Semester VI
Paper M 601 Spectroscopy

Unit 6.1 Introduction to Spectroscopy (Marks 10)

The nature of electromagnetic radiation. The regions of spectrum. Mechanism of interaction of electromagnetic radiation with matter. Absorption and emission spectroscopy. Basic elements of practical spectroscopy. Representation of spectrum – the width of spectral line. Intensity of spectral lines. Selection rules for various transitions. The Beer-Lambert law, molar absorption coefficient and absorbance. Molecular motion and energy – degree of freedom. Moment of inertia.

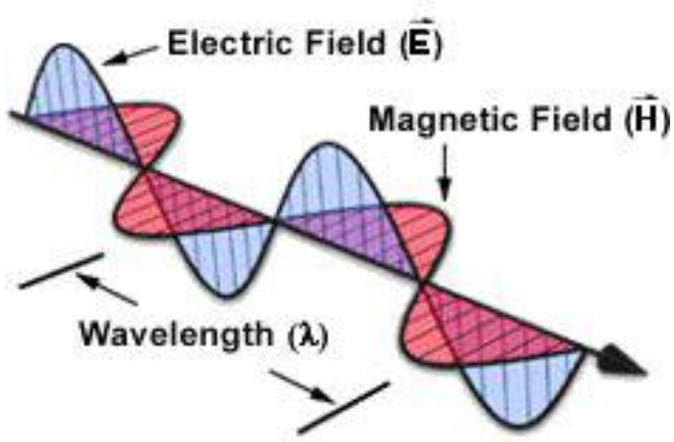
Nature of Electromagnetic Radiation – *Wave Nature*

❖Electromagnetic (EM) radiation is a form of energy propagated through free space or through a material medium in the form of electromagnetic waves.

❖EM radiation is so-named because it has electric and magnetic fields that simultaneously oscillate in planes mutually perpendicular to each other and to the direction of propagation through space.

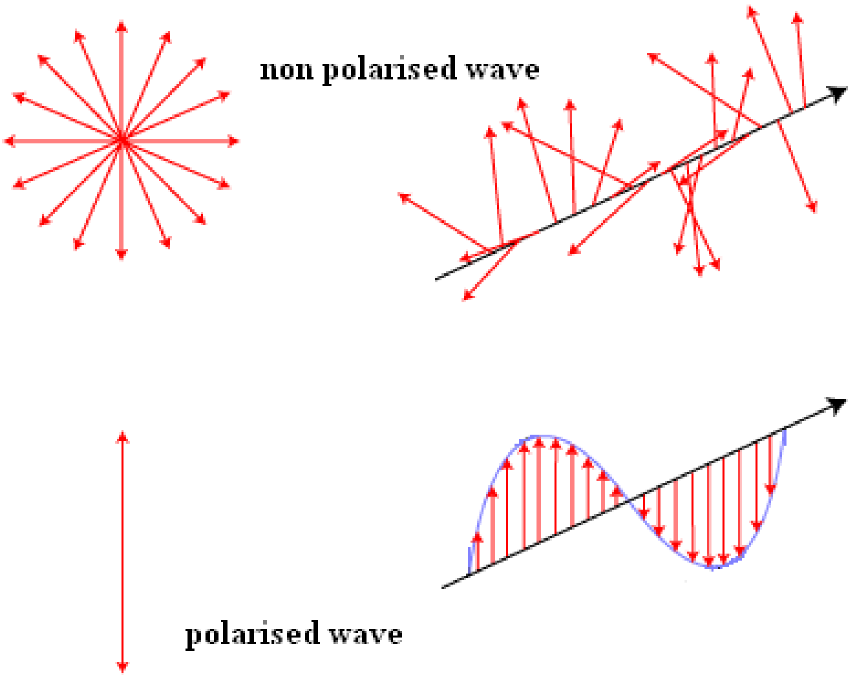
❖Electromagnetic radiation has the dual nature: its exhibits wave properties and particulate (photon) properties.

❖Wave nature of radiation: Radiation can be thought of as a traveling transverse wave.



Nature of Electromagnetic Radiation

❖As a transverse wave, EM radiation can be polarized. **Polarization is the** distribution of the electric field in the plane normal to propagation direction.

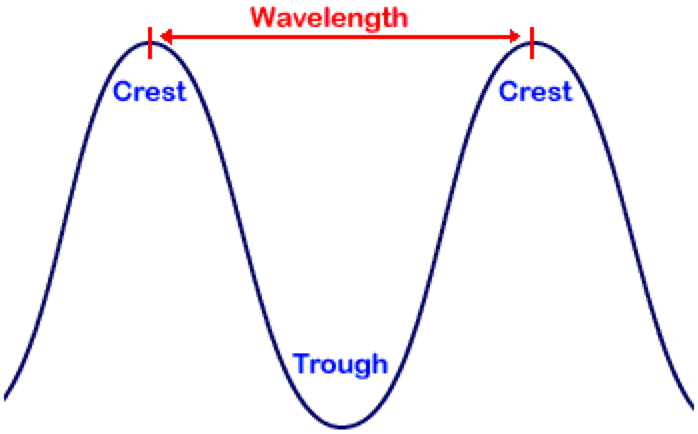


❖Waves are characterized by frequency, wavelength, speed and phase.

❖Frequency is defined as the number of waves (*cycles) per second that pass a given point* in space (symbolized by ν).

❖**Wavelength is the distance between two consecutive peaks or troughs in a wave** (symbolized by the λ).

Nature of Electromagnetic Radiation



❖Relation between λ and ν : $\boldsymbol{\lambda \times \nu = c}$

❖Since all types of electromagnetic radiation travel at the speed of light, short wavelength radiation must have a high frequency.

❖Unlike speed of light and wavelength, which change as electromagnetic energy is propagated through media of different densities, frequency remains constant and is therefore a more fundamental property.

❖Wavenumber is defined as a count of the number of wave crests (or troughs) in a given unit of length (symbolized by ṽ):

$$\tilde{\nu} = \nu / c = 1/\lambda$$

Nature of Electromagnetic Radiation

❖ ***UNITS:***

Wavelength units: length

Angstrom (A) : 1 A = 1×10^{-10} m;
Nanometer (nm): 1 nm=1×10^{-9} m;
Micrometer (μm): 1 μm = 1×10^{-6} m;

Wavenumber units: inverse of length (often in cm^{-1})

❖ **Frequency units: unit cycles per second 1/s (or s^{-1}) is called hertz (abbreviated Hz)**

Properties of Electromagnetic Radiation

1. The oscillating charged particles produce oscillating electric and magnetic fields which are perpendicular to each other and both are perpendicular to the direction of propagation of the wave.

2. Electromagnetic waves do not require a medium i.e., they can travel in a vacuum too.

3. There are many kinds of electromagnetic radiation, differing from one another in terms of wavelength or frequency. This electromagnetic radiation as a whole constitutes the electromagnetic spectrum. For example radio frequency region, microwave region, infrared region, ultraviolet region, visible region etc.

4. The electromagnetic radiation is characterized based on various properties like frequency, wavelength, time period etc.

Nature of Electromagnetic Radiation – *Particle Nature*

❖Radiation can be also described in terms of particles of energy, called photons

❖The energy of a **photon is given as**

$$\varepsilon_{photon} = h\nu = hc/\lambda = hc\tilde{\nu}$$

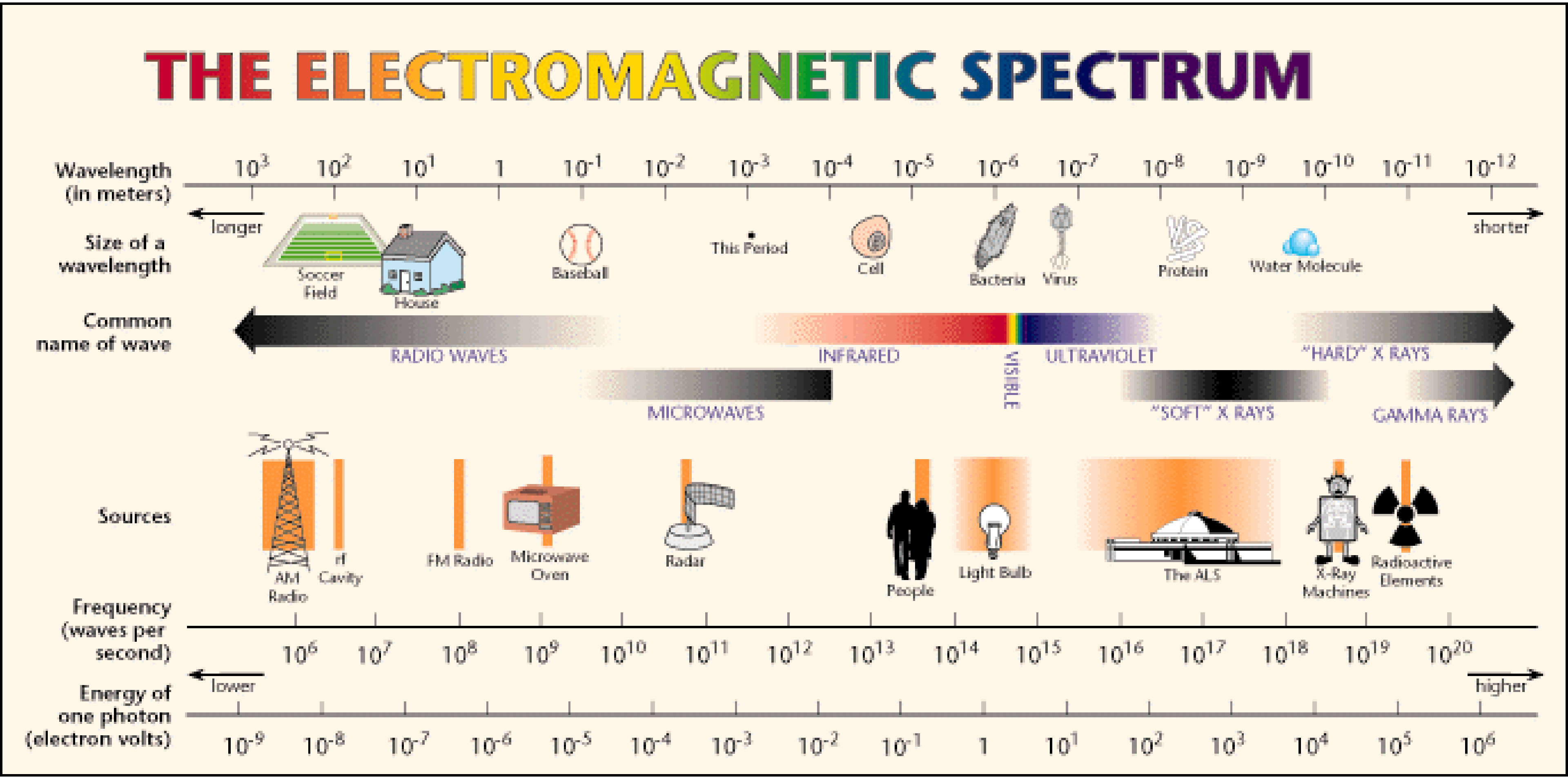
✓where ***h is Plank's constant (h = 6.6256x10^{-34} J s)***

✓Photon has energy but it has no mass and no charge.

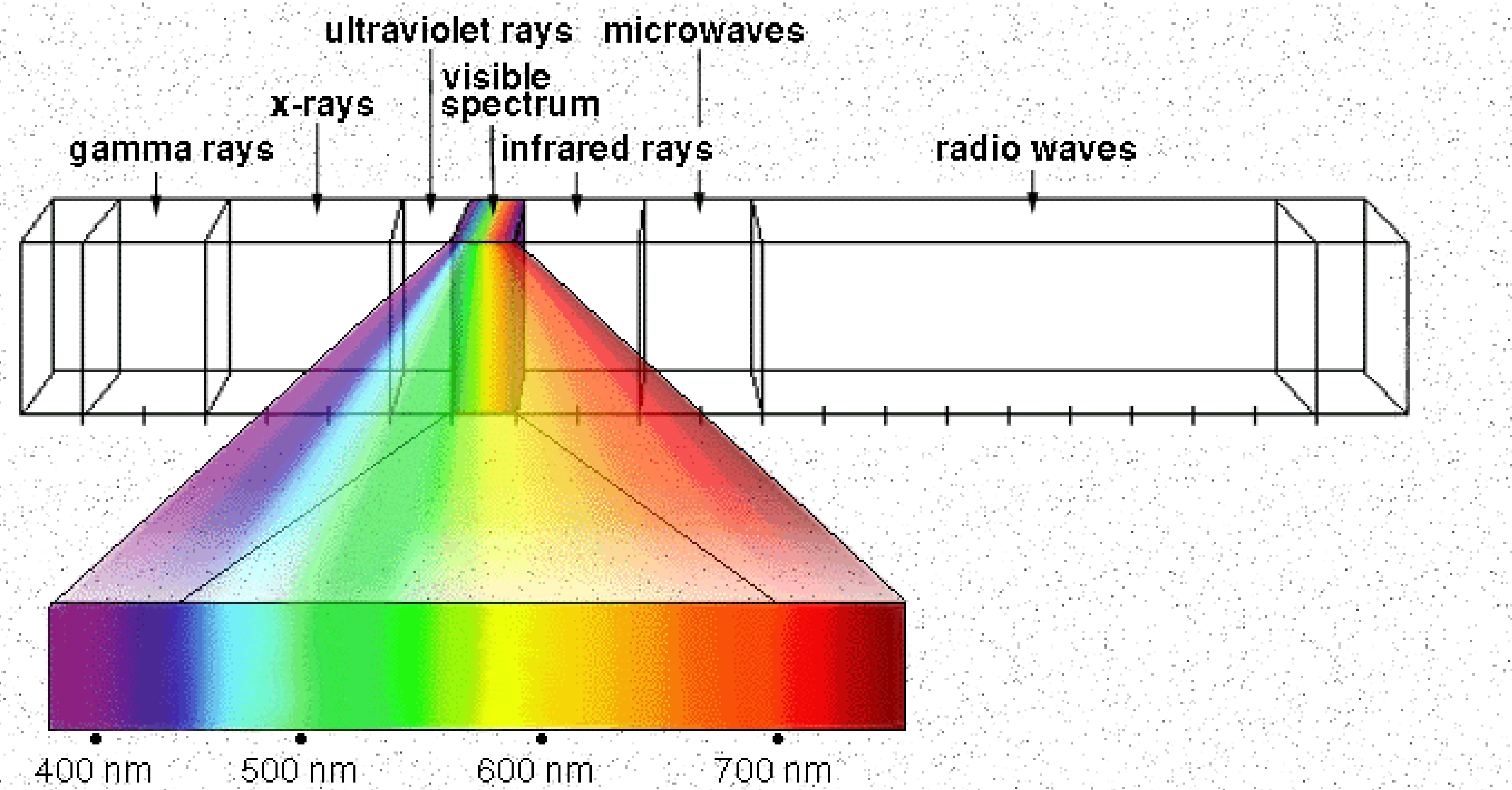
✓Relates energy of each photon of the radiation to the electromagnetic wave characteristics.

Spectrum of Electromagnetic Radiation

❖The electromagnetic **spectrum is the distribution of electromagnetic radiation according** to energy or, equivalently, according to the wavelength or frequency.



Spectrum of Electromagnetic Radiation



Spectrum of Electromagnetic Radiation

Electromagnetic Spectrum

Type of Radiation	Frequency Range (Hz)	Wavelength Range	Type of Transition
gamma-rays	10^{20}-10^{24}	<1 pm	nuclear
X-rays	10^{17}-10^{20}	1 nm-1 pm	inner electron
ultraviolet	10^{15}-10^{17}	400 nm-1 nm	outer electron
visible	4-$7.5x10^{14}$	750 nm-400 nm	outer electron
near-infrared	$1x10^{14}$-$4x10^{14}$	2.5 µm-750 nm	outer electron molecular vibrations
infrared	10^{13}-10^{14}	25 µm-2.5 µm	molecular vibrations
microwaves	$3x10^{11}$-10^{13}	1 mm-25 µm	molecular rotations, electron spin flips*
radio waves	$<3x10^{11}$	>1 mm	nuclear spin flips*

Absorption Spectroscopy

❖**Absorption spectroscopy** refers to spectroscopic techniques that measure the absorption of radiation, as a function of frequency or wavelength, due to its interaction with a sample. The sample absorbs energy, i.e., photons, from the radiating field. The intensity of the absorption varies as a function of frequency, and this variation is the absorption spectrum. Absorption spectroscopy is performed across the electromagnetic spectrum.

❖The most common arrangement is to direct a generated beam of radiation at a sample and detect the intensity of the radiation that passes through it. The transmitted energy can be used to calculate the absorption. The source, sample arrangement and detection technique vary significantly depending on the frequency range and the purpose of the experiment.

Absorption Spectroscopy

❖**Applications: Absorption spectroscopy** is employed as an analytical chemistry tool to determine the presence of a particular substance in a sample and, in many cases, to quantify the amount of the substance present. Infrared and ultraviolet–visible spectroscopy are particularly common in analytical applications. Absorption spectroscopy is also employed in studies of molecular and atomic physics, astronomical spectroscopy and remote sensing.

❖**Types of Absorption Spectroscopy:**

Sr. No	Electromagnetic Radiation	Spectroscopic type
1	X-ray	X-ray absorption spectroscopy
2	Ultraviolet–visible	UV–vis absorption spectroscopy
3	Infrared	IR absorption spectroscopy
4	Microwave	Microwave absorption spectroscopy
5	Radio wave	Electron spin resonance spectroscopy Nuclear magnetic resonance spectroscopy

Absorption Spectroscopy

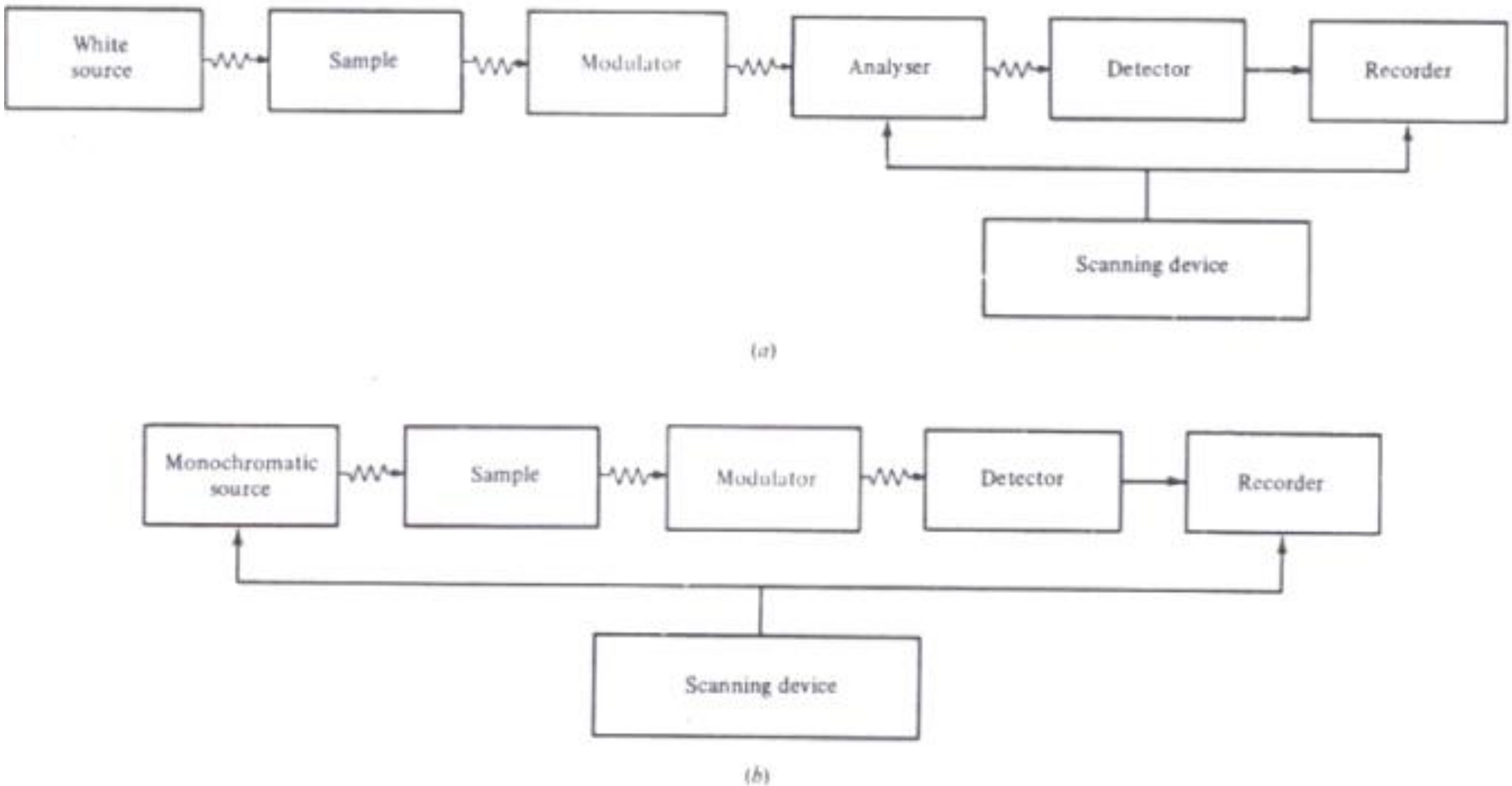
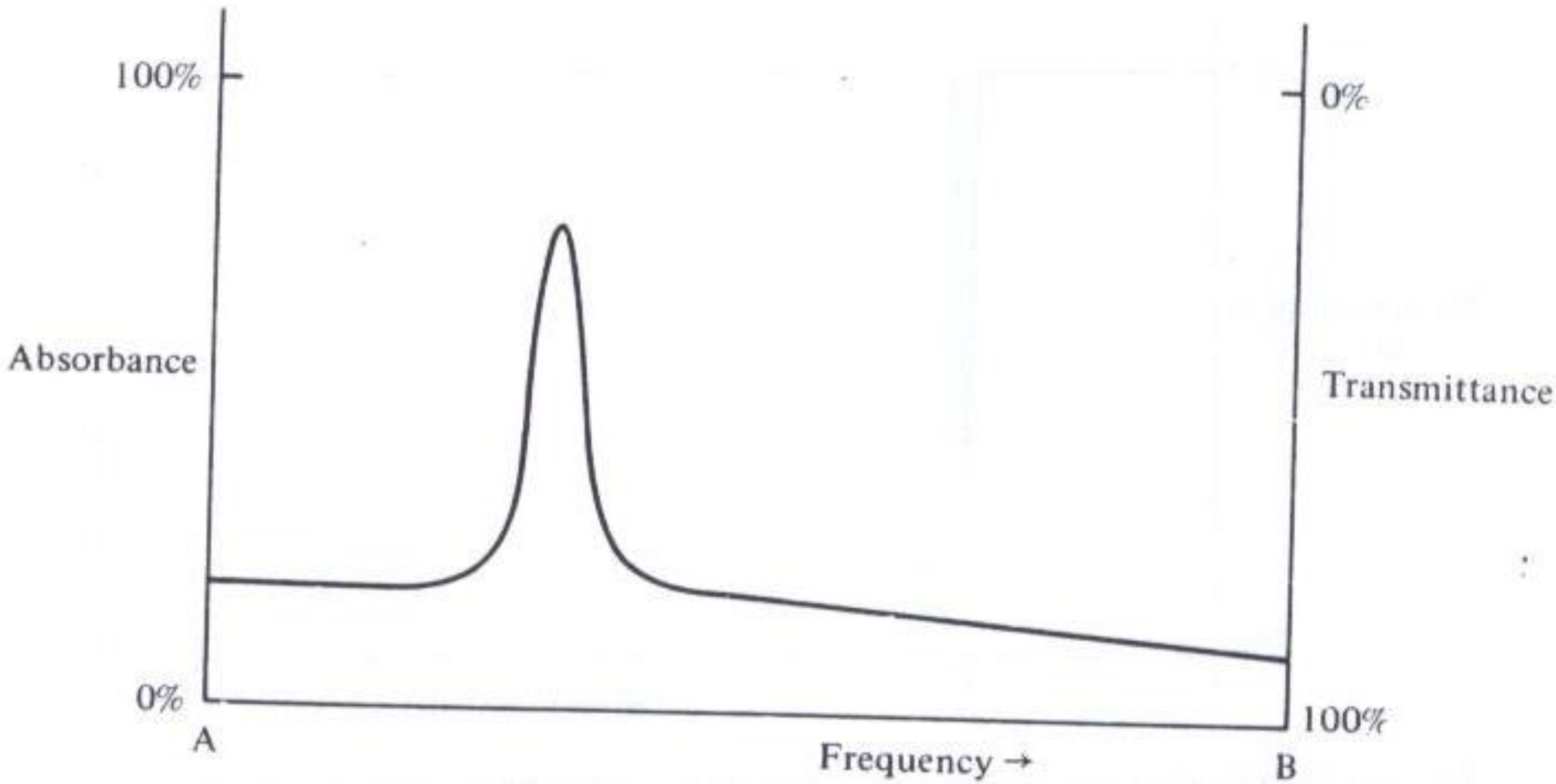


Figure 1.15 Block diagram of a typical absorption spectrometer for use in (*a*) the infra-red, visible, and ultra-violet regions where a 'white' source is available, and (*b*) the microwave and radiofrequency regions where the source can be tuned over a considerable range of frequencies.

Absorption Spectroscopy



Absorption Spectroscopy

❖**Mechanism:** A material's absorption spectrum is the fraction of incident radiation absorbed by the material over a range of frequencies. The absorption spectrum is primarily determined by the atomic and molecular composition of the material. Radiation is more likely to be absorbed at frequencies that match the energy difference between two quantum mechanical states of the molecules. The absorption that occurs due to a transition between two states is referred to as an absorption line and a spectrum is typically composed of many lines.

❖The frequencies where absorption lines occur, as well as their relative intensities, primarily depend on the electronic and molecular structure of the sample. The frequencies will also depend on the interactions between molecules in the sample, the crystal structure in solids, and on several environmental factors (e.g., temperature, pressure, electromagnetic field). The lines will also have a width and shape that are primarily determined by the spectral density or the density of states of the system.

Absorption Spectroscopy - Home Assignments

1. We have an absorption line at 642 nm. Calculate the energy of the absorbed photons.

2. Calculate the energy difference between two absorption lines occurring at 642 nm and 720 nm.

3. Calculate the frequency of following absorption lines and indicated the region of the electromagnetic spectrum.

(i) 640 nm (ii) 411 nm (iii) 180 nm (iv) 900 nm (v) 1100 nm

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Emission Spectroscopy

The **emission spectrum** of a chemical element or chemical compound is the spectrum of frequencies of electromagnetic radiation emitted due to an atom or molecule making a transition from a high energy state to a lower energy state. The photon energy of the emitted photon is equal to the energy difference between the two states. There are many possible electron transitions for each atom, and each transition has a specific energy difference. This collection of different transitions, leading to different radiated wavelengths, make up an emission spectrum. Each element's emission spectrum is unique. Therefore, spectroscopy can be used to identify elements in matter of unknown composition. Similarly, the emission spectra of molecules can be used in chemical analysis of substances. emission is the process by which a higher energy quantum mechanical state of a particle becomes converted to a lower one through the emission of a photon, resulting in the production of light. The frequency of light emitted is a function of the energy of the transition.

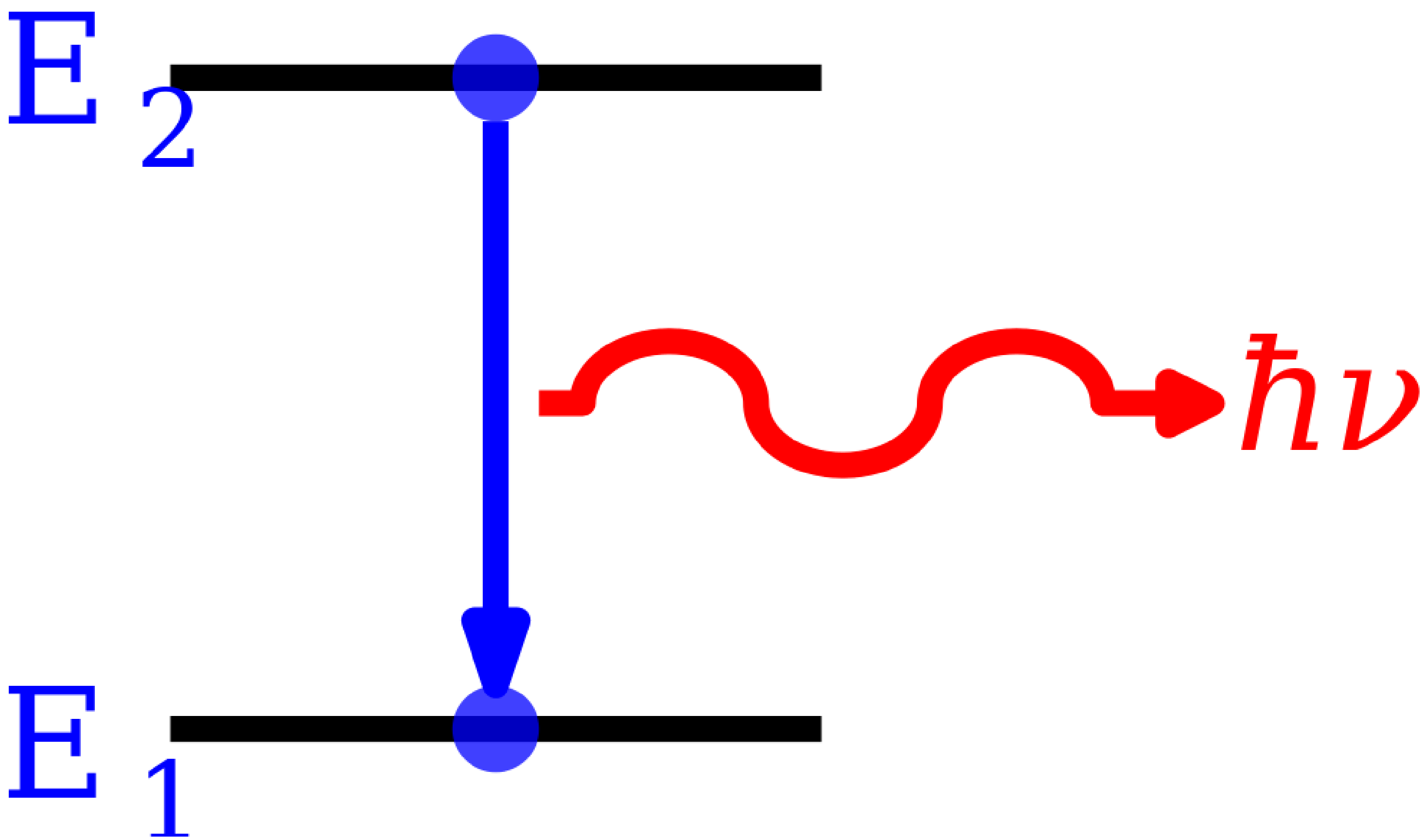
Emission Spectroscopy

When the electrons in the atom are excited, for example by being heated, the additional energy pushes the electrons to higher energy orbitals. When the electrons fall back down and leave the excited state, energy is re-emitted in the form of a photon. The wavelength (or equivalently, frequency) of the photon is determined by the difference in energy between the two states. These emitted photons form the element's spectrum. The fact that only certain colors appear in an element's atomic emission spectrum means that only certain frequencies of light are emitted. Each of these frequencies are related to energy by the formula:

$$\mathbf{E_{photon} = h\nu}$$

Ephoton is the energy of the photon, ν is its frequency, and h is Planck's constant. This oncludes that only photons with specific energies are emitted by the atom. The principle of the atomic emission spectrum explains the varied colors in neon signs, as well as chemical flame test results

Emission Spectroscopy



Emission Spectroscopy

❖**Mechansim:** Light consists of electromagnetic radiation of different wavelengths. Therefore, when the elements or their compounds are heated either on a flame or by an electric arc they emit energy in the form of light. Analysis of this light, with the help of a spectroscope gives us a discontinuous spectrum. A spectroscope or a spectrometer is an instrument which is used for separating the components of light, which have different wavelengths. The spectrum appears in a series of lines called the line spectrum. This line spectrum is called an atomic spectrum when it originates from an atom in elemental form. Each element has a different atomic spectrum. The production of line spectra by the atoms of an element indicate that an atom can radiate only a certain amount of energy. This leads to the conclusion that bound electrons cannot have just any amount of energy but only a certain amount of energy.

Emission Spectroscopy

❖**Applications:** The emission spectrum can be used to determine the composition of a material, since it is different for each element of the periodic table. One example is astronomical spectroscopy: identifying the composition of stars by analysing the received light. The emission spectrum characteristics of some elements are plainly visible to the naked eye when these elements are heated. For example, when platinum wire is dipped into a sodium nitrate solution and then inserted into a flame, the sodium atoms emit an amber yellow color. Similarly, when indium is inserted into a flame, the flame becomes blue. These definite characteristics allow elements to be identified by their atomic emission spectrum. Not all emitted lights are perceptible to the naked eye, as the spectrum also includes ultraviolet rays and infrared radiation. An emission spectrum is formed when an excited gas is viewed directly through a spectroscope.

Emission Spectroscopy

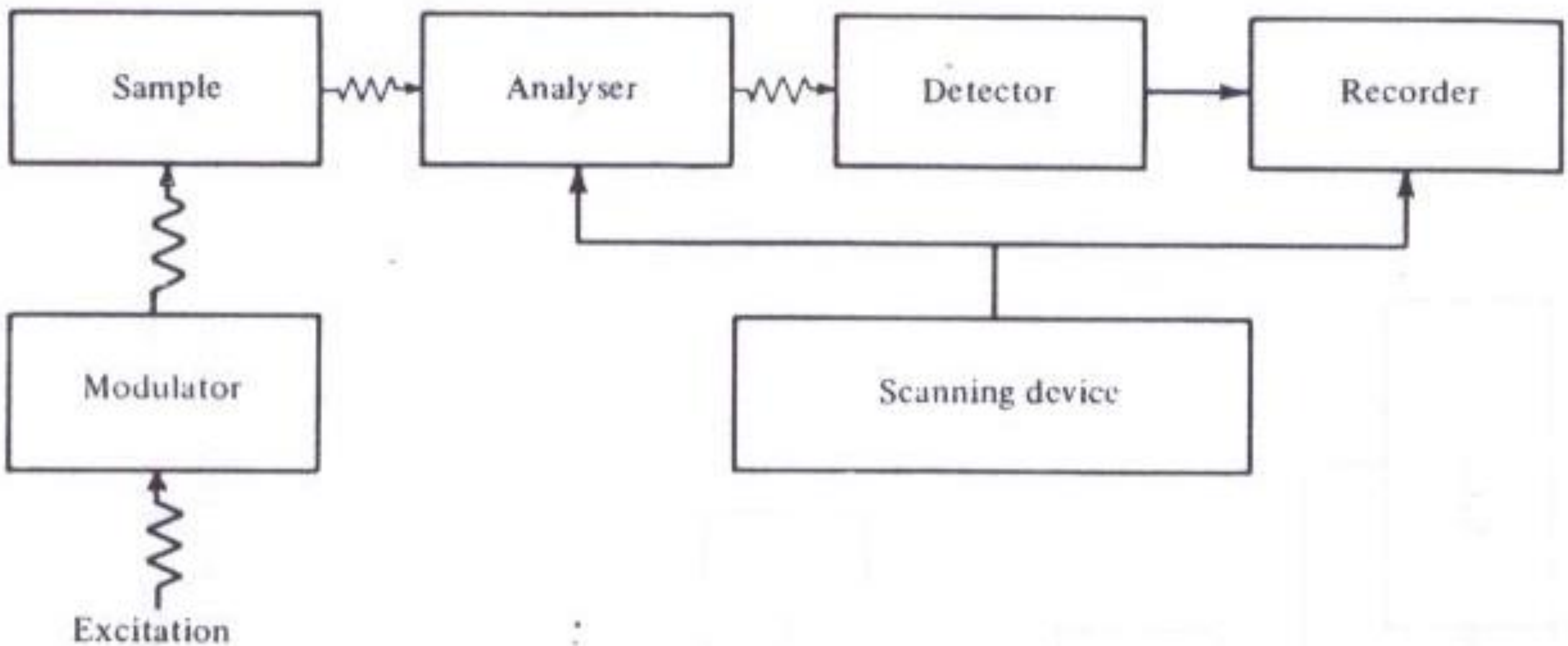


Figure 1.16 Block diagram of a typical emission spectrometer.