda} \text{ J m mol}^{-1} \\ &= \frac{119.71 \times 10^{-3} \times 10^9}{\lambda} \text{ J nm mol}^{-1} \\ &= \frac{119.71 \times 10^6}{\lambda} \text{ J nm mol}^{-1} \\ &= \frac{119.71 \times 10^6}{\lambda \text{ (nm)}} \text{ J mol}^{-1} \\ &= \frac{119.71 \times 10^6}{\lambda \times 4.187 \times 10^3} \text{ kcal mol}^{-1} \\ &= \frac{28600}{\lambda \text{ (nm)}} \text{ kcal mol}^{-1} \end{aligned}$$

Therefore, the amount of energy absorbed (ultraviolet light of wavelength 200 nm) by one mole of substance is 143 kcal mol⁻¹.

Types of Spectroscopy

The field of spectroscopy is divided into emission and absorption spectroscopy. An emission spectrum is obtained by spectroscopic analysis of some light source, such as flame or an electric arc. This phenomenon is primarily caused by the excitation of atoms by thermal or electrical means; absorbed energy causes electrons in a *ground state* to be promoted to a state of higher energy.

The lifetime of electrons in this metastable state is short, and they return to some lower *excited state* or to the *ground state*; the absorbed energy is released as light. The fluorescent lights and colours obtained by heating salts of certain elements in a flame are common example of emission spectra. In some cases, the *excited states* may have appreciable lifetimes such that emission of light continues after excitation has ceased; such a phenomenon is called *phosphorescence*.

Absorption Spectrum

An *absorption spectrum* is obtained by placing the substance between the spectrometer and some source of energy that provides electromagnetic radiation in the frequency range being studied. The spectrometer analyzes the transmitted energy relative to the incident energy for a given frequency. Again, the high-energy states are usually short-lived.

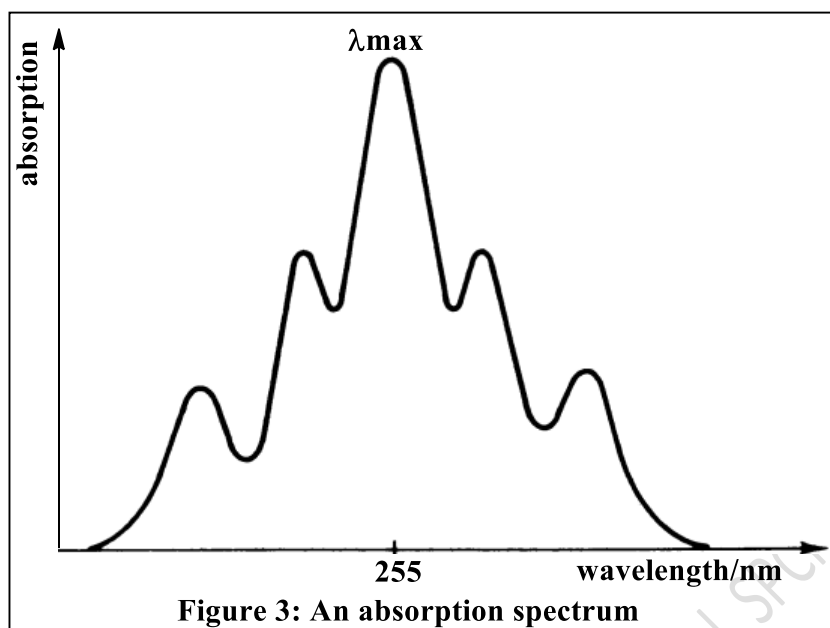
The major fate of absorbed energy in the *infrared region* is heat; thus, the temperature of the substance (or solution) increases while the spectrum is being determined. The major fate of absorbed energy in the *ultraviolet region* is re-emission of light. Occasionally, the absorbed energy may cause photochemically induced reactions.

Absorption of Electromagnetic Radiation by Organic Molecules

When light is passed through a given liquid or a solution, the absorption does not occur at all wavelengths. At a particular wavelength or within a small range of the same, the light is considerably absorbed. Hence, if the amounts of light absorbed (from an observation of the loss of intensity of the emerging radiation) is plotted against the wavelength of the light used, a maximum at the absorption range is obtained. Every substance has got its specific absorption curve.

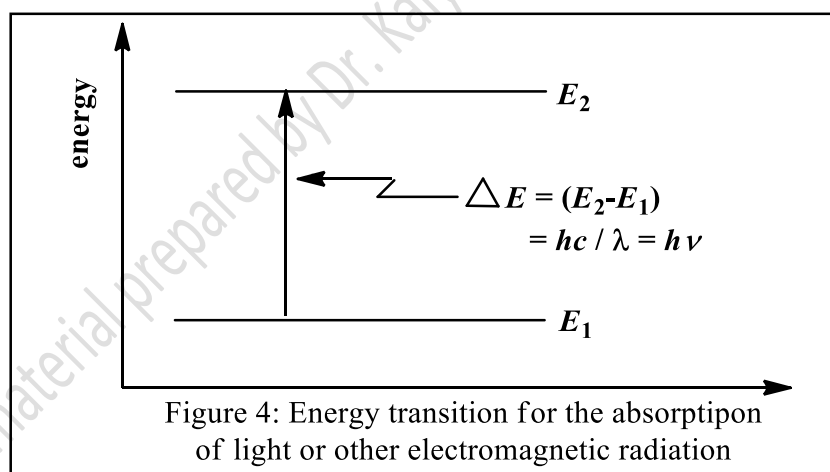
If light from an ultraviolet lamp is passed through a sample of an organic molecule such as benzene, some of the light is absorbed. In particular, some of the wavelengths (frequencies) are absorbed and others are virtually unaffected. The changes in absorption on plotting against wavelength produce an *absorption spectrum* (Figure 3).

The spectrum presented in Figure 3 shows *absorption bands* at several wavelengths-for example, 255 nm. The organic molecule is absorbing light of $\lambda = 255 \text{ nm}$, which corresponds to energy absorption of 470 kJ mol^{-1} ($112.2 \text{ kcal mol}^{-1}$).



Energy of this magnitude is associated with changes in the electronic structure of the molecule, and when a molecule absorbs this wavelength, electrons are promoted to higher-energy orbitals, as represented in **Figure 4**. The energy transition $E_1 \rightarrow E_2$ corresponds to the absorption of energy *exactly* equivalent to the energy of the wavelength absorbed:

$$\Delta E = (E_2 - E_1) = hc / \lambda = h\nu$$



While this example (shown in **Figures 3 and 4**) refers specifically to **ultraviolet light**, the same principle holds for the absorption of energy from any part of the electromagnetic spectrum. *A molecule can only absorb a particular frequency, if there exists within the molecule an energy transition of magnitude $\Delta E = h\nu$.*

Although almost all parts of the electromagnetic spectrum are used for studying matter, in organic chemistry it is mainly concerned with energy absorption from three or four regions—ultraviolet and visible, infrared, microwave and radiofrequency absorption. In *mass spectrometry*, the molecule is bombarded with high-energy electrons (= 70 eV, or 6000 kJ

mol^{-1}), and cause the molecule first to ionize and then to disperse into an array (or spectrum) of fragment ions of different masses.

Although the mechanism of absorption energy is different in the *ultraviolet*, *infrared*, and *nuclear magnetic resonance* regions, the fundamental process is the absorption of a certain amount of energy. The energy required for the transition from a state of lower energy to a state of higher energy is directly related to the frequency of electromagnetic radiation that causes the transition: the energy absorbed is given by $E = h\nu$.

For a given excitation process, a molecule absorbs only one discrete amount of energy, and hence absorbs radiation of only one frequency. If this were the case with all molecules of a substance, one would observe a series of absorption lines. However, a group of molecules exists in a number of different vibrational and rotational states, each state differing from another by a relatively small amount of energy. Thus, a group of molecules absorbs energy over a small range and gives rise to an absorption band or peak.

Interpretations of molecular spectra by the organic chemist are based largely on empirical correlations with extensive compilations of data; consequently, a given absorption can usually be attributed with reasonable assurance to a particular group or arrangement of atoms within the molecule. Absorption of *ultraviolet and visible light* is chiefly caused by electronic excitation; the spectrum provides limited information about the structure of the molecule.

Absorption in the *infrared* region is due to molecular vibrations of one kind or another; the spectrum is generally very complicated and contains many absorption peaks, relatively few of which can be interpreted with a high degree of assurance. On the other hand, the *proton magnetic resonance spectrum* of a compound, owing to nuclear spin transitions, can usually be completely interpreted, and it provides information about the number, nature, and environment of all of the protons in the molecule. **Table 1** shows the kind of information that can be deduced from studying the absorption of these radiations.

Table 1: Summary of spectroscopic techniques in Organic Chemistry and the information obtainable from each	
Radiation absorbed	Effect on the molecule (and information deduced)
ultraviolet-visible λ , 190-400 nm and 400-800 nm	changes in electronic energy levels within the molecule (extent of π -electron systems, presence of conjugated unsaturation, and conjugation with nonbonding electrons)
infrared λ , 2.5-25 μm , $\bar{\nu}$, 400-4000 cm^{-1}	changes in the vibrational and rotational movements of the molecule (detection of functional groups, which have specific vibration frequencies-for example, C=O, NH ₂ , OH, etc.)
microwave ν , 9.5×10^9 Hz	electron spin resonance or electron paramagnetic resonance; induces changes in the magnetic properties of unpaired electrons
radiofrequency ν , 60-600 MHz	nuclear magnetic resonance; induces changes in the magnetic properties of certain atomic nuclei, notably that of hydrogen and the ¹³ C isotope of carbon
electron-beam impact 70 eV, 6000 kJ mol^{-1}	ionization and fragmentation of the molecule into a spectrum of fragment ions [determination of relative molecular mass (molecular weight) and deduction of molecular structures from the fragments produced]

Laws of Photochemistry

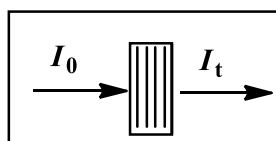
The decrease in intensity of the radiation in its passage through the absorbing medium is governed by two laws - **Lambert's Law and Beer's Law**.

Lambert's Law: This law states that the rate of decrease of intensity with the thickness of absorbing medium is proportional to the intensity of the penetrating radiation. When a monochromatic light is passed through the sample solution, the intensity of the transmitted light decreases exponentially with the thickness of the light absorbing medium. Let us consider, a thin layer of the medium of thickness dl and let I be the intensity of the radiation entering it, then

$$dI/dl = -kI, \text{ on integrating,}$$

$$\ln I_t/I_0 = -kl,$$

where I_0 is the intensity at $l = 0$, and I_t , the intensity at distance l . The constant k is called the '**absorption coefficient**' of the substance.



When the absorbing substance is present in solution, the absorption of light also depends upon the concentration.

Beer's Law: This law states that the rate of decrease in intensity of radiation absorbed is proportional to the intensity of radiation and to the concentration of solute. Hence, using the same symbols,

$$dI/dl = -k'cI, \text{ on integrating,}$$

$$\ln I_t/I_0 = -k'cl,$$

where c is the concentration, and k' is called the '*molar absorption coefficient*' of the substance. Rewriting, $\log I_0/I_t = \epsilon cl$, where ϵ is the molar extinction coefficient and is given by $\epsilon = 0.4343 k'$. The value of ϵ is specific for a given substance for a given wavelength of light.

Molar Extinction Coefficient

The quantity $\log I_0/I_t$ is generally called optical density (or absorbance, A). Therefore, $A = \epsilon cl$. When A ($= \log I_0/I_t$) is plotted against concentration (c) of the solution taken in a column of definite thickness a straight line is obtained. The *molar extinction coefficient* (ϵ) is obtained from the slope of the line.