UNIT 1 ELECTROMAGNETIC RADIATION

Structure

1.1 INTRODUCTION

You would surely have seen a beautiful rainbow showing seven different colours during the rainy season. You know that this colourful spectrum is due to the separation or dispersion of the white light into its constituent parts by the rain drops. The rainbow spectrum is just a minute part of a much larger continuum of the radiations that come from the sun. These are called electromagnetic radiations and the continuum of the electromagnetic radiations is called the electromagnetic spectrum. In the first unit of this course you would learn about the electromagnetic radiation in terms of its nature, characteristics and properties. Spectroscopy is the study of interaction of electromagnetic radiation with matter. We would discuss the ways in which different types of electromagnetic radiation interact with matter and also the types of spectra that result as a consequence of the interaction.

In the next unit you would learn about ultraviolet-visible spectroscopy – a consequence of interaction of electromagnetic radiation in the ultraviolet-visible range with the molecules constituting the matter.

Objectives

After studying this unit, you should be able to:

- describe the wave nature of electromagnetic radiation,
- define the parameters that characterise wave form of electromagnetic radiation,
- outline and explain the properties of the electromagnetic radiation that arise due to its wave nature,
- describe the quantised or particle nature of electromagnetic radiation,
- explain the phenomena of absorption, emission and scattering of electromagnetic radiation, and
- explain the origin of line spectrum and band spectrum.

1.2 WHAT IS ELECTROMAGNETIC RADIATION?

You feel hot while sitting close to a fire. You would say it is obvious, what is so special about it? Fine! But have you ever wondered what makes you feel hot or in other words how does the energy as heat reaches you from the source? This is in the form of **electromagnetic (EM) radiation**. Heat energy reaches us in the form of infra-red radiations which is a type of electromagnetic radiation. Let us learn about EM radiation in general.

An electromagnetic radiation may be defined as the radiant energy which is transmitted through space at enormous velocities. It exists in various forms; the visible light and radiant heat being the easily recognised forms which we experience in daytoday life too. The EM radiation, unlike sound, does not require a medium for transmission and pass readily through vacuum and in vacuum, the velocity of radiation is 3×10^8 m s^{-1}. The study of different ways in which EM radiation can interact with matter is of great importance in Chemistry. In order to understand these interactions it is therefore necessary to have knowledge of the properties of EM radiation. The properties of an electromagnetic radiation could be explained in terms of both classical wave model (wave mechanics) and particle model (quantum mechanics). Let us learn about these models of EM radiation and the properties associated with them.

1.2.1 Wave Mechanical Model of Electromagnetic Radiation

In the wave mechanical model, the electromagnetic radiation is considered to be sinusoidal in nature, i.e., varying like a sine function. According to the Maxwell's theory, an electromagnetic wave can be visualised as oscillatory electric and magnetic fields travelling in the planes perpendicular to each other and also to the direction of propagation (Fig. 1.1). This gives rise to its name viz., **electromagnetic radiation**. However, since it is the electrical effect that is responsible for the phenomenon of interest to a chemist, it is generally represented in terms of the electric field only.

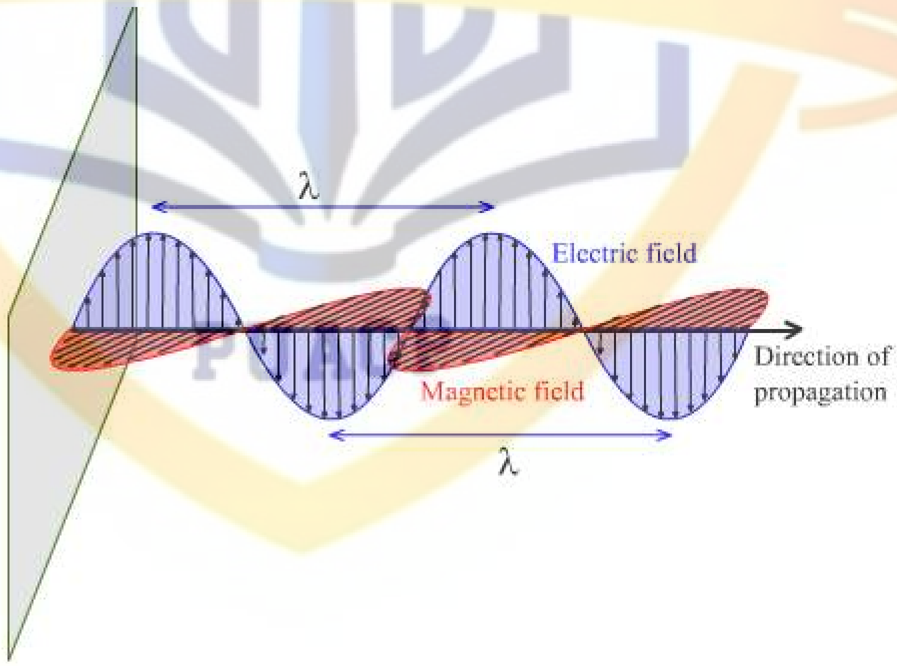


Fig. 1.1: An EM radiation showing oscillatory electric and magnetic fields

Characteristic Parameters of Electromagnetic Radiation

The electromagnetic wave is characterised in terms of a number of parameters. These are as follows:

Amplitude: It refers to the maximum height to which the wave oscillates and equals the height of the crests or depths of the troughs. It is a measure of the radiant power of the radiation. The **radiant power** refers to the energy of the radiation striking at a given area per unit time. It is denoted as *P* and is related to the square of the amplitude. It is important to remember that the radiant power is not related to the wavelength. A closely related term is called **intensity** of the radiation which is denoted as *I* and is defined as the radiant power per unit solid angle.

Wavelength: It is the linear distance between two consecutive wave-crests or wave-troughs or the distance of complete cycle as shown in Fig. 1.1. It is represented by a Greek letter ***lambda*** (λ) and expressed in terms of metre (m), centimetre (cm), micrometre (μm), nanometre (nm) or Angstrom (Å) units. The wavelength of electromagnetic radiation varies from a few Angstroms to several metres.

1 cm = 10^{-2} m
1 μm = 10^{-6} m
1 nm = 10^{-9} m
1 Å = 10^{-10} m

Frequency: It is defined as the number of wave crests or wave troughs that pass through a given point per second. It is represented by a Greek letter ***nu*** (ν) and expressed in terms of second inverse or per second (s^{-1}) or Hertz (Hz). The relationship between wavelength and frequency is given as:

$$\nu = \frac{c}{\lambda}$$

Where, the wavelength λ is in metres, the frequency ν is in reciprocal seconds (s^{-1}) and the velocity of light, $c = 3 \times 10^8 \ m\,s^{-1}$.

Different spectroscopic techniques use different units for wavelength. Nanometre is popular for UV-visible regions while micrometre (μm) is preferred for the IR

Wave number: It equals the number of waves per centimetre or per unit distance. It is denoted as ***nu*** **bar** ($\bar{\nu}$) and is equal to the reciprocal of the wavelength expressed in metres (m). The unit of $\bar{\nu}$ is metre inverse (m^{-1}) though cm^{-1} is also commonly employed; where the wavelength is expressed in the units of cm.

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

Velocity: It is defined as the linear distance travelled by the wave in one second. The velocity in metres per second can be obtained by multiplying frequency in second inverse by wavelength in metres.

$$c = \nu\,(s^{-1})\,\lambda$$

The velocity of EM radiation depends on the medium. It has maximum value in vacuum and equals $3.00 \times 10^8 \ m\,s^{-1}$.

Energy: The energy of the electromagnetic radiation depends on its wavelength or frequency. The relationship is as under.

$$E = h\nu = \frac{hc}{\lambda} \qquad \text{... (1.1)}$$

where, *h* is the Planck's constant and has a value of = 6.626×10^{-34} J s, ν is the frequency *c* is the velocity and λ is the wavelength. As you can probably make out that the energy is directly related to the frequency and inversely related to the wavelength of the radiation. In other words a high frequency radiation will have a higher energy while a longer wavelength radiation will be low in energy. Table 1.1 summarises the important characteristics of the EM radiation, their relationship with wavelength and the common units of their measurement.

Table 1.1: Characteristics of EM radiation, their relationship with wavelength and common units of measurement

Characteristic of EM Radiation	Relationship with Wavelength	Common Units
Wavelength	λ	m, µm, nm
Wave number	$\bar{\nu} = \frac{1}{\lambda}$	m^{-1}, cm^{-1}
Frequency	$\nu = \frac{c}{\lambda}$	s^{-1} (Hz)
Velocity	$c = \nu\lambda$	$m\ s^{-1}$
Energy	$E = \frac{hc}{\lambda}$	Joule (J)

The Electromagnetic Spectrum

Deuterium lamp is commonly employed as the source of UV radiations.

Depending on the wavelengths, electromagnetic radiation is of many types and constitutes what is called an **electromagnetic spectrum** (Fig. 1.2). The EM spectrum is divided into different regions on the basis of the methods required to generate and detect them. The radiations of different regions differ in terms of their characteristics like energy, wavelength, etc. The electromagnetic spectrum is divided into γ-rays, x-rays, ultraviolet, visible, infrared, microwave and radio waves, etc. in terms of increasing wavelengths.

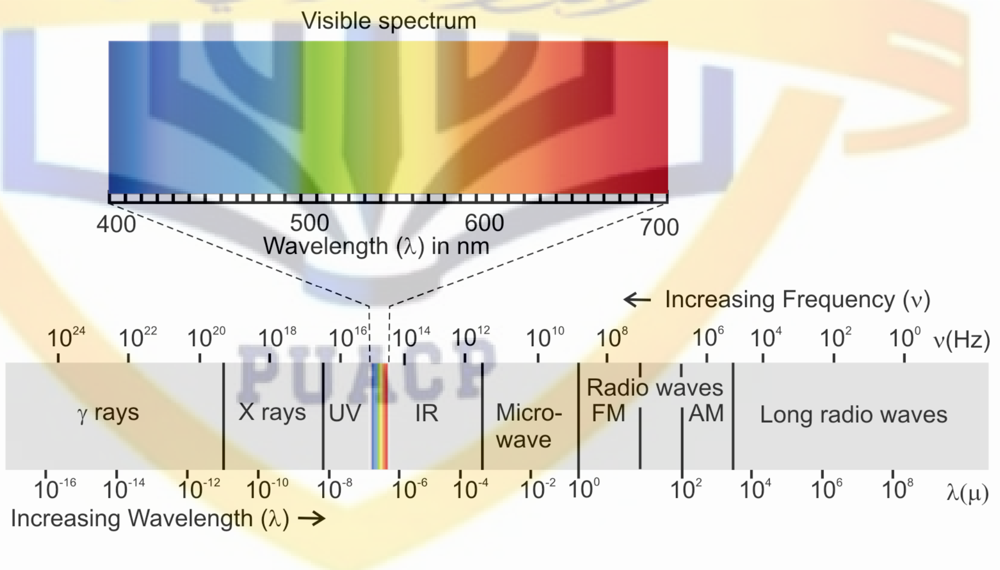


Fig.1.2: Electromagnetic spectrum showing different regions

The visible region of the spectrum which the human eye can sense is very tiny, as compared to the other spectral regions. Since the range of electromagnetic spectrum is quite large, it is expressed in logarithmic or exponential scale.

The sources of radiation mostly give EM radiation spread over a range. In other words the EM radiation emitted by the source contains a number of radiations having slightly different wavelengths. For example, a hot deuterium lamp emits radiations in the wavelength range of approximately 190-380 nm. Such a radiation is called

polychromatic radiation signifying that it consists of many radiations of different wavelengths. We can generate or separate out radiation of a single wavelength from the polychromatic radiation by using a suitable device called **monochromator**. Such a radiation is called a **monochromatic radiation** i.e., consisting of a single wavelength. You would learn about monochromators in the next unit.

Before going ahead, try to answer the following SAQ.

SAQ 1

How is an electromagnetic radiation different from sound waves?

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

1.2.2 Quantum Model of Electromagnetic Radiation

The wave model of electromagnetic radiation described above was successful in explaining a number of observed phenomena however, it fails to account for the absorption, emission and scattering of radiant energy, discussed in Sec 1.3 and 1.4. It is so because when an electromagnetic radiation is absorbed or emitted, there is a permanent transfer of energy which goes against the very concept of wave nature of energy. Therefore a new model for the electromagnetic radiation was required. This is called the **quantum model**. The quantum model (also called **particle model**) of radiation was necessitated by the experimental observations in case of black body radiation and the photoelectric effect. Let us briefly recall these.

Max Planck proposed the concept of quantisation to explain the experimental observations in case of a black body and Einstein used this concept to explain photoelectric effect.

Black Body Radiation

You have learnt earlier that all heated objects emit electromagnetic radiation and the wavelengths of these radiations depend on the temperature of the object. For example, at relatively low temperatures, a metal rod emits infrared radiation which we cannot see but feel as heat. As the temperature is raised to about 600°C a dull red colour is visible and at about 2000 °C it glows white. One can visit a blacksmith and observe the changes in the glow of iron as it is heated to higher and higher temperatures.

However, the energy radiated by a hot surface depends on its nature and surface area, besides the temperature. For a given area and temperature, a black surface radiates more energy per second than a polished surface. At a given temperature the maximum radiation would be given out by a perfectly black surface. The experimentaly observed data on radiant intensity emitted at different wavelengths by a perfect black surface (called black body) at different temperatures could not be explained by classical mechanical principles. This required a relook at the nature of the radiation.

Photoelectric Effect

In 1887, Hertz observed that when a light of appropriate wavelength falls on a clean surface of metal plate placed in an evacuated vessel a stream of electrons is emitted. These electrons are called as **photoelectrons** because these are emitted due to light. As moving electrons constitute electricity, the phenomenon of emission of photoelectrons is referred to as the **photoelectric effect**. Alkali metals with loosely held electrons are better photoelectric metals. Like blackbody radiation, the existence of the photoelectric effect and the related experimental observations could also not be explained by classical physics. These and some other experimental phenomenon could be explained in terms of the quantum mechanical model. Let us learn about it. In the **quantum or particle model**, the radiant energy is considered as stream of discrete particles or packets of energy called as **quanta** (singular, quantum) whose energy is proportional to its frequency. The two are related as,

$$E = h\nu$$

The quantum of light was later called a **photon**.

Alternatively, the energy of the quantum can be related to the wavelength or wave number as follows

$$E = h\frac{c}{\lambda} \quad \text{or} \quad E = hc\bar{\nu}$$

It is important to remember that **energy of the photon** is not same as the radiant power. The radiant power includes the energy of the photon as well as the number of the photons in the radiation.

Let us take an example to understand the application of the relationship between the energy and other characteristics of the radiation.

Example 1: A microwave radiation has a frequency of 12 gigahertz.

a) What would be the energy of the photon corresponding to this radiation?
b) Calculate the wavelength of the radiation.

(h = 6.626 × 10^{-34} J s and 1 gigahertz = 10^9 Hz)

Solution:

The energy of radiation is related to the frequency as, $E = h\nu$

Substituting the values of frequency and Planck's constant, we get

$$E = 6.626\times10^{-34}\,\text{Js}\times1.2\times10^{10}\,\text{s}^{-1} = 7.95\times10^{-24}\,\text{J}$$

∴ The energy of the photon having a frequency of 12 gigahertz = 7.95 × 10^{-24} J

Further, since $E = h\frac{c}{\lambda}$ we can rearrange the equation to get

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

Substituting the values of E, h and c we get

$$\lambda = \frac{7.95\times10^{-24}\,\text{J}}{6.626\times10^{-34}\,\text{J s}\times3.0\times10^{8}\,\text{m s}^{-1}} = 400\text{ nm}$$

∴ The wavelength of the radiation = 400 nm

Try to answer the following SAQ to assess your understanding about the characteristics of the electromagnetic radiation.

SAQ 2

The green light has a wavelength of 535 nm. Calculate the energy of a photon of green light.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

1.3 CONSEQUENCES OF WAVE NATURE OF ELECTROMAGNETIC RADIATION

The wave nature of electromagnetic radiation is manifested in terms of a number of important phenomena. These are interference, diffraction, dispersion, refraction, reflection, scattering, and polarisation etc. Let us learn about these in the following subsections.

1.3.1 Interference

In 1803, an English physicist Thomas Young reported the results of his famous double slit experiment on light. He observed that when a monochromatic light was made to pass through two closely spaced narrow slits and to fall on a distant screen a series of dark and light bands (called fringes) were observed on the screen (Fig. 1.3).

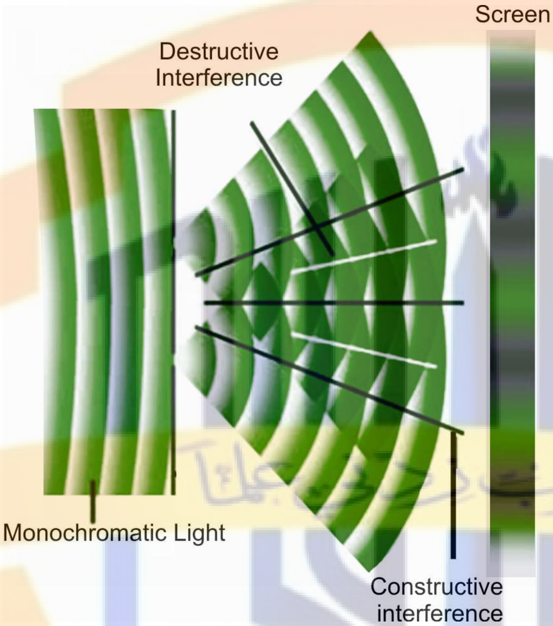


Fig. 1.3: A monochromatic light showing dark and light bands when passed through two closely spaced narrow slits

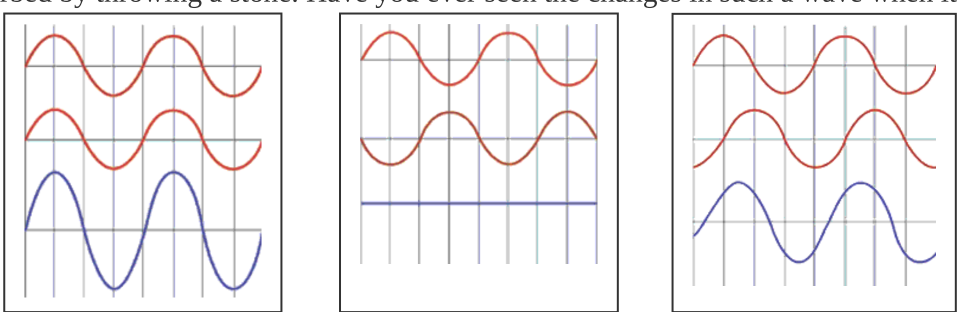
The beautiful coloured patterns observed in the Peacock feathers and in the compact disc are due to interference of light.

The origin of these fringes was explained in terms of the **interference** of the wavelets originating from the two slits. The bright spots were attributed to the **constructive interference** of the wavelets, meaning thereby that the wavelets are in phase and when they interfere, their amplitudes add up to give the bright spot. On the other hand, when the wavelets are not in phase they undergo **destructive interference** whereby these cancel each other's amplitudes and result into a dark spot. The third possibility is that the waves are partially in phase and partially out of phase. In such a situation the resultant amplitude is the sum of the amplitudes of the two wavelets at different times or distance (Fig. 1.4).

Fig. 1.4: Schematic representation of interference of waves

1.3.2 Diffraction

You might have experienced the formation of waves in a pond of still water when disturbed by throwing a stone. Have you ever seen the changes in such a wave when it



encounters a small barrier or a narrow opening? If you have observed, you would recall that these waves bend or change their direction of propagation on meeting a barrier or an opening. This phenomenon of bending of a wave round the corners of sharp barriers or through narrow openings is called **diffraction.** Electromagnetic radiations also show this phenomenon. The consequence of diffraction can be observed by placing a photographic plate in the path of diffracted radiation. The occurrence of a pattern of alternate bright and dark bands is characteristic of the diffraction (Fig.1.5). The intensity is maximum at the central band and decreases gradually as the distance increase and not visible beyond certain distance. The presence of light in the areas that are otherwise expected to be dark accounts for the bending of light.

Diffraction is a wave property, which can be observed not only for electromagnetic radiations, but also for mechanical and acoustical (i.e., related to sound) waves.

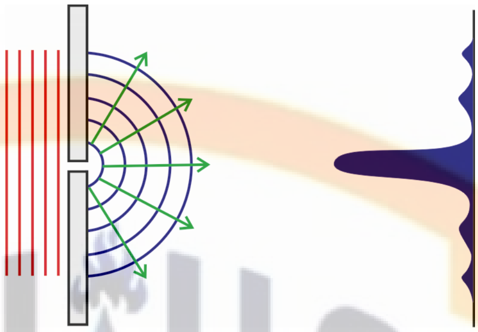


Fig. 1.5: Diffraction of monochromatic radiation through a narrow slit and the resulting intensity pattern

The diffraction phenomenon is a consequence of interference of wavelets originating from different parts of the slit. The inner corners as well as the central part of the slit act as the sources of new wavelets which interfere to give the observed intensity patterns.

The extent of diffraction through narrow openings (slits) depends inversely on the width of the slit i.e., narrower the slit greater the diffraction. The effect becomes observable when the size of the slit is comparable to the wavelength of the light.

1.3.3 Transmission

When radiation passes through a transparent medium, its velocity is found to be reduced as compared to that in the vacuum. This is due to the interaction of radiation with the constituents of matter. The extent of reduction in velocity depends on the nature and concentration of atoms, ions or molecules present in the medium. When the radiation interacts with the atoms and molecules present in the medium, it results in their **periodic polarisation** i.e., the deformation of their electron clouds. In the absence of any absorption, the energy required for polarisation is retained only momentarily ($10^{-14} - 10^{-15}$ s) and reemitted without any alteration and the substance returns to its original state. Since the re emission of the radiation is delayed for some time; i.e. the radiation takes a little longer to travel through a distance, its velocity decreases. However, since there is no absorption of the radiation, the frequency of the radiation does not change. Thus the transmission of radiation involves a series of polarisation processes wherein the atoms, ions and molecules act as intermediates.

Polarisation is a phenomenon of temporary deformation of electron clouds associated with atoms and molecules

The extent of interaction of the radiation with matter can be expressed in terms of an important parameter called the **refractive index** of the medium. It is defined by the following equation:

$$\eta_i = \frac{c}{v_i}$$

where, η_i is the refractive index for the radiation of a given frequency i, and c and v_i are the velocities of the radiation in vacuum and in the medium, respectively. The variation of refractive index of a substance with wavelength of the radiation is called as **dispersion**. If the refractive index increases gradually with increasing frequency, it is called a **normal dispersion**, and if there is a sharp change in refractive index it is termed as an **anomalous dispersion**.

The type of dispersion plays important role in the selection of optical components for instruments.

1.3.4 Refraction

When a beam of light travelling through air falls on glass at an angle, it abruptly changes its direction or in simple words, it bends. A similar effect is observed when the light emerges back into air after passing through the glass. In general, when a radiation falls on the interface of two transparent media of different densities, it abruptly changes its direction. This is called **refraction** of the radiation. Refraction is a consequence of the difference in the velocity of radiation in the two media. When the radiation passes from a rarer medium (say air) to a denser medium (say glass) it bends towards the normal to the interface. If the order of the media is reversed then it bends away from the normal to the interface at the point of incidence. The process of refraction in case of radiation passing from rarer to a denser medium can be depicted diagrammatically as shown in Fig. 1.6.

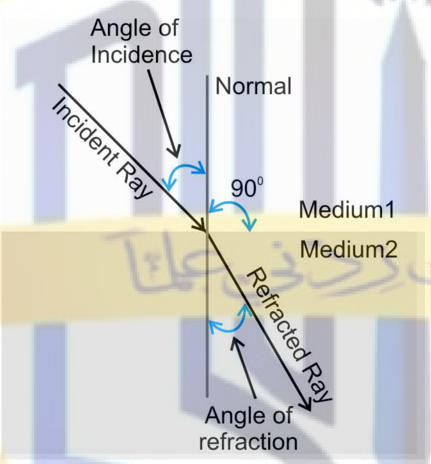


Fig. 1.6: Phenomenon of refraction of radiation

Bending of pencil in a glass of water is a consequence of refraction.

According to **Snell's law**:

$$\frac{\sin\theta_1}{\sin\theta_2} = \frac{\eta_2}{\eta_1} = \frac{v_1}{v_2}$$

where, θ_1 and θ_2, are the angle of incidence between the incident ray and the normal and the angle of refraction between the refracted ray and the normal, respectively. η_1 and η_2 are the refractive indices of the medium that the light is entering into and leaving (or entering from) respectively; v_1 and v_2 correspond to the velocities of light in medium 1 and 2, respectively.

1.3.5 Reflection

When a radiation travelling in a medium is incident on a medium of different refractive index, a fraction of the radiation bounces back at an angle equal to the angle of incidence of the radiation. This is called **reflection** of light. Larger the difference in refractive index the greater is the fraction of reflected radiation. The fraction of the reflected light is given as below:

The fact that the angle of incidence is equal to the angle of reflection is sometimes called the "law of reflection".

$$\frac{P_r}{P_o} = \frac{(\eta_2 - \eta_1)^2}{(\eta_2 + \eta_1)^2}$$

where P_0 and P_r are the radiant powers of the incident and reflected beams, respectively; η_1 and η_2 are the refractive indices of the two media. Fig. 1.7 shows the reflection and the refraction of radiation.

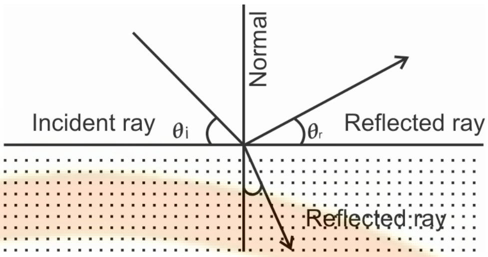


Fig.1.7: Diagrammatical representation of reflection and refraction

SAQ 3

What do you understand by the diffraction of radiation? How is it related to the slit width?

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

1.3.6 Scattering

As we have seen earlier (subsection 1.3.3), interaction of radiation with matter, cause a momentary retention of radiant energy by atoms, ions or molecules due to their polarisation. If the polarised particles are small, destructive interference of the re-emitted radiations eliminates the remitted radiations in all the directions other than original path of the light. What we observe is the radiation transmitted in unaltered direction. Keen experimental observations, however, revealed that a minute fraction of the radiation is transmitted in all directions. This phenomenon is called **scattering** and the radiation is referred to as **scattered radiation**. The intensity of the scattered radiation depends on the size of the particles constituting the medium.

1.3.7 Polarisation

Light emitted by the sun, or a lamp or by a candle flame is unpolarised in nature.

Ordinary radiation is created by vibration of electric charges in all possible directions. Thus a radiation consists of a bundle of electromagnetic waves in which the vibrations are equally distributed among an infinite series of planes perpendicular to the direction of propagation. Such a radiation which is vibrating in more than one plane is referred to as **unpolarised radiation**. If we observe an approaching unpolarised radiation from the direction opposite to its direction of propagation we would observe a set of infinite electrical vectors that oscillate around a fixed point as shown in Fig. 1.8.

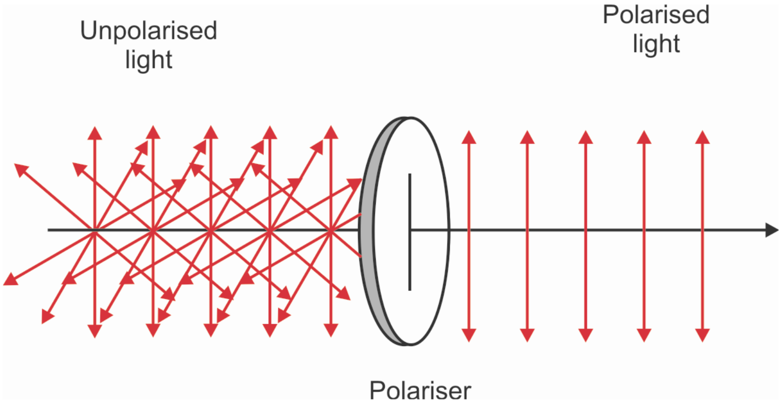


Fig.1.8: An unpolarised radiation passing through a polariser to give a plane polarised light

When such an unpolarised light is passed through a polariser, it cuts off all the radiations oscillating in different planes; and allows only those rays that vibrate in any one particular plane to pass through. The emerging radiation is called as the **plane polarised light**. The electric and magnetic components of the plane polarized light vibrate at right angles to each other as shown in Fig.1.1. The process of transforming unpolarised light into polarised light is known as **polarisation**. Calcite or quartz crystals are commonly used to obtain the polarised radiations.

Polarised light waves are light waves in which the vibrations occur in a single plane.

As mentioned earlier, spectroscopy is a study of interaction of radiation with matter and the consequences there of. Before formally getting into spectroscopy which we will discuss in the next unit, it is worthwhile to understand different possibilities that exist for this kind of interaction. Before studying further you can try answering the following question.

SAQ 4

What is plane polarised light? How is it obtained?

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

1.4 INTERACTION OF EM RADIATION WITH MATTER

In order to understand the nature and mechanism of interaction of radiation with matter we would first like you to recall what you have learnt about nature of matter in earlier classes. You would recall from your understanding of the quantum mechanical description of the electronic structures of atoms and molecules constituting matter, that these have unique set of quantised electronic energy states available to them. These arise from the motion of electrons around the nucleus and the electrons in atoms and molecules are present in the allowed or permissible energy states only. However in case of molecules, the rotation and vibration motions are also quantised in addition to these electronic energy states. The allowed energy level with the least energy is termed as the **ground state** while the rest are called **excited states**. The energy levels for a molecule can be schematically shown as given in Fig. 1.9.

There are a number of vibrational energy levels in an electronic state and a large number of rotational energy levels are there in a vibrational energy level.

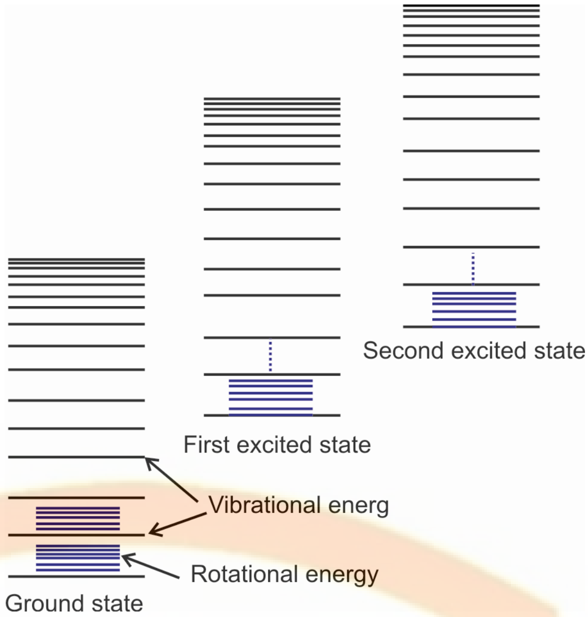


Fig. 1.9: Schematic diagram showing energy levels for a molecule

The transitions amongst these energy states may be brought about by absorption of a photon of suitable energy or these may lead to release of such a photon. In simple words we can say that the system may absorb energy and go from the lower energy state (ground state), E_1, to higher energy state (excited state), E_2 by absorbing a photon of energy equal to the difference of the energies of the two states i.e.,

$$\Delta E = E_2 - E_1 = h\nu$$

where, h is the **Planck's constant** and has the value of 6.626×10^{-34} J s (joules second) ν is the frequency of electromagnetic radiation which is causing the energy changes. Alternatively, a system initially in the higher energy state E_2 can go to the lower energy state E_1 by emitting a photon of the energy equal to the difference in energies. The energy changes can be shown as in Fig. 1.10. As you can see here in ΔE is the energy change associated with the transition between the energy levels E_1 and E_2.

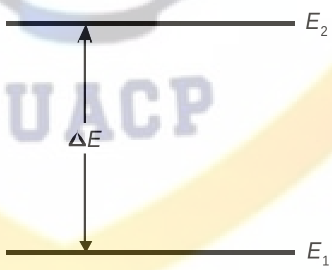


Fig. 1.10: Diagram showing energy change during transition between energy levels

Yet another possibility is of the radiation getting scattered. The three phenomena occurring due to interaction of radiation with matter viz. absorption, emission and scattering are explained in the following subsections.

1.4.1 Absorption

At a given temperature different species (atoms and molecules) are distributed amongst the allowed energy levels in accordance with the **Boltzmann distribution**. According to the Boltzmann statistical distribution, the population of the ground state i.e., the number of species in the ground state is highest and it keeps on decreasing as we go to higher energy levels. The population of any excited state relative to that of the ground state is given by the following formula.

$$\frac{N_i}{N_0} = e^{-\frac{\Delta E}{kT}}$$

where N_i and N_0 are the populations of the i^{th} level and the ground state respectively; ΔE is the difference in the energies of the ground and excited state, k is called the **Boltzmann constant** and T is the absolute temperature. Let us calculate the population of an energy level, having energy of 2 kJ mol^{-1} relative to the energy at ground state at 300 K.

$$\Delta E = E_f - E_i = \frac{2 \times 10^3 \,\text{J mol}^{-1}}{6.022 \times 10^{23}\,\text{mol}^{-1}} = 3.32 \times 10^{-21}\ \text{J}$$

$$\frac{N_i}{N_0} = e^{-\frac{\Delta E}{kT}} = e^{-\frac{3.32 \times 10^{-21}\,\text{J}}{1.38 \times 10^{-23}\,\text{JK}^{-1} \times 300\,\text{K}}} = e^{-0.802} = 0.4484$$

This implies that for every 10000 species at the ground state there are 4484 species at the level that has energy of 2 kJ mol^{-1} relative to it.

Boltzmann constant is gas constant per molecule and can be obtained by dividing the gas constant with the Avagadro's number; $k = R/N_A$; its value is 1.38×10^{-23} J K^{-1}.

Let us see what happens when a polychromatic radiation is made to impinge upon a sample containing atoms or molecules. One simple possibility is that it gets transmitted unaffected through the sample. The other possibility is the radiation coming out of the sample is devoid of the certain frequencies. In the latter case the missing frequencies are said to be absorbed by the sample. Only those photons are absorbed whose energy matches with the difference in energy of any two energy states of the sample provided the transition amongst these levels is allowed. Fig. 1.11 (a) shows that the polychromatic radiation from a source when dispersed with a prism or any suitable device, it gives a **continuous spectrum** of EM radiation. When the radiation is passed through a sample before being dispersed as in Fig. 1.11 (b), certain frequencies are found to be missing. These are absorbed by the sample. The spectrum so obtained is called an **absorption spectrum**.

Whether a transition is allowed or not, is governed by certain rules called selection rules

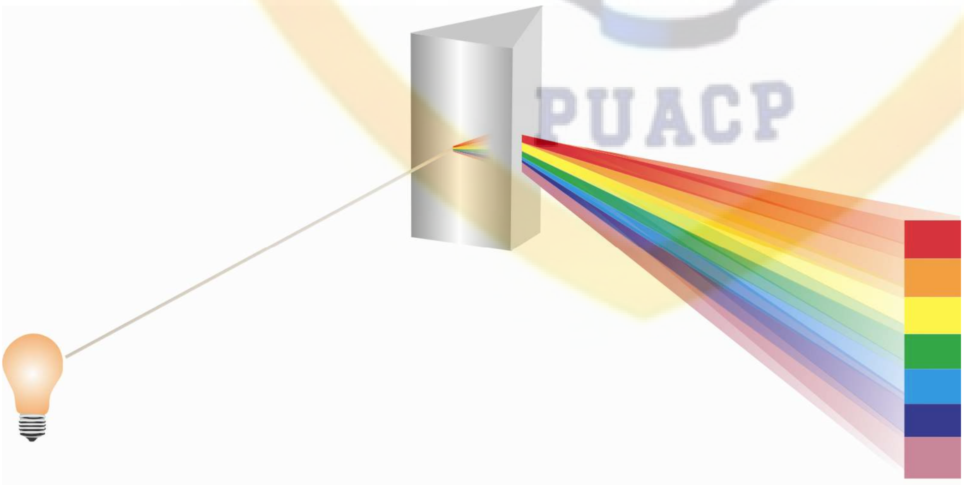


Fig. 1.11 (a): Dispersion of a polychromatic radiation through a prism to give a continuous spectrum

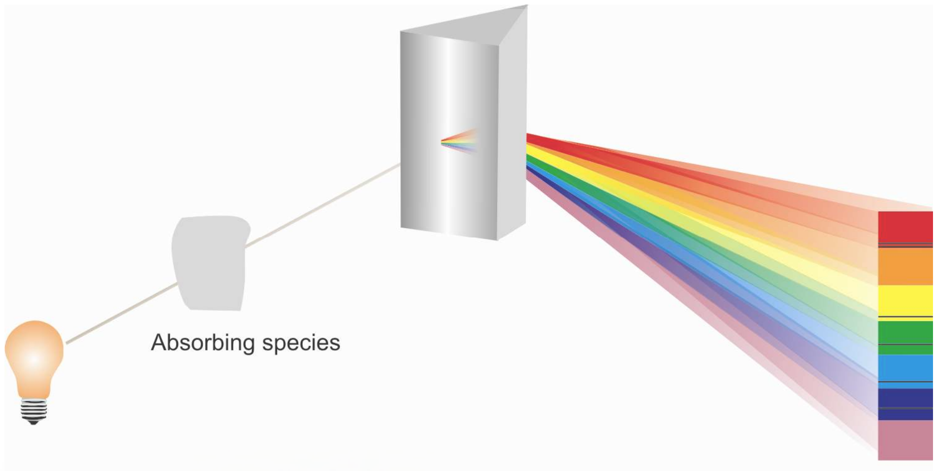


Fig. 1.11 (b): Schematic representation of the set up for getting an absorption spectrum

As the difference in the energy levels is unique for each species, knowledge of the frequencies absorbed by a given species may provide information about the species being studied. The absorption characteristics of a given species are described in terms of the absorption spectrum, which is a plot of the extent of absorption by the species as a function of wavelength or frequency or wave number of the radiation absorbed. The nature of spectrum obtained depends on the nature of the absorbing species. Let us take up the absorption of radiation by atomic and molecular species.

Atomic Absorption

Absorption in the UV and visible regions leads to the transition of outermost electrons while X-ray absorption involves the transition of electrons closest to the nuclei of

Atoms in the gaseous state can absorb ultraviolet or visible radiation or x-rays and result in a spectrum consisting of a number of very sharp absorption lines, characteristic of the atomic species. This is called a **line spectrum**. Let us consider the simple case of absorption by gaseous sodium atom. It exhibits two sharp absorption peaks in the yellow region of visible spectrum (589 nm and 589.6 nm) as shown in Fig.1.12, consequent on excitation of 3s electron to two of the 3p states. Absorption in the UV region on the other hand results in signals at 330 nm and 285 nm due to the excitation of 3*s* election to 4*p* and 5*p* orbital respectively.

The atomic absorption spectrum is composed of a series of sharp and well defined lines characteristic of each element.

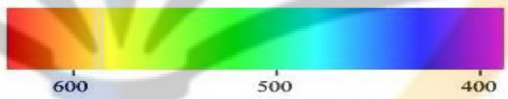


Fig. 1.12: Absorption spectrum of sodium vapours in the visible range

Atomic absorption spectra of alkali and alkaline earth metals are simpler. On the other hand the transition elements give rise to multitudes of lines, yet each element has its own characteristic absorption lines and is useful for qualitative and quantitative studies. You would learn about atomic absorption spectroscopy in detail in Unit 7 of this course.

Molecular Absorption

Each electronic energy level is associated with several vibrational levels and each of the vibrational level is associated with several of the rotational energy levels, possible energy levels are much more for molecules as compared to atoms.

Absorption by molecules is more complex than by atoms, as there are a large number of energy states possible in case of molecules. You would recall that in case of molecules the vibration and rotation motion is also quantised in addition to electronic motion. A molecular energy level in fact has three components and its energy can be given by the following expression.

$$E = E_{electronic} + E_{vibrational} + E_{rotational}$$

Accordingly, three types of quantised transitions occur on excitation with radiations in UV-VIS, IR and microwave regions respectively. The ultraviolet and visible radiations cause transition of electrons from the low energy electronic states to the higher energy states. On the other hand, IR and microwave radiations cause transitions amongst the vibrational and rotational energy levels, respectively.

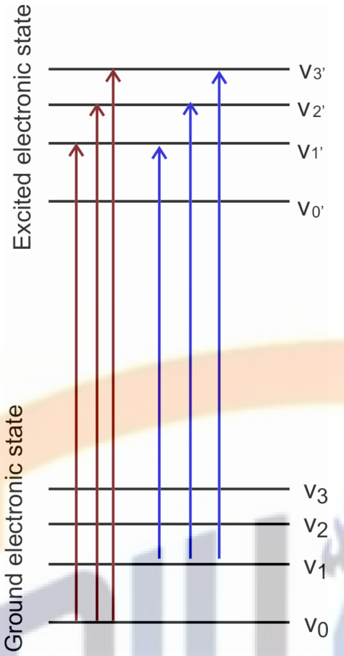


Fig. 1.13: Simplified energy level diagram showing the reason for observing band spectrum in the molecules

Since each electronic energy level is associated with several vibrational levels and each of the vibrational level is associated with several of the rotational energy levels, the transitions caused by UV-VIS radiation have associated vibrational and rotational transitions. Accordingly the molecular spectra are quite complex and consist of a large number of transitions. For this reason, electronic absorption bands for molecules are usually broad and the spectrum is called **band spectrum**. Fig.1.13 gives a simplified energy level diagram for a molecule showing the reason for observing band spectrum. Similarly the transitions caused by radiations in the IR region have an associated rotational component. Sample IR and UV spectra are given in Fig. 1.14.

Molecular spectrum generally consists of a series of closely spaced absorption lines and appears as a band.

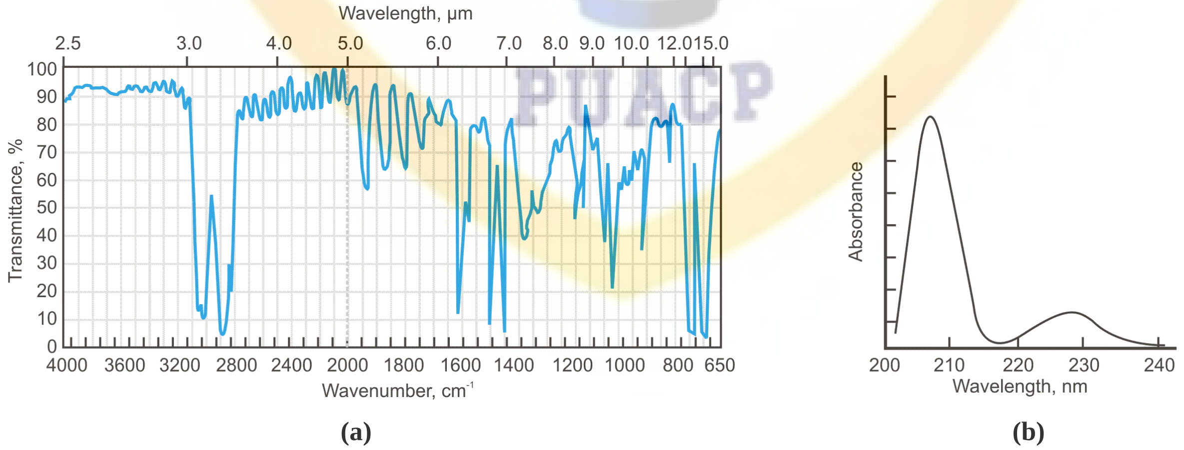


Fig. 1.14: Sample a) IR spectrum and b) UV spectrum

Sometimes the sample does not absorb radiation of a given type under ordinary conditions but on placing the sample in a magnetic field it does. This phenomenon is of immense analytical applications and is the origin of probably the most exploited molecular structure determination technique i.e., nuclear magnetic resonance (NMR). Another important technique of ESR also need magnetic field. Let us learn about the magnetic field induced absorption.

Magnetic Field Induced Absorption

The elementary particles such as electrons and nucleons are associated with magnetic properties. When subjected to external strong magnetic field, the interactions between the internal and external magnetic fields give rise to additional quantised energy levels. The difference in the energies of these levels is small and transitions are brought about by absorption of the radiation of longer wavelength ranges. The transitions amongst the energy levels generated due to the interaction of the nuclear magnetic moment with the applied magnetic field are studied using radio-waves in the range of 30 to 500 MHz and give rise to **Nuclear Magnetic Resonance (NMR) spectroscopy**. The energy separation of the levels created by interaction between the electron magnetic moment with the applied external field is even smaller. These are studied under **Electron Spin Resonance (ESR) Spectroscopy** by using microwaves of a frequency of about 9500 MHz.

The intensity or radiant power (P) of a line or band is directly proportional to the number of excited atoms or molecules present in the system. This provides a method for quantitative determination of the analyte.

You may be wondering that what happens to the absorbing species after it has absorbed the photon. Where does this extra energy go? Does it bring in some kind of a change in the structure of the species? In other words, what is the fate of the absorbed radiation?

Fate of the Absorbed Radiation

As a consequence of the absorption, the energy of the photon is transferred to the absorbing species and it acquires an excited state.

$$M + h\nu \longrightarrow M^* \quad \text{(Excitation)}$$

The concentration of the excited species so obtained is quite small and its life time is very short. The excited species generally loses the extra energy to the other atoms or molecules, present in the medium and reverts back to the ground state. This process is called **non-radiative relaxation** and occurs in a short period of time (10^{-6} to 10^{-9} s). The excess energy is transferred in a series of small steps to the neighboring species as their kinetic energy and is manifested in the form of heat. As a consequence of this, the temperature of the system increases slightly.

$$M^* \longrightarrow M + \text{heat} \quad \text{(Relaxation)}$$

In some cases the relaxation process is accompanied by an emission of radiation and is referred to as **radiative relaxation**. Let us learn about different types of radiative relaxation mechanisms and the spectra which arises due to these.

SAQ 5

Calculate the population of an energy level having energy of 10 kJ relative to the ground state at 327^{o}C.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

1.4.2 Emission

During the festive season or at the times of celebrations, you must have enjoyed the beautiful display of colours by fireworks in the sky. This splendid show is a result of relaxation of excited species from higher energy to the ground level releasing the excess energy in the form of light and heat. The colours we see are electromagnetic radiations in the visible range. The excitation of the species can be brought about by a number of ways, such as, absorption of electromagnetic radiation, bombardment with electrons or other elementary particles, exposure to high potential alternating current, spark, arc or a flame. The radiation emitted by an excited species is characterised in terms of an **emission spectrum**. Like an absorption spectrum, the emission spectra may be a **band spectrum** or a **line spectrum**. Fig.1 .15 shows a schematic emission spectrum.

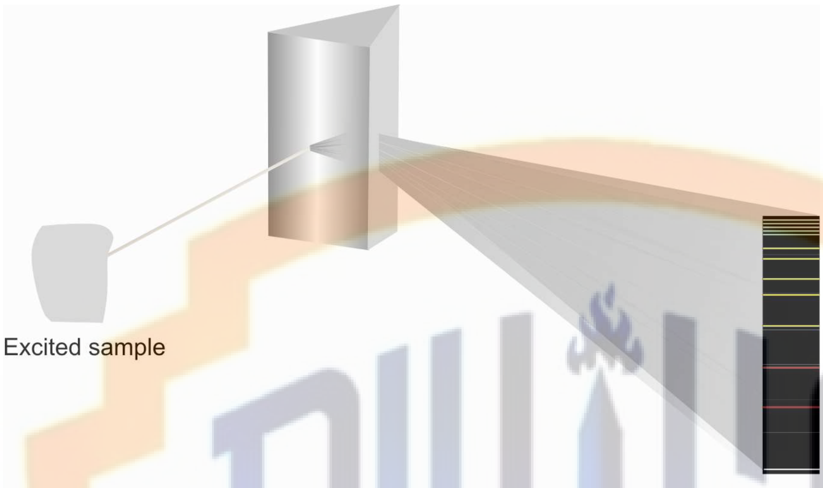


Fig. 1.15: A schematic emission spectrum

The line spectrum is a result of relaxation of atoms or ions and generally consists of a series of well defined lines characteristic of the species involved. On the other hand, the band spectra, which consist of several groups of lines that are closely spaced and not resolved, are given by excited molecules or radicals. In case of incandescent solids we get continuous spectra wherein the line spectra and band spectra are superimposed and appear as a continuum. Let us learn about these types of spectra.

Line Spectra

Line spectra are obtained from individual atoms that are well separated in a gaseous sample of an element. The atomised sample of the element is subjected to a flame, plasma, an electric arc or spark whereby the constituent atoms are excited to higher orbitals. For example, in case of sodium atom, single outer electron in the 3*s* orbital can be excited to higher orbitals. The excited state being unstable and short lived, returns to the ground state by the emission of a photon. The emission from the first excited state (3*p*) of sodium is responsible for the yellow colour emission at 589.6 nm of the flame when sodium salts are introduced into it. Other excited states corresponding to 4*p* and 5*p* levels give emissions at 330.6 nm and 285.3 nm respectively in the ultraviolet region. The flame emission and atomic emission spectroscopic techniques are based on this phenomenon and are useful for qualitative and quantitative measurement of atoms. You would learn about these in the third block of the course.

Band Spectra

Band spectra arise from gaseous radicals or small molecules and consist of a series of closely spaced lines that arise from the radiative relaxation of the excited molecule to any of the available vibrational levels in the ground state Fig. 1.16 illustrates the origin of band spectrum of a molecule. You may note here that the molecule in the vibrational ground state of the excited electronic state may relax to any of the five vibrational levels of the ground state shown here. Accordingly the emission spectrum would consist of five closely spaced lines in the example given here. In complex molecules, the emission band consists of many more lines that are much more closely spaced and appear as a band.

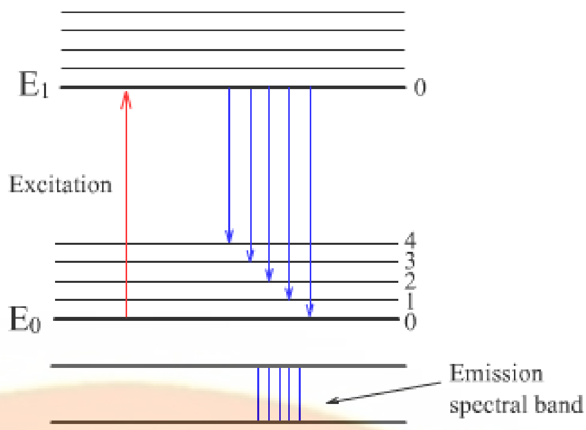


Fig. 1.16: Emission band spectrum of a molecule

Continuous Spectra

As mentioned earlier, the continuous spectra are caused by solids when heated. It is characteristic of the temperature of the emitting surface rather than the bulk of the material. These types of spectra are produced by condensed solids giving rise to innumerable atomic and molecular oscillations. Heated solids are used as radiation sources of analytical instruments involving IR, visible and longer wavelength UV radiations.

Fluorescence and Phosphorescence

In the emission spectra of atoms and molecules discussed above the energy of the emitted radiation is same as that used for excitation. In some atomic and molecular systems the emitted radiation is of different frequency than that of the excitation radiation. These are either due to **fluorescence or phosphorescence**. In such emissions, the excited atom or molecule does not emit radiation directly from the excited state. Instead the excited species relaxes down to excited state of lower energy through non-radiative processes and then from there it comes to the ground state accompanied by the emission of radiation. You would learn these analytically important phenomena in details in Units 5 and 6 of this course.

1.4.3 Raman Scattering

You have read in the subsection 1.3.5 that, when a radiation interacts with matter a part of it gets scattered. If a monochromatic radiation is used then the scattered radiation is of the same frequency as the incident frequency. This is called **Rayleigh scattering.** However, it has been found that in certain cases the radiation may interact with matter in such a way that it involves certain amount of energy exchange. Consequently the scattered radiation has frequencies greater or smaller than that of the incident radiation. This is called **Raman scattering** and is an important analytical tool. You would learn in details about Raman spectroscopy, which is based on this type of scattering, in Unit 4 of this course.

SAQ 6

What is the difference between the radiative and non radiative relaxations?

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

We have so far learnt that the radiation can interact in different ways with the matter and cause transitions amongst different types of quantised energy levels. Table 1.2 summarises different types of spectroscopies, the regions of the wavelength responsible for them and the nature of quantum transitions involved in them. We shall take up different spectroscopic methods in the forthcoming units.

Table 1.2: Spectroscopic methods based on wavelength range and the type of quantum transitions involved

Type of spectroscopic method	Wavelength range	Type of quantum transition
Mossbauer spectroscopy (γ-ray spectroscopy)	0.005 – 1.4 Å	Nuclear transition (change of nuclear configuration)
X-ray (Diffraction, Absorption, Emission, Fluorescence)	0.1 - 100 Å	Inner electron transition (change of electron distribution)
Vacuum UV absorption	10 - 180 nm	Bonding electrons transition (change of electron distribution)
UV and Visible (Absorption, Emission, Fluorescence)	180 - 780 nm	Bonding electrons transition (change of electron distribution)
Infrared (Absorption) and Raman (Scattering)	0.78 - 300 nm	Vibration/Rotation of molecules (change of configuration)
Microwave absorption	0.75 - 3.75 nm	Rotation of molecules. (change of orientation)
Nuclear Magnetic Resonance (NMR)	0.6 - 10 m	Spin of nuclei in a magnetic field (change of nuclear spin)
Electron Spin Resonance (ESR)	3 cm	Spin of electrons in a magnetic field (change of electron spin)

We will begin with the UV-visible spectroscopy in the next unit.

1.5 SUMMARY

Electromagnetic radiation is the radiant energy which is transmitted through space at enormous velocities and does not require a medium for transmission and readily pass through vacuum. According to wave mechanical model it can be visualised as oscillatory electric and magnetic fields travelling in the planes perpendicular to each other and also to the direction of propagation. These waves are characterised by a number of parameters like, amplitude, wavelength, frequency, wavenumber, velocity, energy etc. On the other hand according to the quantum or particle model, the radiant energy is considered as stream of discrete particles or packets of energy called as quanta, whose energy is proportional to its frequency.

The wave nature of electromagnetic radiation is manifested in terms of a number of phenomena. Interference refers to the interaction of two waves as they are travelling. The result of such an interaction depends on whether they interact constructively or destructively. Diffraction is a consequence of interference and refers to the phenomenon of bending of a wave round the corners of sharp barriers or through narrow openings.

When EM radiation passes through a transparent medium, its velocity is reduced due to the interaction of radiation with the constituents of matter. The extent of interaction is expressed in terms of the refractive index of the medium. The variation of refractive index of a substance with wavelength of the radiation is called as dispersion.

When a radiation passes from a given medium to another medium it bends towards or away from the normal to the interface. This is called refraction and is due to the difference in the velocities of the radiation in the two media. A fraction of the radiation however, bounces back at an angle equal to the angle of incidence of the radiation and is termed as reflection.

Ordinary radiation is unpolarised radiation and consists of a bundle of electromagnetic waves having vibrations among an infinite series of planes perpendicular to the direction of propagation. On passing ordinary light through a polariser we can get polarised light having vibrations in a single plane.

The interaction of radiation with matter causes transitions among the quantised energy levels of the interacting species. When a radiation falls on the matter it may either be absorbed or it may excite the interacting species which then may emit a radiation or the radiation undergoes scattering as a consequence of interaction.

The absorption or emission spectra of atomic species consist of a series of discrete lines and is called a line spectrum. On the other hand the molecular spectra are quite complex and the resulting spectra are usually broad and the spectrum is called band spectrum.

The radiations in the different regions of the EM spectrum have different energies. On interacting with the matter these cause transitions amongst different types of quantised energy levels. This leads to different types of spectroscopies.

1.6 TERMINAL QUESTIONS

1. Name the phenomena which could not be explained on the basis of wave mechanical model of EM radiation.
2. What is an electromagnetic radiation? List any three characteristics of electromagnetic radiation.
3. Explain the following in brief.
   a) Constructive interference
   b) Destructive interference
   c) Reflection of light
   d) Refraction of light
4. Express the wavelength 3500 Å in terms of micrometres and nanometres.
5. Calculate the frequency and wave number for the EM radiation having a wavelength of 10 m.
6. Compute and compare the energies of the photon corresponding to the FM radio frequencies of your region.
7. Atomic spectrum consists of sharp lines whereas molecular spectrum contains broad bands. Explain.
8. Name the type of transitions involved in the UV-Visible, IR, and Microwave spectroscopic techniques?

1.7 ANSWERS

Self Assessment Questions

1. The electromagnetic radiations do not need a medium for transmission; these can transmit through vacuum. However, for sound waves a medium is necessary for transmission.

2. We know that $E = h\nu = \frac{hc}{\lambda}$

   $h = 6.626 \times 10^{-34}$ J s

   $c = 3.0 \times 10^{8}$ m s^{-1}

   $\lambda = 535 \times 10^{-9}$ m

   Substituting the values, we get

   $$E = \frac{6.626\times10^{-34}\,\text{J s}\times3.0\times10^{8}\,\text{m s}^{-1}}{5.35\times10^{-7}\,\text{m}} = 3.72\times10^{-19}\,\text{J}$$

3. The phenomenon of bending of a wave round the corners of sharp barriers or through narrow openings is called *diffraction*.

   The extent of diffraction varies inversely with the width of the slit and is observable only when the size of the slit is comparable to that of the wavelength of the light.

4. Plane polarised light is that EM radiation in which the electrical (also magnetic) field oscillates in a single plane. These can be obtained by passing the unpolarised radiation through a polariser made up of calcite or quartz crystals.

5. According to Boltzmann distribution, $\frac{N_i}{N_0} = e^{-\frac{\Delta E}{kT}}$

   Given: ΔE = 10 kJ;   T= 327^{o} C = 327 + 273 = 600 K

   We are given the value of ΔE per mole; first we calculate it per molecule by dividing it with Avogadro's constant

   $$\Delta E = E_{\text{f}} - E_{\text{i}} = \frac{10\times10^{3}\,\text{J mol}^{-1}}{6.022\times10^{23}\,\text{mol}^{-1}} = 1.66\times10^{-20}\,\text{J}$$

   Now substituting it in the Boltzmann formula, we get

   $$\frac{N_i}{N_0} = e^{-\frac{\Delta E}{kT}} = e^{-\frac{1.66\times10^{-20}\,J}{1.38\times10^{-23}\,JK^{-1}\times300\,K}} = e^{-4.10} = 0.0166$$

6. These relaxations refer to the mechanisms by which an excited species relaxes to the ground state. The radiative relaxation is accompanied by the emission of a photon whereas in non-radiative relaxation the energy is emitted as heat.

Terminal Questions

1. The wave mechanical model of electromagnetic radiations could not explain the phenomenon of absorption, emission and scattering of radiant energy.

2. Electromagnetic radiation is a kind energy which is transmitted through space in the form of electric and magnetic fields. It travels with the speed of light and does not need any medium to travel.

   The different characteristics of electromagnetic radiation are

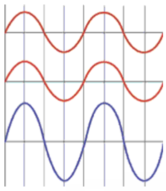
   - Amplitude
   - Wavelength
   - Frequency

- Wave number
- Velocity

3. The terms can be explained as follows:

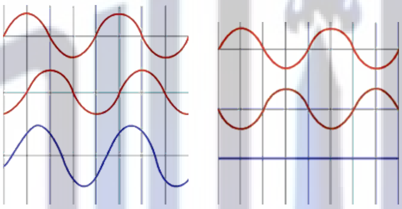
Constructive Interference

When two waves travelling together are in phase then these reinforce each other. The amplitude of the resultant wave is more than that of any of the two waves. In fact it is the sum of the amplitudes of the two waves.



Destructive Interference

When two waves travelling together are out of phase then these cancel each other. The amplitude of the resultant wave is equal to the sum of the amplitudes of the two waves. In case the waves are completely out of phase the waves are destroyed completely.



Reflection of Light

When a radiation travelling in a given medium is incident on a medium of different refractive index at an angle; then a fraction of the radiation bounces back at an angle equal to the angle of incidence of the radiation. This is called reflection of light.

Refraction of Light

The change in the direction of a beam of light when it falls on the interface of two transparent media of different densities is called refraction.

4. We know that $1Å = 1\times10^{-10}$ m

So 3500 Å $= 3500 \times 10^{-10}$ m

We can write it as $= 0.35 \times 10^{4} \times 10^{-10}$ m $= 0.35 \times 10^{-6}$ m $= 0.35$ μm

Similarly, we can write

3500 Å $= 350 \times 10 \times 10^{-10}$ m $= 350 \times 10^{-9}$ m $= 350$ nm

5. We know that $v = \dfrac{c}{\lambda}$ and $c = 3.0 \times 1010$ m s^{-1}

Substituting the values, we get

$$v = \frac{3.0\times10^{10}\,\text{m}\,\text{s}^{-1}}{10\ \text{m}} = 3.0\times10^{9}\ \text{s}^{-1} = 3.0 \times 10^{9}\,\text{Hz}.$$

Further, as wavenumber and wavelength are related as, $\overline{v} = \dfrac{1}{\lambda}$

Substituting the values of the wavelength we get, wave number

$$\bar{v} = \frac{1}{10\,\mathrm{m}} = 0.1\,\mathrm{m}^{-1}$$

6. Energy and frequency are related as $E = hv$

   The frequencies of the FM radio stations range from about 90 to 108 MHz; let us take the frequencies of two FM stations as v_1 and v_2 MHz, respectively

   The energies of the photons corresponding to the radio frequencies of the two stations would be hv_1 and hv_2 respectively and can be calculated by substituting the values of *h* and the frequency.

   The ratios of the energies can be calculated as $\frac{E_2}{E_1} = \frac{hv_2}{hv_1} = \frac{v_2}{v_1}$

   You may substitute the values corresponding to the FM radio frequencies of your region and compute the ratio.

7. In case of atomic spectrum the transitions occur from one electronic energy level to the other and result in sharp lines.

   On the other hand, in case of molecules the vibration and rotation motion is also quantised, and each electronic energy level is associated with several vibrational levels and each of the vibrational level is associated with several of the rotational energy levels.

   Thus, the electronic transitions in the molecules have associated vibrational and rotational transitions and radiations over a range of wavelengths are absorbed. Therefore, the molecular absorption spectra have broad bands.

8. UV-Visible : electronic
   IR : vibrational
   Microwave : rotational