FYUGP BSc. FOOD TECHNOLOGY (Hons.)

OPTICS & SPECTROSCOPY

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Module	**Unit**	**Content**	**Hrs (45 +30)**	**Marks (70)**
I		**Introduction**	**8**	**15**
	1	Properties of light, Laws of reflection, laws of refraction	3	
	2	Refractive index, Optical path	2	
		Electromagnetic spectrum and visible light	1	
	3	Photons, Dual nature of light	2	
	Sections 1.5 – 1.12, Book 1			
II		**Interference and Polarization**	**19**	**25**
	4	Interference, Young double slit experiment	2	
	5	Coherence and conditions for interference	2	
	6	Interference in thin parallel films	3	
	7	Interference in wedge shaped film, Angle of wedge and thickness of spacer,	3	
	8	Colour of thin films		
	9	Polarization: Types of polarization	1	
	10	Brewster's law	1	
	11	Production of plane polarized light	2	

	12	Polarizer and analyser, Malu's law	2	
	13	Double refraction	1	
	14	Optical activity and specific rotation	2	
	Section 14.4 – 14.7,15.2, 15.5, 20.1, 20.2, 20.5, 20.6, 20.8 - 20.11, 20.27 - 20.29 , Book 1			
III	**Introduction to Spectroscopy**		**7**	**15**
	15	Electromagnetic spectrum and Quantization of energy	2	
	16	Types of molecular energies and spectroscopic methods	2	
	17	Spectral line width	1	
	18	Absorption and emission of radiation, Einstein coefficient (excluding derivation)	2	
	Sections : 1.1 - 1.6, Book 2			
IV	**Spectroscopic Methods of sample analysis**		**11**	**15**
	19	Microwave spectroscopy	3	
	20	Infrared Spectroscopy (vibration spectra only)	2	
	21	Electronic spectroscopy	3	
	22	Raman spectroscopy: Introduction, Quantum theory of Raman scattering, Rotational Raman spectra of linear molecules	3	
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which then emit light. Many living organisms such as fireflies, fish and bacteria emit light due to chemical reactions. Such glow is called **chemiluminescence**. The cold light emitted by tube lights is a result of **photoluminescence**. The internal surface of the tube light is coated with a phosphor material, which under the action of UV light emits visible light. The TV screens and computer terminal screens glow because of **cathodoluminescence,** which occurs due to bombardment of the screen by high-energy electrons.

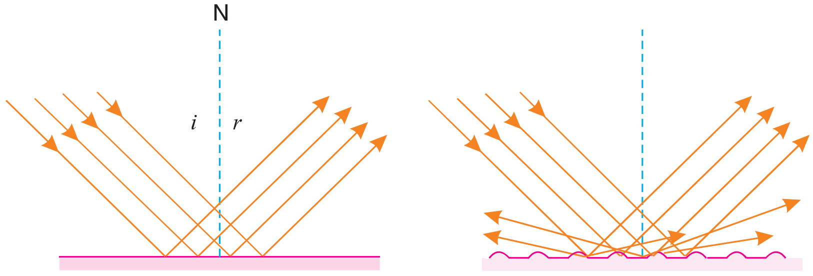
1.5. PROPERTIES OF LIGHT

Reflection, refraction, dispersion and velocity are the important properties of light. We briefly discuss about them here.

1.5.1. REFLECTION OF LIGHT

When light travelling in a medium encounters a boundary leading to a second medium, part of the incident light is returned to the first medium from which it came. This phenomenon is called *reflection*. Reflection of light from a smooth surface is called *regular* or *specular reflection.*

Computer screen glows because of cathodoluminescence, which occurs due to bombardment of the screen by high energy electrons.



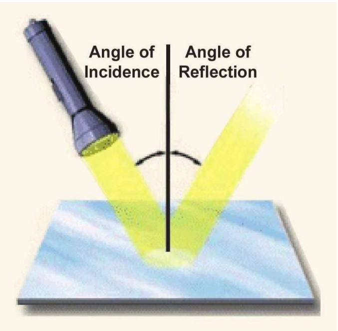
(a) (b)

Fig. 1.5

Reflection from a rough surface is known as *diffuse reflection*. It is largely by diffuse reflection that we see non-luminous objects around us. The difference between diffuse and specular reflection is a matter of surface roughness. In the study of optics, the term reflection is used to mean specular reflection.

1.5.1.1. Laws of reflection

In Fig. 1.6 the light ray AB, passing through air, is incident on a plane mirror and is reflected via the path BC. The point (B) where the light intersects the surface of the mirror is the



Laws of reflection.

point of incidence. A line drawn at B, perpendicular to the mirror, is the *surface normal*. The angle subtended by the surface normal and the incident ray is the *angle of incidence, i.* The angle subtended by the surface normal and the reflected ray is the *angle of reflection, r.* For some reason, it is customary to measure the angles from the surface normal toward the ray.

First Law: The incident ray, the reflected ray and the normal at the point of incidence are in the same plane. This plane is called the *plane of incidence.*

Second Law: The angle of reflection is equal to the angle of incidence. Thus, in Fig. 1.6,

$$i = r \tag{1.1}$$

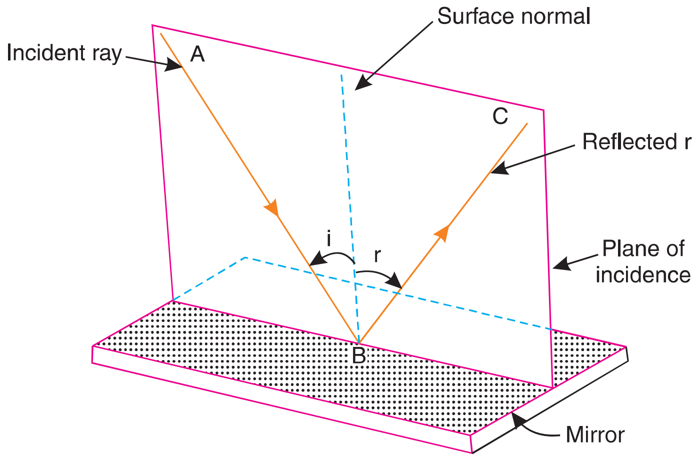
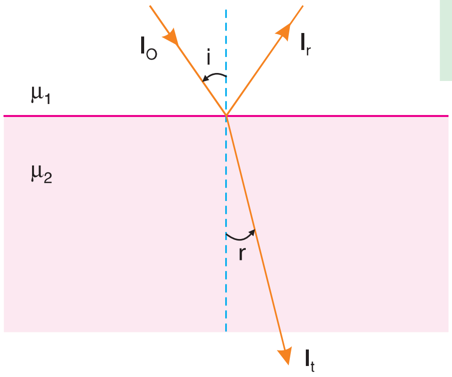


Fig. 1.6

Note — The laws of reflection are obeyed in specular reflection. They do not hold in case of irregular or diffuse reflection.

1.5.2. REFRACTION OF LIGHT

When a ray of light travelling through a transparent medium encounters a boundary leading into another transparent medium, part of the ray is reflected and part of it enters the second medium. The ray that enters the second medium is bent at the boundary and is said to be *refracted*. Thus, refraction means that the light ray follows in the second medium a direction different from its direction in the first medium. The angle '*r*' subtended by the normal and the refracted ray is the *angle of refraction*. This angle is also measured from the surface normal toward the ray.



Phenomenon of refraction—A ray obliquely incident on air-glass interface bends toward the normal in glass.

Fig. 1.7

1.5.2.1. Laws of refraction

First Law: The incident ray, the refracted ray and the normal at the point of incidence lie in the same plane.

Second Law: The ratio of the sine of the angle of incidence to the sine of the angle of refraction for any two given media is constant.

$$\frac{\sin i}{\sin r} = \mu \qquad \ldots (1.2)$$

where μ is called the *refractive index* of the medium.

Note — The laws of reflection and refraction relate only to the directions of the corresponding rays but do not say anything about the intensities of the reflected and refracted rays. These depend on the angle of incidence, the two indexes of refraction, and the polarization of the incident ray. ◀

Note — The laws of reflection and refraction are obtained as experimental results. They can also be derived from Maxwell's equations. The superiority of this treatment is that it enables us to predict the amplitude, intensity, phase, and polarization states of the reflected and refracted rays.

1.6. REFRACTIVE INDEX

The refractive index of a medium is defined as the ratio of velocity of light in a vacuum to the velocity of light in the medium. Refractive index defined as above is called as *absolute refractive index*. Thus,

$$\mu = \frac{c}{\upsilon} \qquad \ldots (1.3)$$

The refractive index is sometimes referred to as *optical density*. A medium with a relatively high refractive index is said to have a high optical density, while one with a lower index is said to have a low optical density.

The relative refractive index μ_{21} of a second medium relative to a first one is defined as the ratio of speeds of light υ_1 and υ_2 in the first and second media respectively.

The numerical value of refractive index is characteristic of the two media, but it also depends on wavelength. Hence, a refractive index is specified definitely only when wavelength is stated. Unless otherwise mentioned, refractive index is usually given for yellow light. The absolute refractive index for air under standard conditions is 1.0002918 for light having wavelength of the D-line of sodium (5893 Å). Since the refractive index for air is nearly equal to unity, it follows that for a solid or a liquid the absolute refractive index and the refractive index relative to air differ only slightly. Therefore, distinction is not made between them.

Note — The refractive index depends not only on the substance but also on the wavelength of the light. The dependence on wavelength is called **dispersion.** ◀

1.7. OPTICAL PATH

The shortest distance, L between two points A and B is called the *geometric path*. The length of geometric path is independent of the medium that surrounds the path AB. When a light ray travels from the point A to point B, it travels with the velocity 'c' if the medium is air and with a lesser velocity υ if the medium is other than air. Therefore, the light ray takes more time to go from A to B located in a medium.

From equation (1.3)

$$\mu = \frac{c}{\upsilon} = \frac{AB/t}{AB/T} = \frac{T}{t}$$

where t and T are the time taken by the light ray in air and in a medium respectively.

$$\therefore \qquad T = \mu t \qquad \ldots (1.4)$$

The above relation means that a light ray takes μ times more time to cover the distance AB in a medium. To take into account the delay, we use another distance called the *optical length*. If a ray of light travels a distance L in a medium of refractive index μ in a certain interval of time, then it would travel a greater distance Δ in air during the same interval of time. Therefore,

$$\frac{\Delta}{L} = \frac{ct}{\upsilon t} = \mu$$

or $$\Delta = \mu L \qquad \text{... (1.5)}$$

i.e., Optical path length = (Refractive index)(Geometric path length)

Thus, ***the optical path length is defined as the product of refractive index and the geometric path length.***

Note that if a ray travels a distance l in a medium of refractive index μ, the optical path length is equal to μl. In a given time light travels the same optical path length in different media. Suppose light travels a distance l_1 in a medium of refractive index μ_1 and a distance l_2 in a medium of refractive index μ_2 in time t. Then

$$\mu_1 l_1 = \mu_2 l_2$$

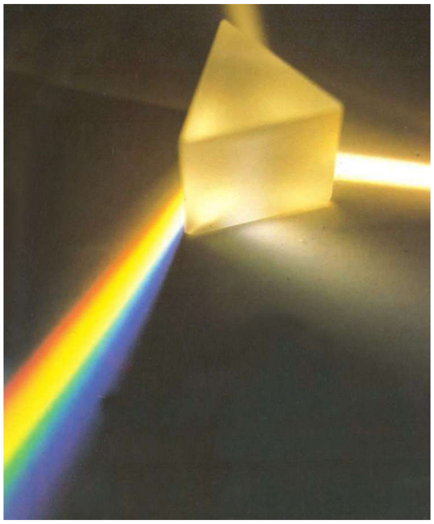
1.8. DISPERSION

The refractive index is a function of wavelength. Generally, it decreases as the wavelength increases. Consequently, light passing through a material medium will be separated according to wavelength. This is known as chromatic dispersion.

With the light at normal incidence, blue light would merely lag behind the red light. With the light incident obliquely, the colors become separated in space, both surfaces refracting blue more than red. With a prism the separation is even more pronounced.

Note that dispersion is not proportional to refraction. Refraction and dispersion bear no simple relationship to one another. Some glasses have a high index of refraction and little dispersion; others have just the opposite.

When a ray of white light falls on a glass prism, it splits up into different colours (see Fig.1.8). This display of colours is known as ***spectrum*** of the source of light. This separation of a composite beam into its constituent colours is called *dispersion* and the medium which produces dispersion is known as a *dispersive medium.* When the colours travel through a refracting medium, their velocities are different. Hence the refractive index of the material is different. Out of the seven colours formed by the white light, violet colour suffers greater deviation than red light.



When white light passes through a glass prism, a rainbow of colours emerges.

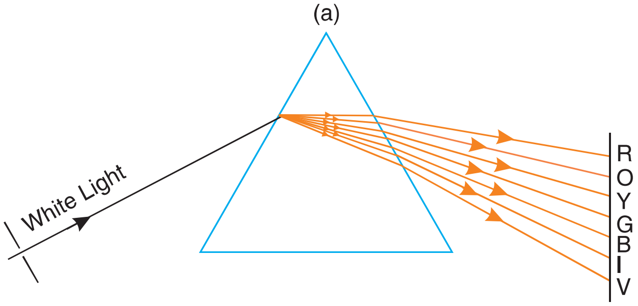


Fig. 1.8

1.9. THE VELOCITY OF LIGHT

The first attempt to measure the velocity of light was made by Galileo in 1667. Two observers were stationed on the tops of two hills about 1.5 km apart. Each observer was provided with one lamp and the experiment was carried out at night. One observer, say A, uncovered his lamp thereby sending a short flash of light to the other observer, say B and noted the instant at which he did so. The other observer B uncovered his lamp as soon as he saw the flash from B's lamp. The interval between these two instants of time noted by A is obviously equal to the time taken by the light to travel the distance AB twice. However, the interval could not be found between the two instants. From this Galileo concluded that velocity of light, if finite, was extremely large.

Eight years later, in 1675, the Danish astronomer, Roemer succeeded in measuring the velocity of light. The satellites of planet Jupiter show eclipses once in every 7 days. He noticed that the time interval between two consecutive eclipses of one of the satellite of Jupiter varied with the relative positions of the earth. This time interval increased as the earth moved away from Jupiter and decreased as it moved toward Jupiter. Roemer correctly attributed this variation to the finite velocity of light and found that light required about 22 minutes to travel a distance equal to the diameter of earth's orbit. The diameter of the earth's orbit was known to be 2.87×10^{11} m.

$$\therefore \qquad c = \frac{2 \times 10^{11}\,\text{m}}{22 \times 60\,\text{s}} = 2.3 \times 10^{8}\ \text{m/s}$$

This value is lower than the actual speed. Regardless of its accuracy it showed that the speed of light was not infinite, as many then believed, but was finite and measurable.

The first laboratory measurement of the speed of light was carried out in 1849 by the French physicist H.L.Fizeau. Later, many experimenters using different methods have measured c. The most precise determination gives a value

$$\therefore \qquad c = 2.997924 \times 10^{8}\ \text{m/s}.$$

which is usually simplified as

$$\mathbf{c = 3 \times 10^{8}\ m/s.} \qquad \ldots (1.7)$$

1.10. VISIBLE RANGE

The arrangement of the various electromagnetic waves in a continuous sequence of frequencies and wavelengths is called an **electromagnetic spectrum**. The spectrum includes waves covering a broad range of wavelengths (see Fig. 1.9). It is bounded at one end by the gigantic radio waves having wavelengths of a few kilometres and at the other end by γ- rays of tiny wavelengths of the order of 10^{-12}m. **Visible range** is that part of the spectrum constituted by waves, which can be detected by the human eye. It extends from the deepest violet to the deepest red. The limiting range of these waves depends in the individual properties of the eye and varies approximately in the interval λ = 4000Å to λ = 7800Å. The regions flanking the visible range are **infrared (IR)** on the longer wavelength side and **ultraviolet (UV)** on the shorter wavelength side. The IR region lies in the wavelength range 7.8×10^{-7}m to 10^{-3}m and the UV region lies between 4000Å to 10Å. The radiation in these three regions, namely visible, IR and UV, put together is called **optical radiation**. Table - 1 lists the wavelengths and the frequencies of each of the coloured region in the visible region.

The sensitivity of the human eye is a function of wavelength. It has peak **sensitivity** at a wavelength of about 5500 Å corresponding to yellow-green.

The wavelengths of light waves are shorter and therefore smaller units are used to express them. They are usually expressed in angstrom or nanometre or micrometre units.

TABLE-1

Colour	*Vacuum wavelength* (*Å*)	*Frequency* (10^{14}*Hertz*)
Red	7800 - 6200	3.84 - 4.82
Orange	6220 - 5970	4.82 - 5.03
Yellow	5970 - 5770	5.03 - 5.20
Green	5770 - 4920	5.20 - 6.10
Blue	4920 - 4550	6.10 - 6.59
Violet	4550 - 3990	6.59 - 7.69

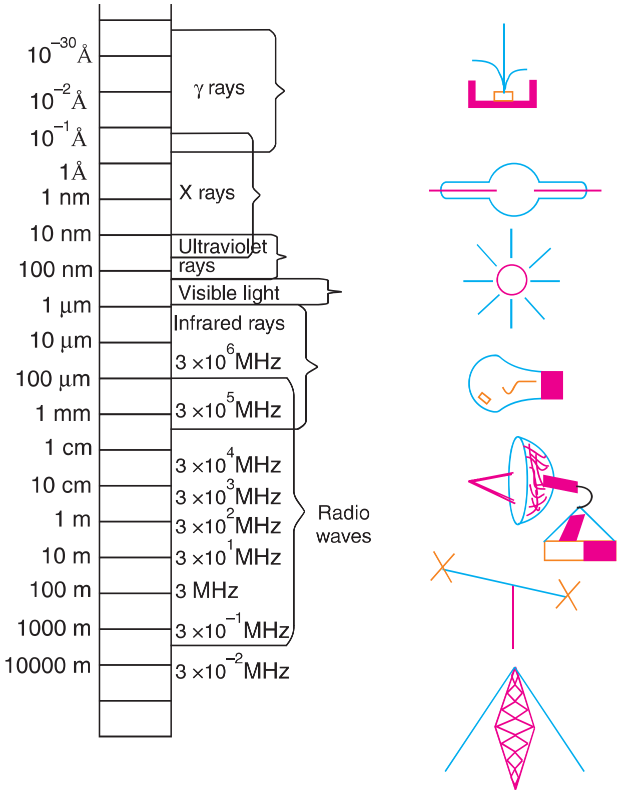


Fig. 1.9

1 angstrom (Å) $= 10^{-10}$ m = 0.1 nm

1 nanometre (nm) $= 10^{-9}$ m = 10 Å

1 micrometre (µm) $= 10^{-6}$ m = 10,000 Å = 1000 nm

1.11. PHOTONS

According to quantum theory, light is considered as a stream of special particles, namely **photons**. Photons do not have rest mass and travel with a velocity equal to the speed of light in a vacuum. The fundamental characteristics of a photon are its energy E and momentum p.

$$E = h\nu \qquad \text{... (1.8)}$$

and
$$p = \frac{h\nu}{c} = \hbar k \qquad \text{... (1.9)}$$

The momentum vector p of a photon has a direction coinciding with that of the wave vector k. k has a magnitude $2\pi/\lambda$ and a direction coinciding with that of wave velocity. Photon mass $m = \dfrac{h\nu}{c^2}$ is the mass of the electromagnetic field and is not associated with a rest mass because photons at rest do not exist.

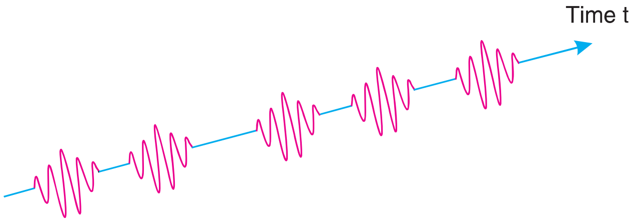


Fig. 1.10 (a) Bursts of light emitted by atoms.

Photons are emitted by individual atoms in light sources. An atom leaving an excited state gives up the excess energy in the form of a burst of light (photon) and jumps to the lower normal state. The process of transition of the atom from an upper state to a lower state lasts for a brief time of about 10^{-8}sec. Therefore, the light emitted by an atom is not a continuous harmonic wave of infinite extension but is a *wave train* of finite length having a certain limited number of oscillations. It is impossible to say exactly when an atom may emit light because the emission is completely a random process. Fig. 1.10(a) pictorially describes the emission of light by a single atom in terms of wave trains. Other atoms in the source behave similarly but with different emission times. Adding together the wave trains generated by all atoms in the light source produces a succession of wave trains (Fig. 1.10 b), which gives an impression of continuous wave.

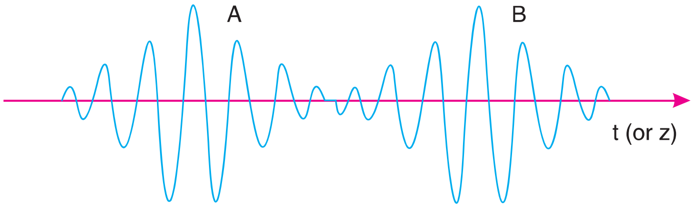


Fig. 1.10 (b) A succession of wave trains gives an impression of continuous wave.

1.12. THE DUAL NATURE

On one hand light appears to be a continuous electromagnetic wave of frequency ν and on the other hand it appears to be a collection of photons having energy E and momentum p. It has been found that neither of the models can separately explain *all* the experimental facts. A particle is precisely localized in space whereas a continuous wave cannot be attributed to a particular location in space. Thus, the corpuscular nature and wave nature appear to be mutually exclusive. However, the experimental evidence points out that light behaves both as a continuous wave and a particle. Therefore, we say that light exhibits **dual nature**. The reason for the wave-particle dualism may be understood as follows. At the lower frequency end of the electromagnetic spectrum are radio waves whose wavelengths are so large that they spread over a very large volume of space (see Fig. 1.11). Therefore, the energy available at any point is insignificantly small and their particle nature cannot be observed. On the higher frequency side of the spectrum, we have x-rays and γ-rays.Their wavelengths are so short that the wave energy is concentrated in a point of very small dimension and the particle nature is readily experienced whereas the wave nature is less noticeable. The visible region represents the transition region in which both the aspects of light can be observed.

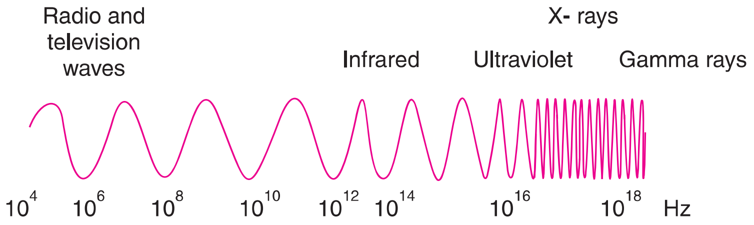


Fig. 1.11

In photon description the light intensity is given by $I = N h\nu$ and in the wave description it is given by $I = |E|^2$. It implies that the square of the amplitude of a light wave at a point in space is proportional to the number of photons arriving at that point. In other words the amplitude of a light wave determines the probability that a photon can be found at a particular point in space. Probability to observe photons is thus proportional to $|E|^2$. Thus, the ultimate connection between the wave behaviour and the particle behaviour are interpreted.

To sum up, light *rays* consist of streams of *photons*, which are basically *electromagnetic wave trains*. We use all the three descriptions namely rays, waves and photons appropriately to describe the behaviour of light. When light is refracted or reflected by optical elements such as lenses, we mostly use the ray description; when light propagates through space or any medium we use the electromagnetic wave description and whenever light interacts with matter we make use of the photon description.

QUESTIONS

1. What is meant by reflection?
2. State and explain the law of reflection.
3. What do you mean by refraction of light?
4. What is absolute refractive index of a medium?
5. What is Snell's law?
6. What is meant by optical path? How is it different from geometrical path length?
7. What are the four important theories of light?
8. Explain briefly the corpuscular theory and its limitations?
9. Describe the Huygens' wave theory?
10. Why light is classified in the category of electromagnetic waves?
11. Explain what the visible region means?
12. What is photon theory of light?
13. Explain the dual nature of light?

14.3. SUPERPOSITION OF WAVES

Frequently it is necessary to find the resultant disturbance at a point when a number of disturbances arrive simultaneously. According to the **principle of superposition—**

when two or more waves overlap, the resultant displacement at any point and at any instant may be found by adding the instantaneous displacements that would be produced at the point by the individual waves if each were present alone.

It means that the resultant is simply the sum of the disturbances. The principle of superposition applies to electromagnetic waves also and is the most important principle in wave optics. In case of electromagnetic waves, the term *displacement* refers to the amplitude of the electric field vector.

Interference is an important consequence of superposition of *coherent* waves.

14.4. INTERFERENCE

If two or more light waves of the same frequency overlap at a point, the resultant effect depends on the *phases* of the waves as well as their *amplitudes*. The resultant wave at *any point* at any instant of time is governed by the **principle of superposition.** The combined effect at each point of the region of superposition is obtained by adding algebraically the amplitudes of the individual waves. Let us assume here that the component waves are of the *same amplitude*.

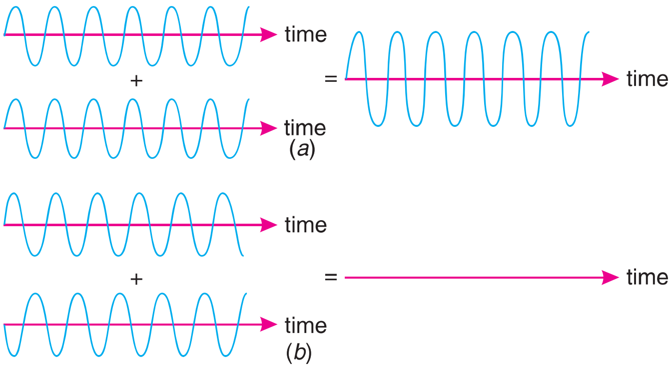


Fig. 14.5

At certain points, the two waves may be *in phase*. The amplitude of the resultant wave will then be equal to the sum of the amplitudes of the two waves, as shown in Fig.14.5(a). Thus, the amplitude of the resultant wave

$$A_R = A + A = 2A. \quad (14.7)$$

Hence, the intensity of the resultant wave is

$$I_R \propto A_R^2 = 2^2 A^2 = 2^2 I. \quad (14.8)$$

It is obvious that the resultant intensity is greater than the sum of the intensities due to individual waves.

$$I_R > I + I = 2I \quad (14.9)$$

Therefore, the interference produced at these points is known as **constructive interference**. A **stationary bright band** of light is observed at points of constructive interference.

At certain other points, the two waves may be *in opposite phase*. The amplitude of the resultant wave will then be equal to the sum of the amplitudes of the two waves, as shown in Fig.14.4 (b). Thus, the amplitude of the resultant wave

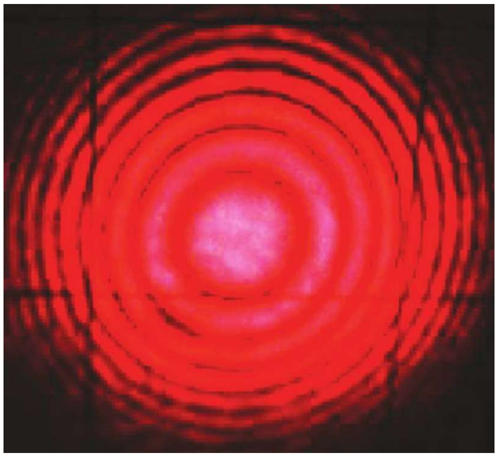
$$A_R = A - A = 0. \tag{14.10}$$

Hence, the intensity of the resultant wave is

$$I_R \propto 0^2 = 0. \tag{14.11}$$

It is obvious that the resultant intensity is less than the sum of the intensities due to individual waves.

$$I_R < 2I \tag{14.12}$$



In the central bright spot, there is constructive interference and then a destructive interference ring and then constructive, and so on.

Therefore, the interference produced at these points is known as **destructive interference.** A **stationary dark band** of light is observed at points of destructive interference. Thus, we see that a redistribution of energy took place in the region.

Thus, when two or more coherent waves of light are superposed, the resultant effect is **brightness** in certain regions and **darkness** at other regions. The regions of brightness and darkness alternate and may take the form of straight bands, or circular rings or any other complex shape. The alternate bright and dark bands are called **interference fringes. The phenomenon of redistribution of light energy due to the superposition of light waves from two or more coherent sources is known as interference.**

Whether the condition (14.7) occurs or (14.10) occurs at a point is *solely* determined by the difference in the optical paths traversed by the waves that are superposing at that point.

Let us consider two sources of light S_1 and S_2, as shown in Fig. 14.6. Let us assume that the sources are identical and produce harmonic waves of same wavelength and that the waves are in the same phase at S_1 and S_2. Light from these sources travel along different paths, S_1P and S_2P, and meet at a point P. We now wish to know whether we get brightness or darkness at P due to the superposition of waves.

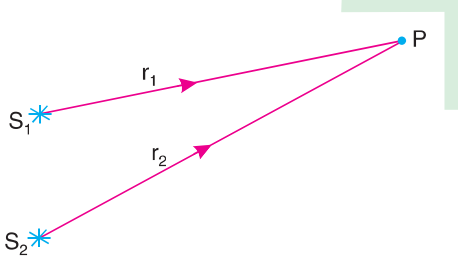


Fig. 14.6

Referring to Fig. 14.6, we find that the waves move along the geometric paths $S_1P = r_1$ and $S_2P = r_2$, which are different in length. Also, the media through which the two waves travelled, may be different. As a result, the optical path lengths are different. If μ_1 is the refractive index of the medium in which the ray S_1P travelled, the corresponding optical path length is $\mu_1 r_1$. Similarly, if μ_2 is the refractive index of the medium in which the ray S_2P travelled, the corresponding optical path length is $\mu_2 r_2$. These optical paths accommodate different number of waveforms along their lengths. The optical path difference between the waves at the point P is $(\mu_2 r_2 - \mu_1 r_1)$. It may come to a few full waves or a mixed fraction of waves. It means that though the waves started with the same phase, they may arrive at P with different phases because they travelled along different optical path lengths.

If the optical path difference $\Delta = (\mu_2 r_2 - \mu_1 r_1)$ is equal to zero or an integral multiple of wavelength λ, then the waves arrive in phase at P and superpose with crest-to-crest correspondence. That is, if

$$\Delta = m\lambda \tag{14.13}$$

where m is an integer and takes values, m = 0,1,2,3,4,5,……,then the waves are in phase (see Fig.14.5a) and their overlapping at P produces constructive interference or brightness.

On the other hand, if the optical path difference $\Delta = (\mu_2 r_2 - \mu_1 r_1)$ is equal to an odd integral multiple of half-wavelength, λ/2 , then the waves arrive out of phase at P and superpose with crest-to-trough correspondence. That is, if

$$\Delta = (2m+1)\frac{\lambda}{2} \tag{14.14}$$

where m is an integer and takes values, m = 0,1,2,3,4,5,…….,then the waves are inverted with respect to each other (see Fig. 14.5b) and their overlapping at P produces destructive interference or darkness.

The regions of brightness and darkness are also known as regions of **maxima** and **minima**.

14.4.1. THEORY OF INTERFERENCE

(a) Analytical Method: Let us assume that the electric field components of the two waves arriving at point P vary with time as

$$E_A = E_1 \sin \omega t \tag{14.15}$$

and

$$E_B = E_2 \sin (\omega t + \delta) \tag{14.16}$$

where δ is the phase difference between them. According to Young's principle of superposition, the resultant electric field at the point P due to the simultaneous action of the two waves is given by

$$E_R = E_A + E_B \tag{14.17}$$

$$= E_1 \sin \omega t + E_2 \sin (\omega t + \delta)$$

$$= E_1 \sin \omega t + E_2 (\sin \omega t \cos\delta + \cos \omega t \sin \delta)$$

$$= (E_1 + E_2 \cos \delta) \sin \omega t + E_2 \sin \delta \cos \omega t \tag{14.18}$$

Equ. (14.18) shows that ***the superposition of two sinusoidal waves having the same frequency but with a phase difference produces a sinusoidal wave with the same frequency but with a different amplitude E.***

Let

$$E_1 + E_2 \cos \delta = E \cos \phi \tag{14.19}$$

and

$$E_2 \sin \delta = E \sin \phi \tag{14.20}$$

where E is the amplitude of the resultant wave and ϕ is the new initial phase angle. In order to solve for E and ϕ, we square the equ.(14.19) and (14.20) and add them.

$$(E_1 + E_2 \cos \delta)^2 + E_2^2 \sin^2 \delta = E^2 (\cos^2 \phi + \sin^2 \phi)$$

or

$$E^2 = E_1^2 + E_2^2 \cos^2 \delta + 2E_1E_2 \cos \delta + E_2^2 \sin^2 \delta$$

or

$$E^2 = E_1^2 + E_2^2 + 2E_1E_2 \cos \delta \tag{14.21}$$

Thus, it is seen that the square of the amplitude of the resultant wave is not a simple sum of the squares of the amplitudes of the superposing waves, there is an additional term which is known as the *interference term.*

(b) Phasor diagram *and* phasor addition: A wave may be viewed either sideways or end-on. In sideways view, as the wave travels through a distance λ, the phase angle changes from 0 to 2π radians. In the end-on view we find a point on the profile of the wave oscillating linearly. The two

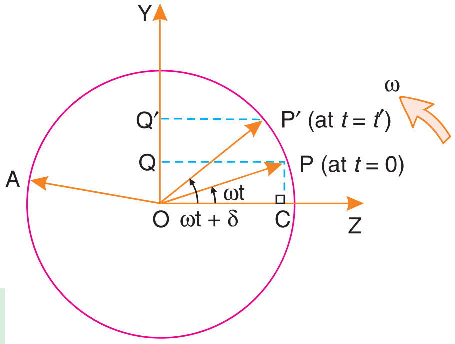
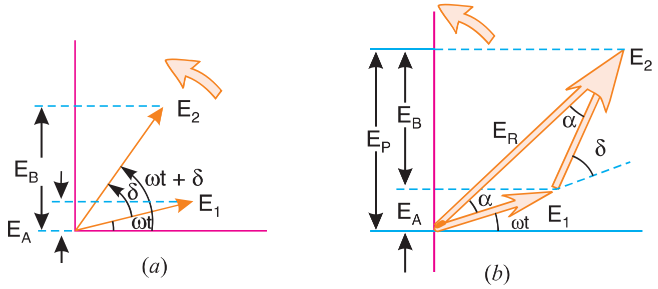


Fig. 14.7

perspectives may be combined as follows. A circle having a radius OA equal to the amplitude of the wave motions is drawn (see Fig. 14.7). Now consider a point P on the circumference of the circle; Q is the projection of P on the vertical axis. As P moves around the circumference with constant angular velocity ω, Q oscillates vertically. This is the end-on view. The Fig. 14.7 is called the **phasor diagram**. OP is called a **rotating vector** or a **phasor**. It means that the *length* of a phasor is proportional to the *amplitude* of the sinusoidal wave and the *projection* of a phasor on the vertical axis is proportional to the *instantaneous value* of the alternating quantity.

Phasor representation may be used to *add sinusoidal functions* with a phase difference. The wave E_A is represented with a vector of amplitude E_1 rotating about the origin in a counter clockwise direction with an angular frequency ω (See Fig. 14.8 a). As the phasor E_1 rotates, the projection E_A oscillates along the vertical axis. The second wave, E_B, has amplitude E_2 and angular frequency ω but its phase is δ with respect to wave E_A. It is also shown in Fig. 14.8 (a). The resultant E_R is the sum of E_A and E_B obtained by drawing the phasors end to end, by placing the foot of one arrow at the head of the other (as in Fig. 14.8b), maintaining the proper phase difference. The whole assembly rotates counterclockwise about the origin. The sum of the projections on the vertical axis at any time gives the instantaneous value of the total field at a point. The amplitude E_R of the resultant sinusoidal wave at P is the *vector sum* of the other two phasors, as shown in Fig. 14.8 (b).



(*a*) (*b*)

Fig. 14.8

To find E_R, we use the law of cosines.

$$E_R^2 = E_1^2 + E_2^2 - 2E_1E_2 cos(\pi\text{-}\delta)$$

or $$E_R^2 = E_1^2 + E_2^2 + 2E_1E_2 \cos\ \delta$$

This is the same as the equ.(14.21). This method is particularly convenient when several wave amplitudes have to be added.

14.4.2. INTENSITY DISTRIBUTION

The intensity of a light wave is given by the square of its amplitude.

$$I = \tfrac{1}{2}\varepsilon_o c E^2 \propto E^2$$

Using this relation into (14.21), we get

$$I = I_1 + I_2 + 2\sqrt{I_1 I_2}\cos\delta \tag{14.22}$$

We see that the resultant intensity at P on the screen is not just the sum of the intensities due to the separate waves. The term $2\sqrt{I_1 I_2}\cos\delta$ is known as the **interference term**. Whenever the phase difference between the waves is zero, i.e. $\delta = 0$, we have maximum amount of light. Thus,

$$I_{\max} = I_1 + I_2 + 2\sqrt{I_1 I_2} \tag{14.23}$$

When $I_1 = I_2 = I_o$

$$I_{\max} = 4I_o \tag{14.23a}$$

It means that the resultant intensity I will be *more than the sum* of the intensities due to the two sources.

When the phase difference is $\delta = 180^o$, $\cos 180^o = -1$ and we have a minimum amount of light.

$$I_{\min} = I_1 + I_2 - 2\sqrt{I_1 I_2} \tag{14.24}$$

which, when $I_1 = I_2$, becomes

$$I_{\min} = 0 \tag{14.24a}$$

It means that the resultant intensity I will be *less than the sum* of the intensities due to the two sources.

At points that lie between the maxima and minima, when $I_1 = I_2 = I_0$, we get

$$I = I_o + I_o + 2I_o\cos\delta$$

$$= 2I_o(1 + \cos\delta)$$

Then using the identity $1 + \cos\delta = 2\cos^2\left(\frac{1}{2}\delta\right)$, we get

$$I = 4I_o\cos^2\left(\tfrac{1}{2}\delta\right) \tag{14.25}$$

Equ. (14.25) shows that the intensity varies along the screen in accordance with the ***law of cosine square.*** Fig. 14.9 shows the variation of intensity as a function of phase angle δ.

It is seen from the plot that the intensity varies from zero at the fringe minima to $4I_o$ at the fringe maxima.

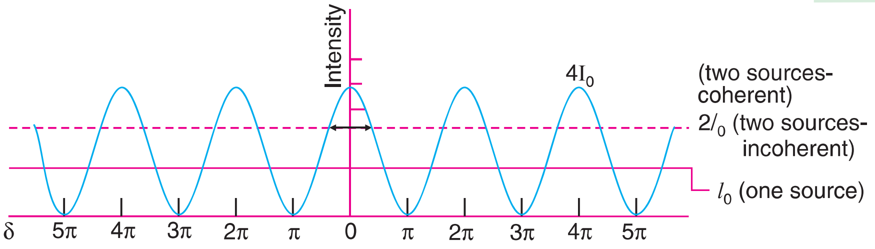


Fig. 14.9

14.4.3. SUPERPOSITION OF INCOHERENT WAVES

Incoherent waves are the waves that do not maintain a constant phase difference. Then the phase of the waves fluctuate irregularly with time and independently of each other. In case of light waves the phase fluctuates randomly at a rate of about 10^8 per second. Light detectors such as human eye, photographic film etc cannot respond to such rapid changes. The detected intensity is always the average intensity, averaged over a time interval which is very much larger than the time of fluctuation. Thus,

$$I_{ave} = I_1 + I_2 + 2\sqrt{I_1 I_2}\ \langle \cos \delta \rangle$$

The average value of the cosine over a large time interval will be zero and hence the interference term becomes zero. Therefore, the average intensity of the resultant wave is

$$I_{ave} = I_1 + I_2$$

If $I_1 = I_2$, then $$I_{\text{ave}} = 2\,I \tag{14.26}$$

It implies that the superposition of incoherent waves does not produce interference but gives a uniform illumination. The average intensity at any point is simply equal to the sum of the intensities of the component waves.

14.4.4. SUPERPOSITION OF MANY COHERENT WAVES

The result (14.23) may be written as

$$I_{\max} = 2^2 I_o$$

which gives the resultant intensity when two coherent waves superpose. The resultant maximum intensity due to N coherent waves will be therefore

$$I_{\max} = N^2 I_o \tag{14.27a}$$

and the minimum intensity $$I_{\min} = 0 \tag{14.27b}$$

where N represents the number of coherent waves superposing at a point.

14.5. YOUNG'S DOUBLE SLIT EXPERIMENT – WAVEFRONT DIVISION

As early as in 1665 Grimaldi attempted to produce interference between two beams of light. He directed sunlight into a dark room through two pinholes in a screen, with an expectation that bright and dark bands would be observed in the area where the beams overlap on each other. He observed uniform illumination instead. In 1801, about one hundred thirty six years later, Thomas Young gave the first demonstration of the interference of light waves. Young admitted the sunlight through a single pinhole and then directed the emerging light onto two pinholes. Finally the light was received on a screen. The spherical waves emerging from the pinholes interfered with each other and a few coloured fringes were observed on the screen. The amount of light that emerged from the pinhole was very small and the fringes were faint and difficult to observe. The pinholes were later replaced with narrow slits that let through much more light. The sunlight was replaced by monochromatic light. Young's experiment is known as **double-slit experiment**.

Fig. 14.10 shows a plan view of the basic arrangement of the double slit experiment. The primary light source is a monochromatic source; it is generally a sodium lamp, which emits yellow light of wavelength at around 5893Å. This light is not suitable for causing interference because emissions from different parts of any ordinary source are ***not*** coherent. Therefore, the monochromatic light is allowed to pass through a narrow slit at S. The light coming out of the slit originated from only a small region of the light source and hence behaves more nearly like an ideal light source. Cylindrical wavefronts are produced from the slit S, the primary light source, which fall on the two narrow closely spaced slits, S_1 and S_2 as shown in Fig. 14.10. The slits at S_1 and S_2 are very narrow. The cylindrical waves emerging from the slits overlap. If the slits are *equidistant* from S, the *phase* of the wave at S_1 will be the same as the *phase* of the wave at S_2. Further, waves leaving S_1 and S_2 are therefore always *in phase*. Hence, sources S_1 and S_2 act as *secondary coherent sources*. The waves leaving from S_1 and S_2 interfere and produce alternate bright and dark bands on the screen at T.

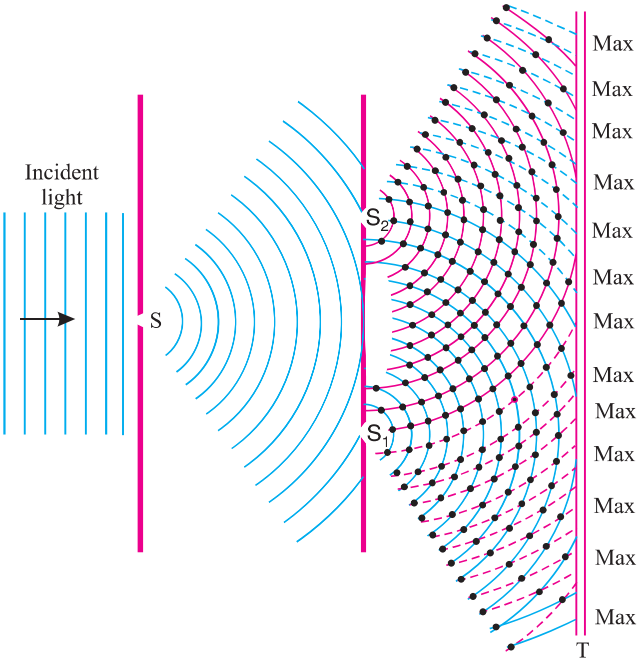


Fig. 14.10

14.5.1. OPTICAL PATH DIFFERENCE BETWEEN THE WAVES AT P:

Let P be an arbitrary point on screen T, which is at a distance D from the double slits. Let θ be the angle between MP and the horizontal line MO. Let S_1N be a normal on to the line S_2P. The distances

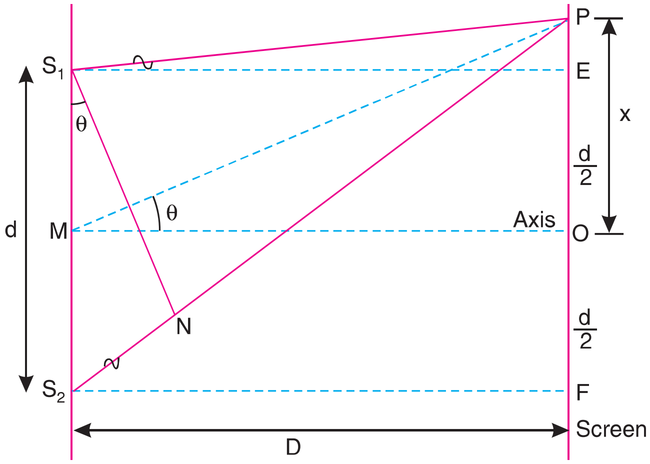


Fig. 14.11

PS_1 and PN are equal. The waves emitted at the slits, S_1 and S_2 are initially in phase with each other. The difference in the path lengths of these two waves is S_2N. We assume that the experiment is carried out in air. Therefore, the optical paths are identical with geometrical paths. The nature of the interference of the two waves at P depends simply on how many waves are contained in the length of the path difference S_2N. If S_2N contains an integral number of wavelengths, the two waves interfere constructively, producing a maximum in the intensity of light on the screen at P. If it contains an odd number of half-wavelengths, then the waves interfere destructively and produce a minimum intensity at P.

Let the point P be at a distance x from O (Fig.14.11). Then

PE = $x - d/2$ and PF = $x + d/2$.

$$(S_2P)^2 - (S_1P)^2 = \left[D^2 + \left(x + \frac{d}{2}\right)^2\right] - \left[D^2 + \left(x - \frac{d}{2}\right)^2\right]$$

$$(S_2P)^2 - (S_1P)^2 = 2xd$$

$$S_2P - S_1P = \frac{2xd}{S_2P + S_1P}$$

We can approximate that $S_2P \cong S_1P \cong D$.

$$\therefore \text{ Path difference} = S_2P - S_1P = \frac{xd}{D} \tag{14.28}$$

We now find out the conditions for observing bright and dark fringes on the screen.

14.5.2. BRIGHT FRINGES

Bright fringes occur wherever the waves from S_1 and S_2 interfere constructively. The first time this occurs is at O, the axial point. There, the waves from S_1 and S_2 travel the same optical path length to O and arrive in phase. The next bright fringe occurs when the wave from S_2 travels one complete wavelength further the wave from S_1. In general constructive interference occurs if S_1P and S_2P differ by a whole number of wavelengths.

The condition for finding a bright fringe at P is that

$$S_2P - S_1P = m\lambda$$

Using the equation (14.28), it means that

$$\frac{xd}{D} = m\lambda \tag{14.29}$$

where m is called the **order of the fringe**.

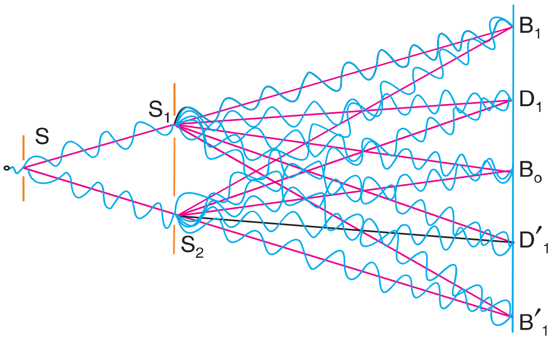
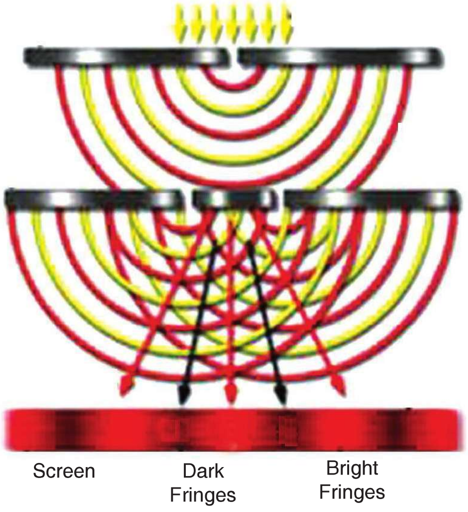


Fig. 14.12

The bright fringe B_o (at O), corresponding to m = 0, is called the *zero-order* fringe. It means the path difference between the two waves reaching at O is zero. Fringe at B_1 is the *first-order bright fringe* from the axis corresponding to m = 1; the path difference between the two waves reaching at B_1 is one λ. The *second order bright fringe* (m = 2) will be located where the path difference is 2λ and so on.



14.5.3. DARK FRINGES

The first dark fringe occurs when $(S_2P - S_1P)$ is equal to λ / 2. The waves are now in opposite phase at P. The second dark fringe occurs when $(S_2P - S_1P)$ equals 3λ / 2. The mth dark fringe occurs when

$$(S_2P - S_1P) = (2m + 1)\,\lambda / 2$$

The condition for finding a dark fringe is $\frac{xd}{D} = (2m+1)\frac{\lambda}{2}$ (14.30)

The *first-order dark fringe* D_1 (Fig. 14.12) from the axis corresponds to m = 0, where the path difference between the two waves is λ/2. The second order dark fringe (m = 1) will be produced where the path difference is 3λ/2 and so on.

14.5.4. SEPARATION BETWEEN NEIGHBOURING BRIGHT FRINGES

The mth order fringe occurs when $x_m = \frac{m\lambda\, D}{d}$

and the (m+1)th order fringe occurs when $x_{m+1} = \frac{(m+1)\lambda\, D}{d}$

The fringe separation, β is given by $\beta = x_{m+1} - x_m = \frac{\lambda D}{d}$ (14.31)

The same result will be obtained for dark fringes. Thus, the distance between any two consecutive bright or dark fringes is known as the ***fringe width*** and is the *same* everywhere on the screen. Further, the width of the bright fringe is equal to the width of the dark fringe. Therefore, the alternate bright and dark fringes are *parallel*. From the equ.(14.31), we find the following:

(*i*) The fringe width β is independent of the *order* of the fringe.It is directly proportional to the wavelength of light, i.e.$\beta \propto \lambda$. The fringes produced by red light are less closer compared to those produced by blue light.

(*ii*) The width of the fringe is *directly proportional* to the distance of the screen from the two slits, $\beta \propto D$. The farther the screen, the wider is the fringe separation.

(*iii*) The width of the fringe is *inversely proportional* to the distance between the two slits. The closer are the slits, the wider will be the fringes.

14.6. COHERENCE

Interference fringes did not appear on the screen in the experiment of Grimaldi as he did not keep the slit S before the double slit arrangement. He obtained only a uniform illumination. It was so because the beams arriving at the screen were not coherent and the phase difference between them varied with time in a haphazard way. The reason for the lack of coherence lies in the very process of light emission. In ordinary sources of visible light, individual atoms are responsible for the emission of light. An atom leaving an excited state gives up the excess energy in the form of a burst of light (photon) and jumps to the lower normal state. The process of transition of the atom from an upper state to a lower state lasts for a brief time of about 10^{-8}sec. Therefore, the light emitted by an atom is not a continuous harmonic wave of infinite extension but is a *wave train* of finite length having a certain limited number of oscillations. It is impossible to say exactly when an atom may emit light because the emission is completely a random process.

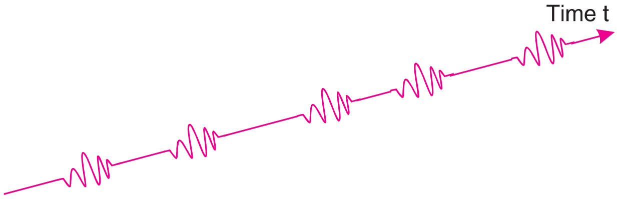


Fig. 14.13

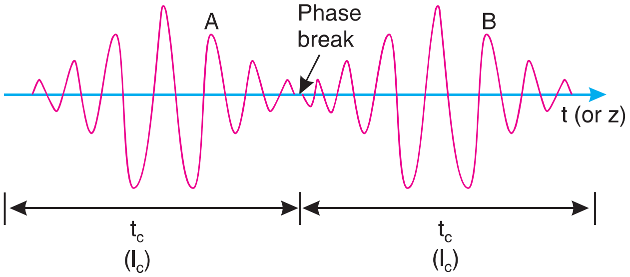


Fig. 14.14

Fig. 14.13 pictorially describes the emission of light by a single atom in terms of wave trains. Other atoms in the source behave similarly but with different emission times. Adding together the wave trains generated by all atoms in the light source produces a succession of wave trains which have their phases distributed randomly. In passing from one wave train to the next there is an abrupt change in phase. Therefore, it is not possible to relate the phase at a point in wave train B to a point in wave train A. The phase of the wave train from an atom would remain constant with respect to the phase of the wave train from another atom only for about 10^{-8} sec. It implies that the two wave trains can be coherent for a maximum time of about 10^{-8} sec. Therefore, light from conventional sources is characterized by two important parameters, namely coherence time and coherence length.

Coherence time: It is *the average time during which the wave remains sinusoidal and phase of the wave packet can be predicted reliably.*

Coherence length: It is *the length of the wave packet over which it may be assumed to be sinusoidal and has predictable phase.*

Light from a sodium discharge lamp has a coherence length of about 2 to 3 cm, while the coherence length of white light is a fraction of a cm. In the double slit experiment, the presence of slit S ensures that the same group of wave trains are incident on slits S_1 and S_2. When the phase of the wave changes at S this change is communicated simultaneously to S_1 and S_2.Therefore, the waves emerging from S_1 and S_2 will be coherent with respect to each other and a *stationary* interference pattern is produced on the screen.

14.7. CONDITIONS FOR INTERFERENCE

We may now summarize the conditions that are to be fulfilled in order to observe a distinct well-defined interference pattern.

(A) Conditions for sustained interference:

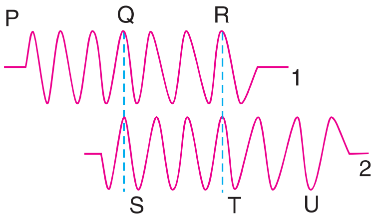
(*i*) **The waves from the two sources must be of the same frequency.**

If the light waves differ in frequency, the phase difference fluctuates irregularly with time. Consequently, the intensity at any point fluctuates with time and we will not observe steady interference.

(*ii*) **The two light waves must be coherent.**

If the light waves are coherent, then they maintain a fixed phase difference over a time and space. Hence, a stationary interference pattern will be observed.

(*iii*) **The path difference between the overlapping waves must be less than the coherence length of the waves.**



Partial overlap of the wavetrains

Fig. 14.15

We have already learnt that light is emitted in the form of wave trains and a finite coherence length characterizes them. If we consider two interfering wave trains, having constant phase difference, as in Fig. 14.15, the interference effects occur due to parts QR of wave 1 and ST of wave 2.

For the parts PQ and TU interference will not occur. Therefore, the interference pattern does not appear distinctly. When the entire wave train PR overlaps on the wave train SU, interference pattern will be distinct. On the other hand, when the path difference between the waves 1 and 2 becomes very large, the wave trains arrive at different times and do not overlap on each other. Therefore, in such cases interference does not take place. The interference pattern completely vanishes if the path difference is equal to the coherence length. It is hence required that

$$\Delta < l_{coh} \tag{14.32}$$

(*iv*) **If the two sets of waves are plane polarized, their planes of polarization must be the same.** Waves polarized in perpendicular planes cannot produce interference effects.

(B) Condition for formation of distinct fringe pattern:

(v) **The two coherent sources must lie close to each other in order to discern the fringe pattern.** If the sources are far apart, the fringe width will be very small and fringes are not seen separately.

(*vi*) **The distance of the screen from the two sources must be large.**

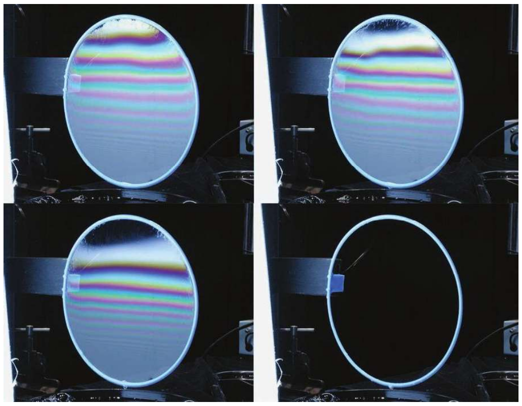
(*vii*) **The vector sum of the overlapping electric field vectors should be zero in the dark regions** for obtaining distinct bright and dark fringes. The sum will be zero only if the vectors are anti-parallel and have the same magnitude.

14.8. TECHNIQUES OF OBTAINING INTERFERENCE

The phase relation between the waves emitted by two independent light sources rapidly changes with time and therefore they can *never* be coherent, though the sources are identical in all respects. However, if two sources are derived from a single source by some device, then any phase change occurring in one source is simultaneously accompanied by the same phase change in the other source. Therefore, the phase difference between the waves emerging from the two sources remains constant and the sources are *coherent*. The techniques used for creating coherent sources of light can be divided into the following two broad classes.

15

CHAPTER



Interference In Thin Films

15.1. THIN FILM

An optical medium is called a **thin film** when its thickness is about the order of 1 wavelength of light in visible region. Thus, a film of thickness in the range 0.5 µm to 10 µm may be considered as a thin film. A thin film may be a thin sheet of transparent material such as glass, mica, an air film enclosed between two transparent plates or a soap bubble. When light is incident on such a film, a small part of it gets reflected from the top surface and a major part is transmitted into the film. Again, a small part of the transmitted component is reflected back into the film by the bottom surface and the rest of it emerges

Soap bubble.

At a Glance

- Thin Film
- Plane Parallel Film
- Interference Due to Transmitted Light
- Haidinger Fringes
- Variable Thickness (Wedge-Shaped) Film
- Newton's Rings
- Michelson's Interferometer
- Applications of Michelson Interferometer
- Twyman and Green Interferometer
- Mach-Zehnder Interferometer
- Multiple Beam Interference
- Fabry-Perot Interferometer and Etalon
- Lummer and Gehrcke Plate
- Applications of Thin Film Interference
- Antireflection Coatings
- Dielectric Mirrors
- Interference Filters

out of the film. A small portion of the light thus gets reflected partially several times in succession within the film (see Fig. 15.1).

In transparent thin films, the two bounding surfaces strongly transmit light and only weakly reflect the incident light. Therefore, only the first reflection at the top surface and the first reflection at the bottom surface will be of appreciable strength. For example, if we consider a glass plate, having a refractive index 1.52, the reflectivity of the top surface is given by

$$r = \left[\frac{1.52-1}{1.52+1}\right]^2 = 0.042$$

It means that about 4% of the incident light is reflected by the top surface of the glass plate, while 96% of it is transmitted into the plate. Out of the light reaching the bottom surface, again 3.8% is reflected and 92% is transmitted out of the plate. Then, again out of the 3.8% of the light 0.15% is reflected at the inner boundary of the top surface and about 3.65% is transmitted out into the air. After two reflections, the intensity will become insignificantly small. At each reflection, the intensity and hence the *amplitude of light wave is divided* into a reflected component and a refracted component. The reflected and refracted components travel along different paths and subsequently overlap to produce interference. Therefore, the interference in thin films is called interference by division of amplitude. Newton and Robert Hooke first observed the thin film interference. However, Thomas Young gave the correct explanation of the phenomena. A thin film may be uniform or non-uniform in its structure. However, as long as its thickness lies within the specified limits, interference of light occurs.

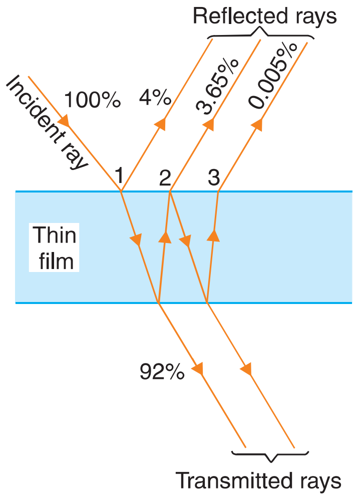


Fig. 15.1

15.2. PLANE PARALLEL FILM

A transparent thin film of uniform thickness bounded by two parallel surfaces is known as a *plane parallel thin film.*

When light is incident on a parallel thin film, a small portion of it gets reflected from the top surface and a major portion is transmitted into the film. Again, a small part of the transmitted component is reflected back into the film by the bottom surface and the rest of it is transmitted from the lower surface of the film. Thin films transmit incident light strongly and reflect only weakly. After two reflections, the intensities of reflected rays drop to a negligible strength. Therefore, we consider the first two reflected rays only (see Fig. 15.2). These two rays are derived from the same incident ray but appear to come from two sources located below the film. The sources are virtual coherent sources. The reflected waves 1 and 2 travel along parallel paths and interfere at infinity. This is a case of *two-beam* interference.

The condition for maxima and minima can be deduced once we have calculated the optical path difference between the two rays at the point of their meeting.

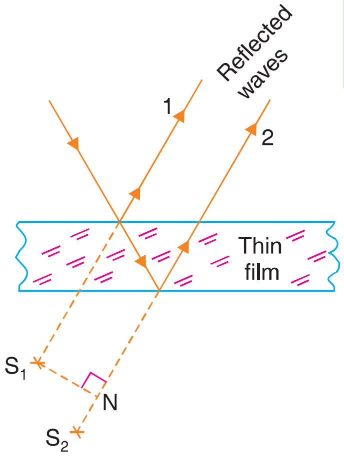
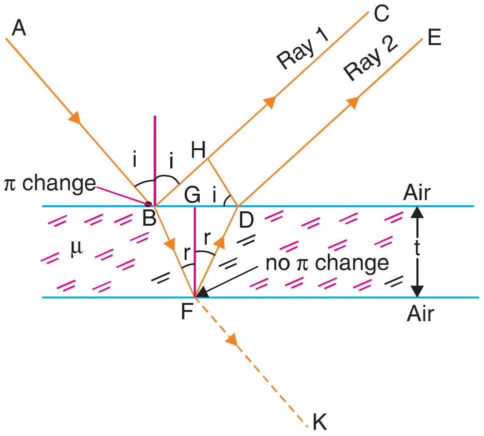


Fig. 15.2

15.2.1. INTERFERENCE DUE TO REFLECTED LIGHT

Let us consider a transparent film of uniform thickness ‘t’ bounded by two parallel surfaces as shown in Fig. 15.3. Let the refractive index of the material be μ. The film is surrounded by air on both the sides. Let us consider plane waves from a monochromatic source falling on the thin film at an angle of incidence *‘i’*. Part of a ray such as AB is reflected along BC, and part of it is transmitted into the film along BF. The transmitted ray BF makes an angle ‘r’ with the normal to the surface at the point G. The ray BF is in turn partly reflected back into the film along FD while a major part refracts into the surrounding medium along FK. Part of the reflected ray FD is transmitted at the upper surface and travels along DE. Since the film boundaries are parallel, the reflected rays BC and DE will be parallel to each other. The waves travelling along the paths BC and BFDE are derived from a single incident wave AB. Therefore they are coherent and can produce interference if they are made to overlap by a condensing lens or the eye.



BF = t/cos r
BG = t.tan r
BH = 2t.tan r . sin i
$\Delta = 2\mu t \cos r - \lambda/2$

Fig. 15.3

(*i*) Geometrical Path Difference:

Let DH be normal to BC. From points H and D onwards, the rays HC and DE travel equal path. The ray BH travels in air while the ray BD travels in the film of refractive index μ along the path BF and FD. The geometric path difference between the two rays is

BF+FD – BH.

(*ii*) Optical Path Difference:

Optical path difference $\Delta_a = \mu L$

$\therefore$ $\Delta_a = \mu\,(BF+FD) - 1(BH)$ (15.1)

$\therefore$ In the ΔBFD, ∠BFG = ∠GFD = ∠r

BF = FD

$$BF = \frac{FG}{\cos r} = \frac{t}{\cos r}$$

$$\therefore \quad BF + FD = \frac{2t}{\cos r} \qquad (15.2)$$

Also, BG = GD

$\therefore$ BD = 2BG

$$BG = FG \tan r = t \tan r$$

$\therefore$ $$BD = 2\, t\ \tan r$$

In the Δ^{le} BHD $$\angle HBD = (90 - i)$$

$$\angle BHD = 90^0$$

$\therefore$ $$\angle BDH = i$$

$\therefore$ $$BH = BD \sin i = 2\, t \tan r \sin i \qquad (15.3)$$

From Snell's law,

$$sin\ i = \mu \sin r$$

$\therefore$ $$BH = 2t \tan r\, (\mu \sin r) = \frac{2\mu\ t\ \sin^2 r}{\cos\ r} \qquad (15.4)$$

Using the equations (15.2) and (15.4) into eq.(15.1), we get

$$\Delta_a = \mu\left[\frac{2t}{\cos\ r}\right] - \left[\frac{2\mu\ t\ \sin^2\ r}{\cos\ r}\right]$$

$$= \frac{2\mu\ t}{\cos\ r}\left[1 - \sin^2\ r\right]$$

$$= \frac{2\mu\ t}{\cos\ r}\ \cos^2 r$$

$\therefore$ $$\Delta_a = 2\mu\ t\ \cos\ r \qquad (15.5)$$

(*iii*) Correction on account of phase change at reflection:

When a ray is reflected at the boundary of a rarer to denser medium, a path change of λ/2 occurs for the ray BC (see Fig.15.3). There is no path difference due to transmission at D. Including the change in path difference due to reflection, the true path difference

$$\Delta_t = 2\ \mu\ t \cos\ r - \frac{\lambda}{2} \qquad (15.6)$$

15.2.2. CONDITIONS FOR MAXIMA (BRIGHTNESS) AND MINIMA (DARKNESS)

Maxima occur when the optical path difference $\Delta = m\ \lambda$. If the difference in the optical path between the two rays is equal to an *integral number of full waves*, then the rays meet each other in phase. The crests of one wave falls on the crests of the others and the waves *interfere constructively*. Thus, when

$$2\mu\ t\ \cos\ r - \frac{\lambda}{2} = m\lambda \qquad (15.7)$$

the reflected rays undergo constructive interference to produce brightness or maxima at the point of their meeting.

$$2\mu\ t\ \cos\ r = m\lambda + \lambda / 2$$

or $$2\mu\ t\ \cos\ r = (2m+1)\lambda\ / 2 \qquad \textbf{Condition for Brightness} \qquad (15.8)$$

Minima occur when the optical path difference is $\Delta = (2m+1)\ \lambda / 2$. If the difference in the optical path between the two rays is equal to an *odd integral number of half-waves*, then the rays meet each other in opposite phase. The crests of one wave falls on the troughs of the others and *the waves interfere destructively*. Thus, when

$$2\mu\ t\ \cos\ r - \lambda\ / 2 = (2m+1)\ \lambda\ / 2 \qquad (15.9)$$

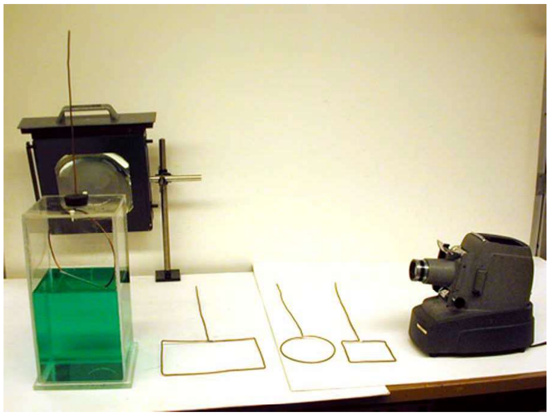
the reflected rays undergo destructive interference to produce darkness. Equ.(15.9) may be rewritten as

$$2\mu\ t\ \cos\ r\ = (m+1)\ \lambda$$

The phase relationship of the interfering waves does not change if one full wave is added to or subtracted from any of the interfering waves. Therefore (m + 1)λ can as well be replaced by mλ for simplicity in expression. Thus,

$$2\mu\ t\ \cos\ r = m\lambda \qquad \textbf{Condition for Darkness} \qquad (15.10)$$

15.2.3. SOME IMPORTANT POINTS



Thin film interference -soap films.

(a) It is seen that the conditions of interference depend on four parameters, namely μ, t, λ and r. In the case of constant thickness (parallel) film, (μt) is constant. When a parallel beam of light is incident on such a film, r also remains constant. Then the interference conditions solely depend on the wavelength λ.

(b) When monochromatic light falls on a parallel beam, the whole film will appear *uniformly* dark or bright. If the condition of constructive interference is satisfied, the film will show intense colour corresponding to the incident light.

(c) If a parallel beam of white light falls on a parallel film, those wavelengths for which the path difference is mλ, will be absent from the reflected light. The other colours will be reflected. Therefore, the film will appear uniformly coloured with one colour being absent.

15.2.4. NARROW LIGHT SOURCE VERSUS EXTENDED LIGHT SOURCE

In case of Fresnel's biprism and Lloyd's mirror, interference fringes were produced by two coherent sources. The initial source is narrow. The fringes obtained on a screen are viewed with an eyepiece. In case of a thin film, a narrow source limits the area of the film that can be viewed. Consider a thin film illuminated by a narrow source of light S (Fig. 15.4). The ray 1 produces

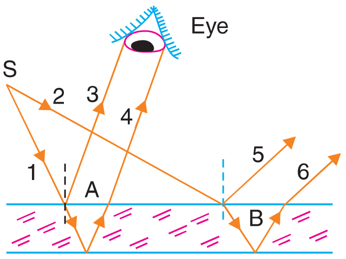


Fig. 15.4

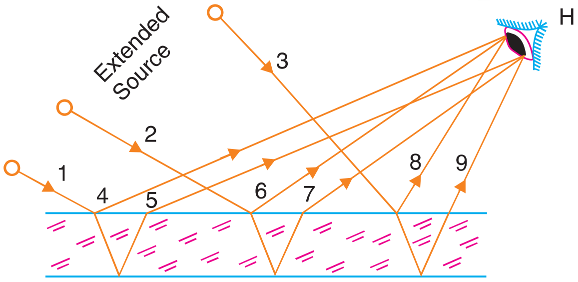


Fig. 15.5

interference fringes because rays 3 and 4 reach the eye. The ray 2 is incident on the surface of the film at a different angle and is reflected along 5 and 6. The rays 5 and 6 do not reach the eye. Similar is the case for other rays incident at different angles on the film surface. The reflected rays do not reach the eye. Thus, *only* the portion A of the film is visible to the eye.

If an extended (or broad) light source is used to illuminate the film, as in Fig.15.5, a larger area of the film surface is observed. The ray 1 after reflection from the upper and the lower surface of the film emerges as rays 4 and 5, which reach the eye. Ray 2 from some other point of the source after reflection from the upper and lower surfaces of the film emerge as rays 6 and 7 which also reach the eye. Also, ray 3 from some other point of the source after reflection from the upper and lower surfaces of the film emerge as rays 8 and 9 which also reach the eye. Therefore, the rays incident at different angles on the film are accommodated by the eye and the field of view is large. Therefore, a broad source of light is required to observe interference in thin films.

15.2.5. RESTRICTION ON THICKNESS OF THE FILM

We know that interference colours are observed only in thin films but not in thick plates such as windowpanes or glass slabs. This is due to the fact that light waves can interfere only when both the conditions of temporal and spatial coherence are satisfied. In Fig. 15.3 we have assumed that a monochromatic wave of infinite length is incident on the film. In reality, the incident light consists of wave trains of finite length and coherence extends over the length of each wave train only. Interference can occur only when parts of the same group of wave trains overlap. Superposition of different wave trains cannot produce interference because they will be incoherent and do not maintain any constant phase relationship with each other.

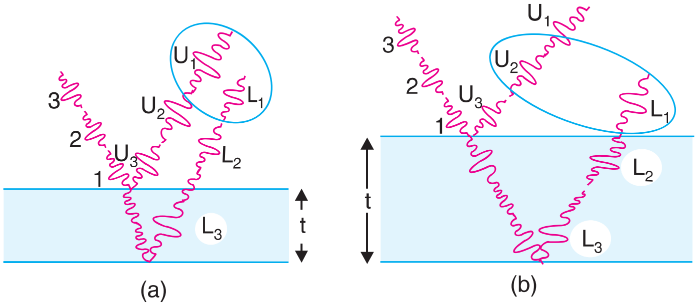
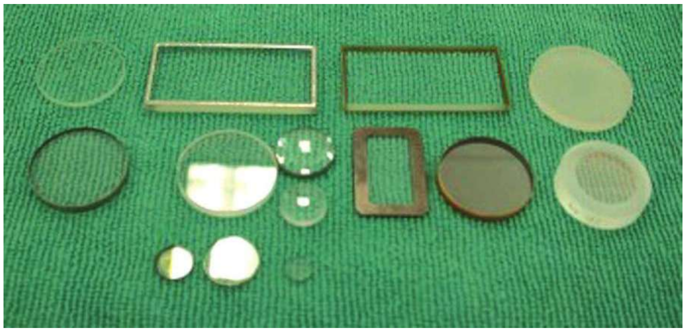


Fig. 15.6



Thick films do not exhibit interference.

Fig. 15.6 shows the real situation. Wave trains 1,2,3 of finite length are incident in succession on a thin film. Portions of each wave train are reflected by the top and bottom surfaces of the film. Each wave train is divided into two reflected wave trains (U_1, L_1, U_2, L_2 and U_3, L_3). In Fig. 15.6 (a) the film is thin and the difference in the optical path lengths of U_1 and L_1 is small compared to the length of the wave train. Their superposition produces interference, as U_1 and L_1 are parts of the same wave train 1 and hence are coherent. In Fig.15.6 (b) the film is thicker and the optical path difference between U_1 and L_1 is large than the coherence length. Consequently, superposition takes place between parts of different wave trains, U_2 and L_1 and U_3 and L_2. Therefore interference does not take place.

It implies that interference occurs *only when* the optical path difference, Δ, between the superposing waves is less than the coherence length (see § 16.3).

i.e., $\Delta << l_{coh}$ (15.11)

∴ $(2\mu t \cos r - \lambda/2) << l_{coh}$ (15.12)

But $l_{coh} = \dfrac{\lambda^2}{\Delta\lambda}$ (Refer to equ. 16.11)

∴ $(2\mu t \cos r - \lambda/2) < \lambda^2/\Delta\lambda$

Rearranging the terms, we obtain

$$t < \frac{\lambda\left[\frac{\lambda}{\Delta\lambda} + \frac{1}{2}\right]}{2\mu \cos r} \tag{15.13}$$

$\lambda/\Delta\lambda >> 1/2$ and for normal incidence $\cos r = 1$.

$$\therefore \quad t < \frac{\lambda^2}{2\mu\Delta\lambda} \tag{15.14}$$

The above equation indicates that *interference in thin film will be observed if the thickness of the film is less than the coherence length of the incident light waves.* Normally, the coherence length of the light from ordinary sources is of the order of a fraction of a millimeter. Therefore, interference is seen with the films of thickness of the order of a few hundred microns only. It is because of this reason that thick films do not exhibit interference.

15.3. INTERFERENCE DUE TO TRANSMITTED LIGHT

Consider a thin transparent film of thickness t and refractive index μ. A ray SA after refraction goes along AB. At B it is partly reflected along BC and partly refracted along BR. The ray BC, after reflection at C, finally emerges along DQ. Here at B and C reflection takes place at the rarer medium. Therefore, no phase change occurs. Draw BM normal to CD and DN normal to BR. The optical path difference between DQ and BR is given by

$$\Delta = \mu(BC + CD) - BN$$

Also, $\mu = \dfrac{\sin i}{\sin r} = \dfrac{BN}{MD}$ or $BN = \mu.MD$

In Fig.15.7, $\angle BPC = r$ and CP = BC = CD

∴ BC + CD = PD

∴ $\Delta = \mu(PD) - \mu(MD) = \mu(PD - MD) = \mu.PM$

In ΔBPM, $\cos r = \dfrac{PM}{BP}$ or $PM = BP.\cos r$

But $BP = 2t$

∴ $PM = 2t \cos r$

$$\therefore \quad \Delta = \mu.PM = 2\mu t \cos r \tag{15.15}$$

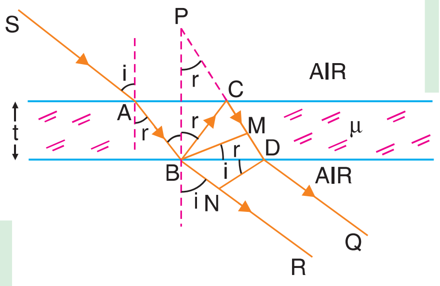


Fig. 15.7

Bright Fringes:

When the optical path difference $\Delta = m\lambda$, bright fringe occurs.

$$\therefore \quad 2\mu t \cos r = m\lambda \tag{15.16}$$

where m = 0,1,2,3,….

Dark Fringes:

When the optical path difference $\Delta = (2m + 1)\,\lambda / 2$, dark fringe occurs.

$$\therefore \qquad 2\mu\, t\, \cos\, r = \frac{(2m+1)}{2}\lambda \tag{15.17}$$

where m = 0,1,2,3,….

In case of transmitted light, the fringes are less distinct because the difference in amplitudes of BR and DQ is very large. However, when the angle of incidence is nearly 45° the fringes are more distinct.

15.4. HAIDINGER FRINGES

In thin films interference fringes are produced due to the path difference $2\mu\, t \cos r$ between the overlapping rays. For a given film the path difference may arise due to (*i*) the angle of refraction r inside the film or (*ii*) the change in thickness. We can express the change in path difference by differentiating the expression $2\,\mu\, t \cos r$.

$$\text{Change in path difference, } \delta(\Delta) = 2\mu\, t \cdot \delta(\cos\, r) + 2\mu\, \cos\, r\ (\delta\, t) \tag{15.18}$$

When the film is of **uniform** (constant) thickness, the change in path difference is only due to the change in r. If the thickness of the film is large, the path difference will change appreciably

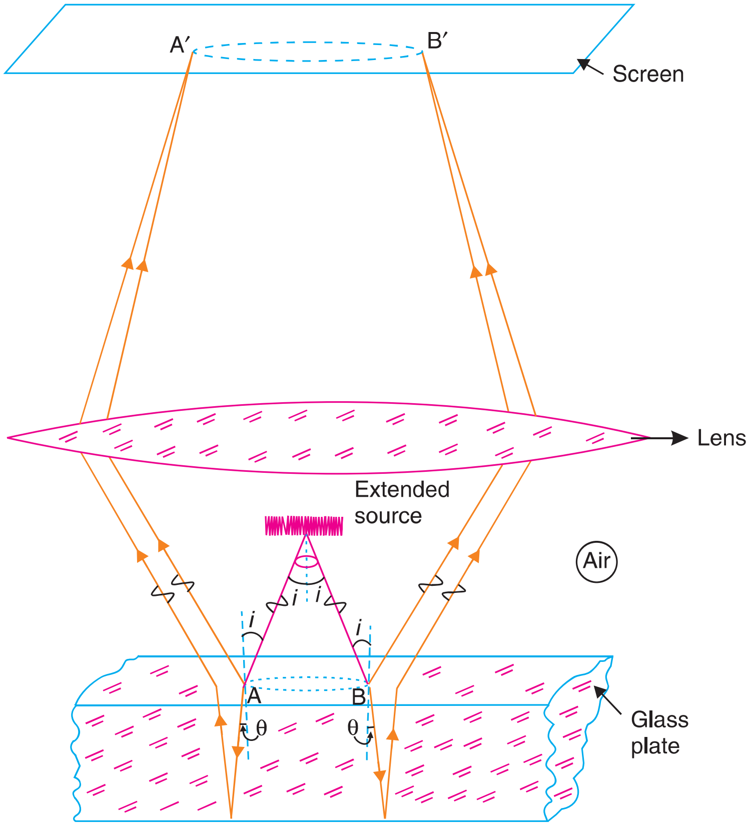


Fig. 15.8

even when *r* changes in a small way. Fringes are produced in this case due to the superposition of rays, which are equally inclined to the normal. These fringes are called **fringes of equal inclination**. The fringes of equal inclination are known as **Haidinger fringes.** In this case all the pairs of interfering rays of equal inclination pass through the plate as a parallel beam and hence meet at infinity. The other pairs of differrent inclination meet at different points at infinity. Therefore, they can be located with a telescope focussed to infinity. The fringes are therefore said to be *localized at infinity*.

To produce Haidinger fringes, the source must be an extended source, the film thickness must be appreciably large and the observing instrument is to be focussed for parallel rays.

Fig. 15.8 shows the formation of Haidinger fringes. Let us consider that a thin plate is illuminated by an extended monochromatic light source. A lens is arranged parallel to the plate and a screen is kept in the focal plane of the lens. Light from the extended source is incident on the plate in diverse directions. The waves propagating parallel to the plane of the page and falling on the plate at an angle *i* at points A and B get reflected from the top and bottom surfaces of the plate. The reflected pairs of waves will meet at points A′ and B′ respectively on the screen due to the focussing action of the lens. Depending on their path difference, the reflected waves produce either brightness or darkness on the screen. In fact the waves incident at the top surface of the plate at an angle *i* travel along the generators of a cone as shown in Fig. 15.8. Each pair of parallel reflected waves interfere at diametrically opposite points. Thus, a circular fringe is produced. Similarly, the waves incident at a different angle will produce a collection of identical points arranged along a circle of another radius. As a result, a system of alternating bright and dark circular fringes with a common centre will be observed on the screen.

Each fringe is characterized by a particular value of *m*. Bright fringes are produced when the condition $2\mu t \cos r = m\lambda$ is satisfied; and dark fringes are produced where the condition

$2\mu t \cos r = (2m+1)\lambda/2$ is satisfied. The parallel pairs of reflected rays meet only at infinity; therefore a lens is used to focus them. Accordingly, these fringes of equal inclination are said to be localized at infinity.

15.5. VARIABLE THICKNESS (WEDGE-SHAPED) FILM

Let us now study the interference of light in a film of varying thickness. *A thin film having zero thickness at one end and progressively increasing to a particular thickness at the other end is called a wedge.* A thin wedge of air film can be formed by two glass slides resting on each other at one edge and separated by a thin spacer at the opposite edge.

The arrangement for observing the interference pattern in a wedge shaped film is shown in Fig. 15.9(a). The wedge angle is usually very small and of the order of a fraction of a degree. When a parallel beam of *monochromatic* light illuminates the wedge from above, the rays reflected from its two bounding surfaces will not be parallel. They appear to diverge from a point near the film. The path difference between the rays reflected from the upper and lower surfaces of the air film varies along its length due to variation in film thickness. Therefore, alternate bright and dark fringes are observed on its top surface (see Fig. 15.9b). The fringes are localized at the top surface of the film.

When the light is incident on the wedge from above, it gets partly reflected from the glass-to-air boundary at the top of the air film. Part of the light is transmitted through the air film and gets reflected partly at the air-to-glass boundary, as shown in Fig. 15.10. The two rays BC and DE, thus reflected from the top and bottom of the air film, are coherent as they are derived from the same ray AB through *division of amplitude*. The rays are close enough if the thickness of the film is of the order of a wavelength of light. For small film thickness the rays interfere producing darkness or brightness depending on the phase difference. The thickness of the glass plates is large compared

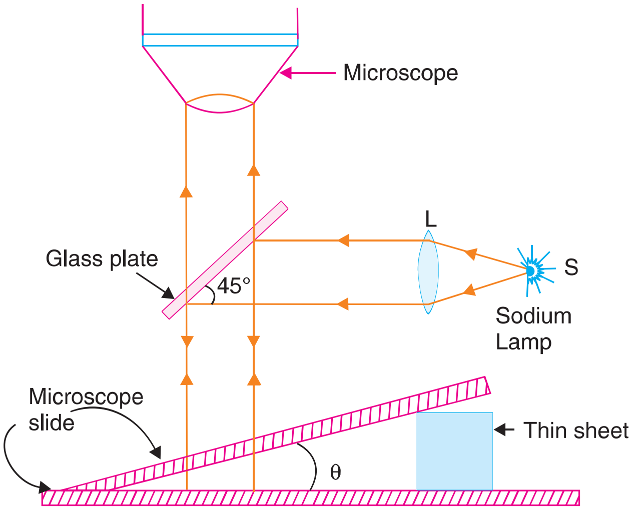


Fig. 15.9 (a)

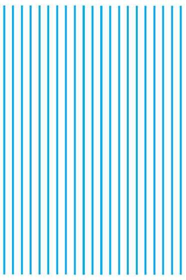


Fig. 15.9 (b)

with the wavelength of the incident light. Hence, the observed interference effects are entirely due to the wedge-shaped air film.

The optical difference between the two rays BC and DE is given by

$$\Delta = 2\mu\, t \cos r - \lambda/2$$

where λ/2 takes account the gain of half–wave due to the abrupt jump of π radians in the phase of the wave reflected from the bottom boundary of air – to – glass.

Maxima occur when the optical path difference $\Delta = m\,\lambda$. If the difference in the optical path between the two rays is equal to an *integral number of full waves*, then the rays meet each other in phase. The crests of one wave falls on the crests of the others and the waves *interfere constructively*. This needs that

$$\Delta = 2\mu\, t \cos r - \lambda/2$$

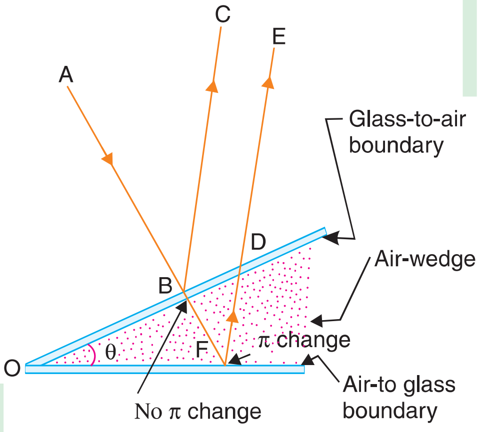


Fig. 15.10

Minima occur when the optical path difference is $\Delta = (2\text{ m} + 1)\,\lambda/2$. If the difference in the optical path between the two rays is equal to an *odd integral number of half-waves*, then the rays meet each other in opposite phase. The crests of one wave falls on the troughs of the others and *the waves interfere destructively*. It needs that

$$2\mu\, t \cos r = m\lambda.$$

Referring to Fig.15.11, let us say a dark fringe occurs at A where the relation

$$2\mu\, t \cos r = m\lambda$$

is satisfied. If normal incidence is assumed, $\cos r = 1$ and if the thickness of air film at A is denoted by $t_{1,}$ then at A

$$2\mu\, t_1 = m\lambda \tag{15.19}$$

The next dark fringe will occur, say, at C where the thickness CL = t_2. Then at C

$$2\mu\, t_2 = (m+1)\,\lambda \tag{15.20}$$

Subtracting eq. (15.19) from eq. (15.20), we get

$$2\mu\,(t_2 - t_1) = \lambda \tag{15.21}$$

But $\quad (t_2 - t_1) = BC$

$\therefore \quad 2\mu(BC) = \lambda$

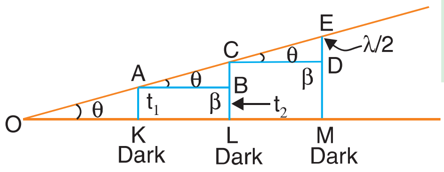


Fig. 15.11

or $$BC = \frac{\lambda}{2\mu} \tag{15.22}$$

From the Δ^{le}ABC, ∠CAB = θ and BC = AB tan θ

$$\therefore \quad (AB)\ \tan\,\theta = \frac{\lambda}{2\mu} \tag{15.23}$$

AB is the distance between successive dark fringes and it also equals the separation of the successive bright fringes. It is, therefore, called the **fringe width,β**. That is AB = β. We may write eq. (15.23) as

$$\beta = \frac{\lambda}{2\mu\,\tan\,\theta} \tag{15.24}$$

For small values of θ, tan θ ≈ θ.

$$\therefore \quad \beta = \frac{\lambda}{2\mu\theta} \tag{15.25}$$

As the quantities on the right side of the above equation are all constant, β is constant for a given wedge angle. According to equ.(15.25), an increase in the angle θ makes the fringes move closer. At an angle θ ≈ 1°, the interference pattern vanishes. On the other hand, if θ is gradually decreased, the fringe separation increases, and ultimately the fringes disappear as the faces of the film become parallel.

The interference pattern has the following salient features.

(*i*) Fringe at the apex is dark.
(*ii*) Fringes are straight and parallel.
(*iii*) Fringes are equidistant.
(*iv*) Fringes are localized.
(*v*) Fringes are of equal thickness.

(*i*) Fringe at the apex is dark: At the apex, the two glass slides are in contact with each other. Therefore, the thickness of the air film at the contact edge is negligible ($t \cong 0$). The optical path difference there becomes

$$\Delta = 2\mu t - \lambda/2 = 0 - \lambda/2 = -\lambda/2 \tag{15.26}$$

It implies that a path difference of λ/2 or a phase difference of π occurs between the reflected waves at the edge. The two waves interference destructively. Therefore, the fringe at the apex is always dark (See Fig. 15.12).

(*ii*) Straight and parallel fringes: Each fringe in the pattern is produced by the interference of rays reflected from sections of the wedge having the same thickness. The locus of points having the same thickness lie along lines parallel to the contact edge. Therefore, the fringes are straight. Since the fringes are equidistant [see (iii)], they will be parallel (See Fig. 15.12).

(*iii*) Equidistant fringes: The fringe width β is given by

$$\beta \approx \lambda/2\theta \qquad (15.27)$$

where λ is the wavelength of the incident light and θ is the angle of the wedge. As the quantities λ and θ are constants, β is constant for a given wedge angle. Therefore, the fringes are equidistant (see Fig.15.12).

(*iv*) Localized fringes: The fringes form very close to the top surface of the wedge and can be seen with a microscope.

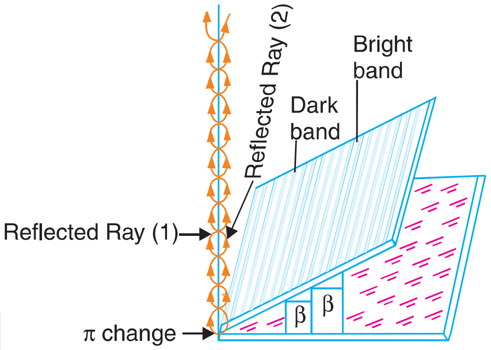


Fig. 15.12

(*v*) Fringes of equal thickness: In thin films of thickness of the order of a few λ, the rays from various parts of the film have almost the same inclination and hence the path difference between the overlapping waves changes mainly due to change of thickness. The fringes produced in such cases are mainly due to the variation in thickness of the film. Each fringe will be the locus of points of the same thickness. Such fringes are called **fringes of equal thickness**.

15.5.1. DETERMINATION OF THE WEDGE ANGLE

The wedge angle θ can be experimentally determined with the help of a travelling microscope. Using the microscope the positions of dark fringes at two distant points Q and R are noted (Fig. 15.13). Let the distance OQ be x_1 and OR be x_2. Let the thickness of the wedge be t_1 at Q and t_2 at R.

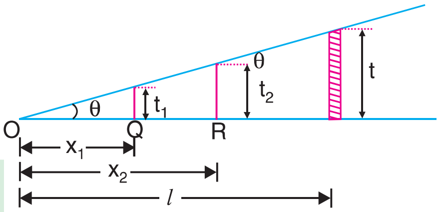


Fig. 15.13

The dark fringe at Q is given by

$$2\mu t_1 = m\lambda \qquad (15.28)$$

But as θ is very small, we can write

$$t_1 = x_1 \tan\theta \cong x_1\theta$$

$$\therefore \quad 2\mu\, x_1\, \theta = m\lambda \qquad (15.29)$$

We can write similarly for the dark fringe at R as

$$2\mu\, x_2\, \theta = (m+N)\lambda \qquad (15.30)$$

where N is the number of dark fringes lying between the positions Q and R. Subtracting equ.(15.29) from equ.(15.30), we get

$$2\mu(x_2-x_1)\theta = N\lambda$$

$$\therefore \quad \theta = \frac{N\lambda}{2\mu\left(x_2 - x_1\right)} \qquad (15.31)$$

In case of air μ = 1 and the above relation reduces to

$$\theta = \frac{N\lambda}{2\left(x_2 - x_1\right)} \qquad (15.32)$$

15.5.2. DETERMINATION OF THE THICKNESS OF THE SPACER

The thickness of the spacer used to form the wedge shaped air film between the glass slides can be determined from the above measurements. If ‘t’ is the thickness of the spacer (foil or wire) used, we can write from Fig.15.13 that

$$t = l \tan \theta \cong l\,\theta \qquad (15.33)$$

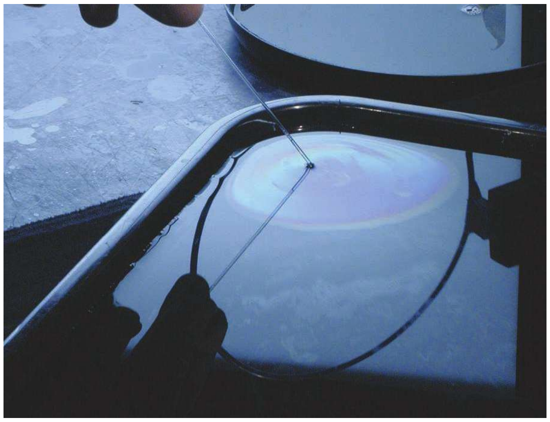
where l is the length of the air wedge. Using the equ.(15.32) into equ.(15.33), we obtain

$$\therefore \qquad t = \frac{lN\lambda}{2(x_2 - x_1)} \qquad (15.34)$$

15.5.3. FIZEAU FRINGES

If a parallel beam of light is incident perpendicularly or nearly perpendicular on a variable thickness film, then dark and bright fringes are seen in reflected light. These fringes are fringes of equal thickness, because each fringe corresponds to lines of equal optical thickness. These fringes or localized fringes and are observed at the top of the film. These localized fringes of equal thickness are known as *Fizeau fringes*. Contours following lines of equal optical thickness are seen if the area is large. The fringes may be obtained in case of thick films also if the source is small.

15.5.4. COLOURS IN THIN FILMS


Colours in thin films of oil.

The colours exhibited in reflection by thin films of oil, mica, soap bubbles and coatings of oxides on heated metals etc are due to interference of light from an extended source such as sky. Thomas Young explained the origin of colours in thin films. It may be understood as follows. The films are usually observed by reflected light. The eye looking at the thin film receives light waves reflected from the top and bottom surfaces of the film. The reflected rays are very close to each other and are in a position to interfere. The optical path difference between the interfering rays is $\Delta = 2\mu t \cos r - \lambda/2$. It is seen that the path difference depends upon the thickness t of the film, the wavelength λ and the angle r, which is related to the angle of incidence of light on the film. White light consists of a range of wavelengths and for specific values of t and r, waves of only certain wavelengths (colours) constructively interfere. Therefore, only those colours are present in the reflected light. The other wavelengths interfere destructively and hence are absent from the reflected light. Hence, the film at a particular point appears coloured. As the thickness and the angle of incidence vary from point to point, different colours are intensified at different places. The colours seen are not isolated colours, as at each place there is a mixture of colours. The composition of colours is different at different places and contours of impressive hues are observed over the entire surface of the film.

15.6. NEWTON’S RINGS

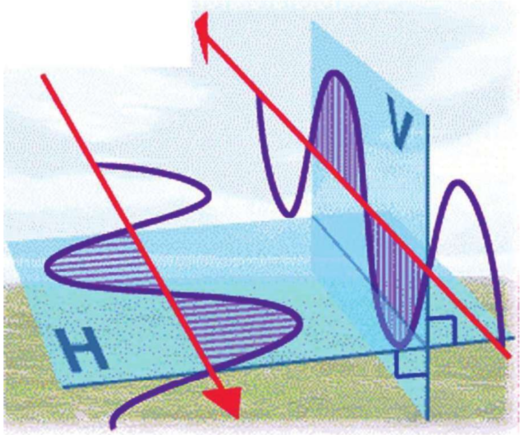
Newton’s rings are an example of fringes of equal thickness. Newton’s rings are formed when a plano-convex lens P of a large radius of curvature placed on a sheet of plane glass AB is illuminated from the top with monochromatic light (Fig. 15.14). The combination forms a thin circular air film of variable thickness in all directions around the point of contact of the lens and the glass plate. The

20
CHAPTER

Polarization

20.1. INTRODUCTION

Interference and diffraction phenomena proved that light is a wave motion and enabled the determination of the wavelength. However, they do not give any indication regarding the character of the waves. Whether the light waves are longitudinal or transverse, or whether the vibrations are linear or circular cannot be deduced from the above two phenomena, as all kinds of waves under suitable conditions exhibit interference and diffraction. In 1816 Arago and Fresnel showed that light waves vibrating in mutually perpendicular planes do not interfere. In 1817 Thomas Young postulated that light waves are *transverse waves* and explained



Polarization

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- Types of Polarization
- Polaroid Sheets
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- Effect of Polarizer on Light of Different Polarizations
- Experimental Determination of Principal Refractive Indices
- Phase Difference Between E-ray and O-ray
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- Anisotropy Induced by Mechanical Strain
- Photoelasticity

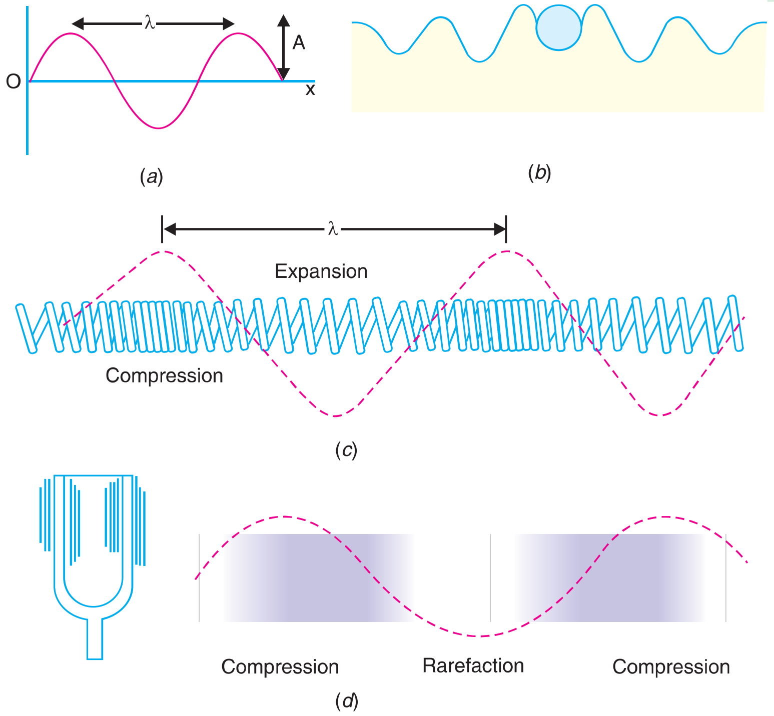
the absence of interference between light waves polarized in mutually perpendicular planes. Thus, the existence of polarization property is a direct consequence of light being a transverse wave. Light coming from common light sources is unpolarized. It can be transformed into different types of polarization using optical devices. The state of polarization cannot be perceived by an unaided human eye. An understanding of polarization is essential for understanding the propagation of electromagnetic waves guided through wave-guides and optical fibres. Polarized light has many important applications in industry and engineering. One of the most important applications is in liquid crystal displays (LCDs), which are widely used in wristwatches, calculators, TV screens, etc.

20.2. POLARIZATION

Waves are basically of two types: (*i*) longitudinal waves and (*ii*) transverse waves.

(*i*) A wave in which particles of the medium oscillate to and fro along the direction of propagation is called a **longitudinal wave**. Waves produced on a spring and sound waves are examples of longitudinal waves. The longitudinal wave consists of alternate compressions and rarefactions, as shown in Fig.20.1 (c) & (d).

(*ii*) A wave in which every particle of the medium oscillates up and down at right angles to the direction of wave propagation is called a **transverse wave**. Ripples on water surface and waves on a rope are examples of transverse waves. The wave propagates in the form of alternating crests and troughs, as shown in Fig.20.1 (a) & (b).



(*a*) (*b*)

(*c*)

(*d*)

Fig. 20.1

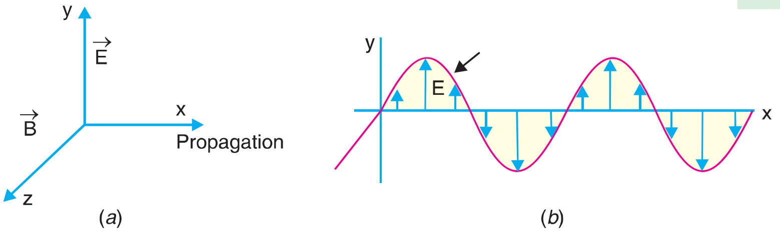
In a longitudinal wave, all directions perpendicular to the wave propagation are equivalent. On the other hand, a preferential direction normal to the wave propagation exists in a transverse wave.

The preferential direction in a transverse wave is the direction of vibration of the particles and it differs from all other directions. The existence of a preferential direction for a transverse wave leads to the characteristic phenomenon known as polarization. Polarization is not found with longitudinal waves as they do not possess a directional property. Thus, polarization is specific to transverse waves.

Light waves are transverse waves consisting of electric and magnetic fields vibrating perpendicular to each other and to the direction of propagation. The vibrating electric field vector and the direction of propagation of the wave constitute a plane. There is an infinite number of such planes around the direction of propagation. In an ideal light wave, the vibrations of electric vector are confined to a single plane. In practice, light sources emit a mixture of light waves whose planes of vibration are randomly oriented about the direction of propagation. Such random orientation of vibration planes gives rise to symmetry about the wave propagation direction. As a result, the transverse nature of the wave gets concealed. The process of removing the symmetry and bringing in one-sidedness in the light wave is called **polarization**.

20.3. UNPOLARIZED AND POLARIZED LIGHT

Light wave is a transverse electromagnetic wave made up of mutually perpendicular, fluctuating electric and magnetic fields. Fig.20.2 (*a*) shows the electric field in the *xy*- plane, the magnetic field in the *xz*-plane and the propagation of the wave in the *x*- direction. The right-hand part of the diagram shows the variation of the electric field in space as the wave propagates. Traditionally, light wave is described by the **electric field vector**, ***E***, and accordingly, only the electric field vector is shown in Fig.20.2 (*b*).



(*a*) (*b*)

Fig. 20.2: A light wave is described by the electric field vector, *E*

As the electric field is a vector, it points in a particular direction in space. The **polarization** of an electromagnetic wave refers to the orientation of its electric field vector *E*. If we could view a light wave coming from an ordinary source towards us, then we would observe that the direction of *E* is randomly varying with time on a very fast scale. The light from an incandescent bulb, for example, emits a mixture of light waves with electric field components that change randomly on a scale of 10^{-14} s, almost as fast as the optical frequency itself. As a result, the **direction of oscillation of the electric field vector in an ordinary light beam occurs in all the possible planes perpendicular to the beam direction,** as illustrated in Fig.20.3. A light wave, in which **E-**vector oscillates in more than one plane, is referred to as **unpolarized light**. Light emitted by the sun, by an incandescent lamp, or by a candle flame is unpolarized light.

Polarized Light

Polarized light is not produced naturally. It is obtained by converting natural light into polarized light using optical elements. The process of transforming unpolarized light into polarized light is polarization. A polarized light wave is a light wave with a definite direction of oscillation of the *E*- vector, which occurs in a *single plane* or in *some specific way*. For example, the wave in Fig.20.2 (b) is a polarized wave. **Polarized light** is the light that contains waves that only fluctuate in one specific plane.

We designate the plane created by the direction of oscillation of the electric field vector ***E*** and the direction of propagation of the beam as the **plane of polarization of light wave**. Thus, the *xy*-plane is the plane of polarization in Fig.20.2 (*b*).

20.4. NATURAL LIGHT IS UNPOLARIZED LIGHT

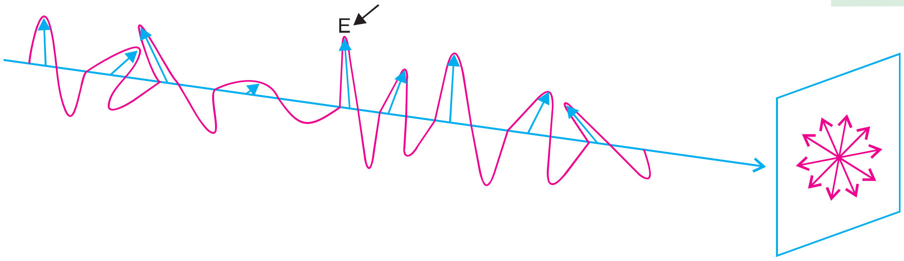


Fig. 20.3: Natural light is unpolarized

We mentioned earlier that light from the ordinary light sources is unpolarized. Let us find out the reason. We know that atoms emit light. Any light source consists of a very large number of atomic emitters. Each atom radiates, at a specific instant, a **wave packet** (also known as a **wave train**) that lasts for about 10^{-8} s. Light radiated by a source is a mixture of wave packets emitted by different atoms at different instances (see Fig.20.3). Individual wave packets will be polarized, but each wave packet has its own polarization, and they are not correlated in any way. There is no continuity of plane of polarization and the plane of polarization varies from wave packet to wave packet in a completely random manner. The polarization of the waves determined at any particular spot will fluctuate randomly, and very rapidly, with no preferred direction. Any direction is equally likely, and the usual graphical representation of ordinary light is shown in the right-hand figure in Fig.20.4 (*a*). Fig.20.4 (*a*) is a fictitious diagram. It only implies that the natural light consists of electric field vectors of many possible orientations lying at different angles between 0 and 360º and hence symmetrically distributed about the direction of propagation.

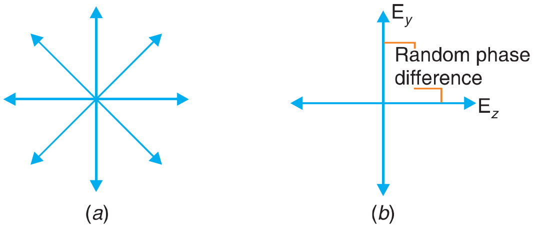


Fig.20.4: (*a*) Pictorial representation of Natural light. (*b*) Unpolarized light is viewed as a combination of *incoherent* vertically and horizontally polarized waves.

The concept of unpolarized light is rather difficult to visualize. In general, it is looked upon as consisting of an average of half of its vibrations horizontally polarized and half of its vibrations vertically polarized. Due to the random distribution of the optical vectors, the amplitude of the vertical and horizontal component vectors are taken as equal; however, the **two components are incoherent**, *i.e.* have a randomly changing phase difference. In view of this, unpolarized is pictorially represented by two electric vectors as shown in Fig.20.4 (*b*).

A comparison of Unpolarized and Polarized light

Unpolarized light	Polarized light
1. Consists of waves with planes of vibration equally distributed in all directions about the ray direction.	Consists of waves having their electric vector vibrating in a single plane normal to ray direction.
2. Symmetrical about the ray direction	Asymmetrical about the ray direction.
3. Produced by conventional light sources.	Is to be obtained from unpolarized light with the help of polarizers.
4. May be regarded as the resultant of two *incoherent* waves of equal intensity but polarized in mutually perpendicular planes.	May be regarded as the resultant of two mutually perpendicular *coherent* waves having zero phase difference.

20.5. TYPES OF POLARIZATION

The polarization of a light wave describes *the shape and locus of the tip of the E vector* (in the plane perpendicular to the direction of propagation) *at a given point in space as a function of time*. Depending upon the locus of the tip of the *E* vector, light may exhibit three different states of polarization. They are

(*i*) plane or linear polarization,
(*ii*) elliptical polarization and
(*iii*) circular polarization.

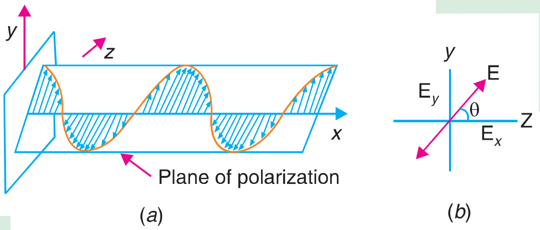
Apart from these, the light may also be partially polarized.

An unaided human eye cannot identify the state of polarization of light. However, some insects and animals possess polarization sensitive vision.

20.5.1 PLANE POLARIZED LIGHT

Plane polarized light waves are light waves in which the oscillations occur in a single plane. In a plane-polarized wave, the oscillations of electric field vector *E* are strictly confined to a single plane *perpendicular* to the direction of propagation. As the direction of the field vector at some point in space and time lies along a line in a plane perpendicular to the direction of wave propagation, a plane-polarized wave is also known as a **linearly polarized** wave.

With linear polarization, the orientation of the *E*-vector stays constant at a point in space. That is, the direction of *E* does not vary with time, but its magnitude varies sinusoidally with time. If the field is pointing either up or down, we call it **vertical polarization**, and if it's pointing either right or left, we call it **horizontal polarization**. Electric fields are not restricted to pointing exactly along vertical or horizontal axes, but can be at any arbitrary angle to those axes. Linearly polarized light, polarized at any arbitrary angle, may be regarded as a combination of horizontally and vertically polarized light, with appropriate amplitude, and which are oscillating **in phase** or **180° out**



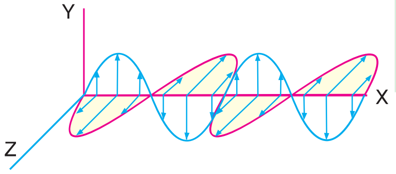
(*a*) (*b*)

A light wave polarized in an arbitrary direction

Fig.20.5

of phase. The **key point** is that the two component waves are **coherent**.

Let ***x*** be the direction of travel of the light and, *y* and *z* be directions in the plane of the electric field. The electric field makes a constant angle to the *z*-direction, as shown in the Fig.20.5 (*a*). The wave in Fig.20.5 (*a*) is the resultant wave due to superposition of two **coherent** linearly polarized waves, oscillating in phase, as shown in Fig.20.6.

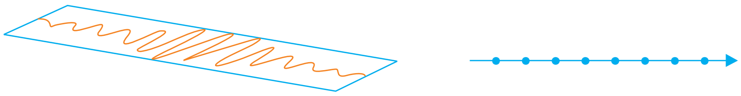


A linearly polarized wave is viewed as a combination of *coherent* vertically and horizontally polarized waves.

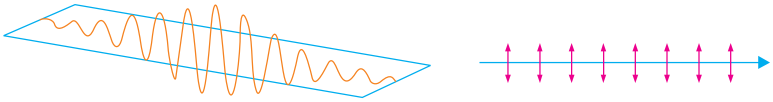
Fig.20.6

Representation of linearly polarized light in diagrams

Linearly polarized light is represented in diagrams as shown in Fig.20.7. When the electric field vector oscillates horizontally in a direction perpendicular to the plane of the paper, the light wave is represented by dots (Fig.20.7 *a*). When the electric field vector oscillates vertically in the plane of the paper, the light wave is represented by arrows, as shown in Fig.20.7 (*b*).



(*a*) Horizontal Linear Polarization



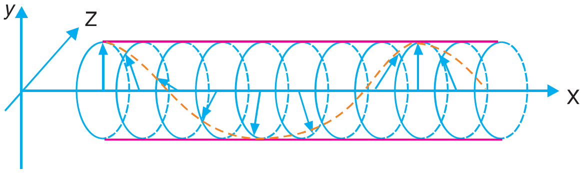
(*b*) Vertical Linear Polarization

Representation of linearly polarized light in diagrams

Fig. 20.7

20.5.2 CIRCULARLY POLARIZED LIGHT

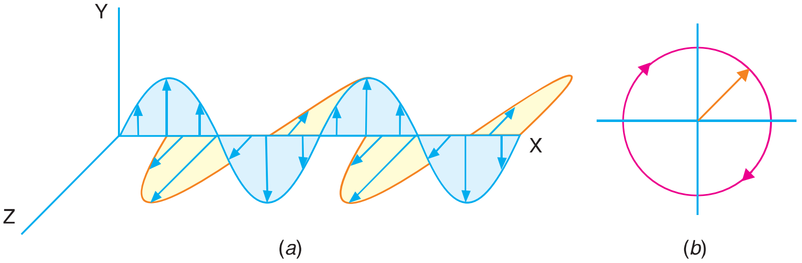
A light wave is said to be ***circularly polarized***, if in the course of wave propagation, the magnitude of the electric vector *E* stays constant but it rotates at a constant rate about the direction of propagation and sweeps a circular helix in space, as shown in Fig.20.8. This is a picture in terms of the **space variation** of *E***.** Alternately, if we could see the wave advancing towards our eyes, we would find that the tip of the *E* vector tracing a circle in space, completing one revolution within one wavelength. Hence, the state of polarization is called *circular polarization*. In, circularly polarized light, there is no preference to specific direction of oscillation.



Space variation of *E*; *E* vector sweeps a circular helix in space

Fig. 20.8

A circularly polarized light wave may be regarded as the resultant wave produced due to superposition of two coherent linearly polarized waves of *equal amplitude* oscillating in mutually perpendicular planes, and are out of phase by 90°.

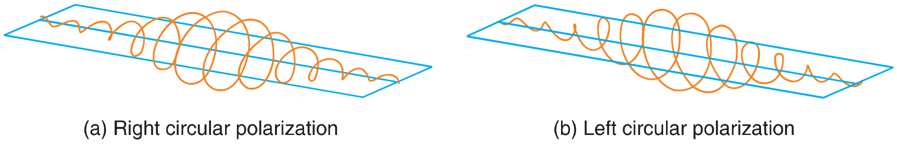


Circularly polarized wave is a combination of horizontally polarized and vertically polarized waves that are out of phase by 90° and having equal amplitudes.

Fig. 20.9

Let us again consider two linearly polarized waves having equal amplitude, out of which one is polarized in *z*-direction (horizontally polarized wave) and the other in *y*-direction (vertically polarized wave). Let us further assume that they are **coherent** and out of phase by 90° (see Fig.20.9a). At some instant, the *E*-field vector of *z*-polarized wave will have maximum amplitude and the *E*-field vector of y-polarized wave will be at zero. At that instant, the polarization is horizontal. A little time later, the *z*-polarized wave has decreased a little, while the *y*-polarized wave has started to increase. Then, the light looks like it is polarized at a slight angle— mostly horizontal, but with a small vertical component. A little while later, the *z*-component has decreased some more, and the *y*-component has increased some more, and the angle is greater. And so on. Eventually, the *y*-polarized wave is at a maximum, and the *z*-polarized wave is zero, and we have pure vertical polarization. If we stand at one point in space, and look at the direction of the wave, we will observe that the *E*-vector sweeps a circle in space. Hence, it is called circularly polarized wave. Note that the *oscillations of the resultant E-vector do not take place in a single plane.*

If the rotation of the tip of *E* is clockwise as seen by an observer looking back towards the source, then the wave is said to be **right-circularly polarized** (Fig.20.10 *a*). If the tip of *E* rotates anti-clockwise, then the wave is said to be **left-circularly polarized** (Fig.20.10. *b*). This is a description of circular polarization in terms of the **time variation** of *E*.



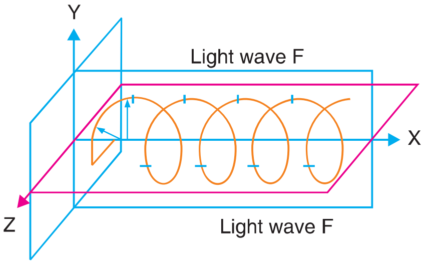
(a) Right circular polarization

(b) Left circular polarization

Fig. 20.10

20.5.3 ELLIPTICALLY POLARIZED LIGHT

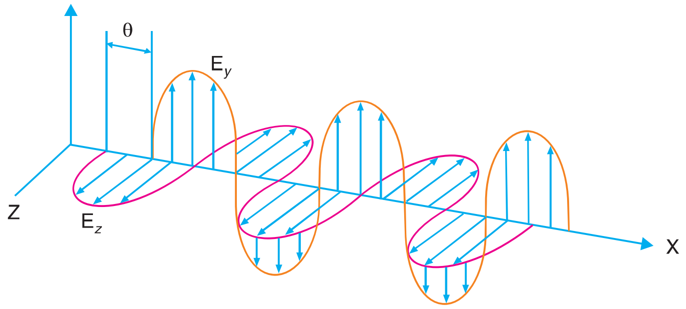
A light wave is said to be ***elliptically polarized***, if the magnitude of electric vector *E* changes with time and the vector *E* rotates about the direction of propagation and sweeps a flattened helix in space, as shown in Fig.20.11. This is a description of elliptically polarized light in terms of the **space variation** of ***E***. Alternately, if we imagine that we are looking at the light wave advancing towards us, we would observe that the tip of the *E* vector traces an ellipse in space. Hence, it is called elliptically polarized light. This is a description of elliptical polarization in terms of the **time variation** of *E*.



Space variation of **E**; **E** vector sweeps a flattened helix in space

Fig. 20.11

An elliptically polarized light wave may be regarded as the resultant wave produced due to superposition of two **coherent** linearly polarized waves of different amplitudes, oscillating in mutually perpendicular planes and are out of phase. If waves of differing amplitude are related in phase by 90°, or if the relative phase difference is other than 90° then the resultant light wave is elliptically polarized.



Elliptically polarized wave is a combination of horizontally polarized and vertically polarized waves that are of different amplitudes and out of phase by θ

Fig. 20.12

Let us consider two linearly polarized waves having different amplitudes, out of which one is polarized in *x*-direction and the other in y-direction. Let us further assume that they are **coherent** and out of phase by an arbitrary angle θ (see Fig.20.12). The *E*-field vector of *Z*-polarized wave will have maximum amplitude at times when the *E*-field vector of *y*-polarized wave is a minimum and vice versa (Fig.20.12). Then the oscillations of the resultant *E*-vector do not take place in a single plane. The magnitude of resultant *E*-vector varies at each point in space and the overall rotation of the *E*-vector has the appearance of a flattened helix.

When we are looking back towards the source, if the rotation of *E* vector occurs clockwise, it is said to be a **right-elliptically-polarized** wave. If it rotates anti-clockwise, it is said to be a **left-elliptically polarized** wave.

20.5.4 PARTIALLY POLARIZED LIGHT

Usually, light is neither totally polarized nor unpolarized but a mixture of the two types. It can be viewed as a mixture of plane polarized light and unpolarized light. Partially polarized light is represented as shown in Fig.20.13.

Partially polarized light, like natural light, can be represented in the form of a superposition of two incoherent plane-polarized waves with mutually perpendicular planes of oscillations. In case of natural light the amplitude of these waves is the same and for partially polarized light, it is different.

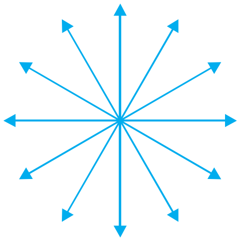


Fig. 20.13

Degree of Polarization:

If we pass partly polarized light through a polarizer, and if we rotate the polarizer about the direction of the ray, the intensity of the transmitted light will change within the limits from I_{max} to $I_{min.}$. The transition from one of these values to the other will occur upon rotation through an angle of 90°. We define the degree of polarization with the help of the following expression.

$$P = \frac{I_{max} - I_{min}}{I_{max} + I_{min}} \qquad \text{... (20.1)}$$

% polarisation

$$\% \text{ polarization} = \frac{(I_{max} - I_{min})}{(I_{max} + I_{min})} \times 100 \qquad \text{... (20.2)}$$

For plane polarized light $I_{min} = 0$, and hence $P = 1$ and the % polarization is 100%. For natural light, $I_{max} = I_{min}$, and hence $P = 0$ and the % polarization is zero. If $I_{max} = 2I_{min}$, $P = 0.33$ and % polarisation = 100/3 = 33%.

The concept of the degree of polarization cannot be applied to elliptically and circularly polarized light.

20.6. PRODUCTION OF PLANE POLARIZED LIGHT

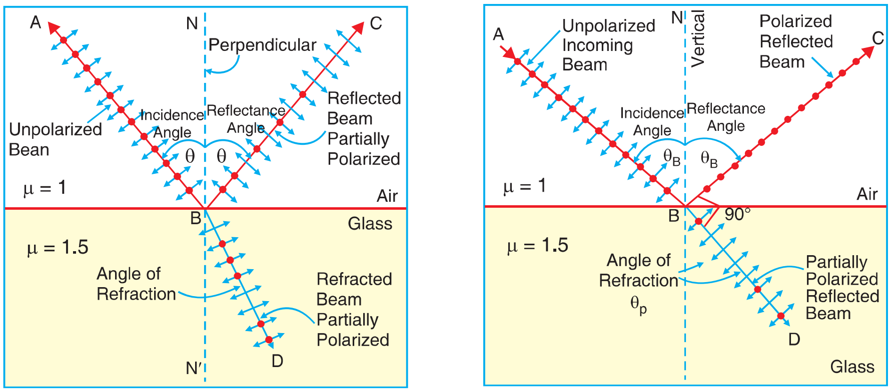
We now study the methods of producing plane-polarized light. Plane polarized light may be produced from unpolarized light using the following five optical phenomena:

(*i*) reflection, (*ii*) refraction, (*iii*) scattering, (*iv*) selective absorption (dichroism), and (*v*) double refraction. Out of these five, the phenomena of selective absorption and double refraction are helpful in practical production of plane polarized light.

20.6.1 POLARIZATION BY REFLECTION FROM DIELECTRIC SURFACES

E.L.Malus, French engineer discovered in 1808 polarization of light by reflection. He noticed that when natural light is incident on a smooth surface, at a certain angle the reflected beam is plane polarized. The extent to which polarization occurs is dependent upon the angle at which the light is incident on the surface and upon the material, which the surface is made of. Metallic surfaces reflect light with a variety of vibrational directions; such reflected light is unpolarized. However, light that is specularly reflected from dielectric surfaces, such as asphalt roadways, water etc, is linearly polarized. If the extent of linear polarization is large, a person perceives **glare** from such surfaces. On bright sunny days, the glare caused by sunlight on a roadway or a field of snow, may be almost blinding to the human eye.

When light wave is incident on a boundary between two dielectric materials, part of it is reflected, and part of it is transmitted.



(*a*) (*b*)

(*a*) Reflection and Refraction at the surface between two media (*b*) Brewster Law

Fig. 20.14

Fig.20.14 (*a*) shows an unpolarized light beam AB incident on a glass surface. The incident ray AB and the normal NBN′ define the plane of incidence. The electric vector *E* of the ray AB can be resolved into two components, one perpendicular to the plane of incidence and the other lying in the plane of incidence. The perpendicular component is represented by **dots** and is called the ***s*-component**. The parallel component is represented by the **arrows** and is called the ***p*-component**. In case of completely unpolarized light the two components are of equal magnitude. At a particular angle θ_B, the reflection coefficient for *p*-component goes to zero and the reflected beam does not contain any *p*-component (see Fig.20.14 *b*). It contains only *s*-component and is totally *plane polarized.* The angle θ_B is called the **polarizing angle** or **Brewster's angle**.

This particular method of polarizing light is not advantageous, as the intensity of the reflected beam is very small.

20.6.1.1 Brewster's Law

Sir David Brewster performed a series of experiments on the polarization of light by reflection at a number of surfaces. He found that the polarizing angle depends upon the refractive index of the medium. In 1892, Brewster proved that **the tangent of the angle at which polarization is obtained by reflection is numerically equal to the refractive index of the medium.** If θ_B is the angle and m is the refractive index of the medium, then

$$\mu = \tan \theta_B \qquad \text{... (20.3)}$$

This is known as Brewster's law.

If natural light is incident on a smooth surface at the polarizing angle, it is reflected along *BC* and refracted along *BD*, as shown in Fig.20.14 (*b*). Brewster found that the maximum polarization of reflected ray occurs when it is at right angles to the refracted ray. It means that $\theta_B + r = 90^\circ$.

$$\therefore \quad r = 90^\circ - \theta_B \qquad \text{... (20.4)}$$

According to Snell's law,

$$\frac{\sin \theta_B}{\sin r} = \frac{\mu_2}{\mu_1} \qquad \text{... (20.5)}$$

where μ_2 is the absolute refractive index of reflecting surface and μ_1 is the refractive index of the surrounding medium. It follows from equ.(20.4) and equ.(20.5) that

$$\frac{\sin \theta_B}{\sin (90° - \theta_B)} = \frac{\mu_2}{\mu_1}$$

or
$$\frac{\sin \theta_B}{\cos \theta_B} = \frac{\mu_2}{\mu_1}$$

∴
$$\tan \theta_B = \frac{\mu_2}{\mu_1} \qquad \text{... (20.6)}$$

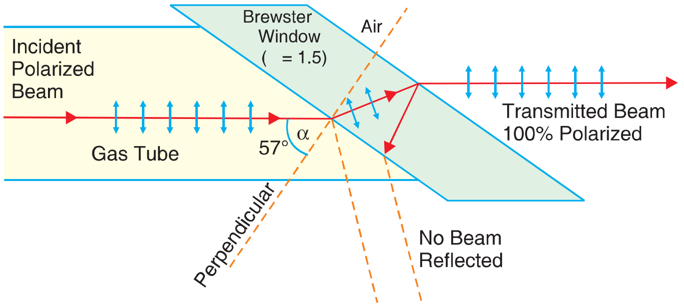
Equ.(20.6) shows that the polarizing angle depends on the refractive index of the reflecting surface. The polarizing angle q_B is known as **Brewster angle**. Light reflected from any angle other than Brewster angle is partially polarized.

Application of Brewster's law:

(*i*) Brewster's law can be used to determine the refractive indices of opaque materials.

(*ii*) It helps us in calculating the polarizing angle necessary for total polarization of reflected light for any material if its refractive index is known. However, the law is not applicable for metallic surfaces.

(*iii*) In gas lasers it is common to arrange two glass windows at the two ends of the laser tube. The windows are arranged at Brewster angle to the axis of the laser tube and hence they are called **Brewster windows**. The light beam traveling between the mirrors of the laser is reflected many times from these mirrors. Since the mirrors are at Brewster angle, all the light that is polarized perpendicular to the beam plane is emitted out of the laser cavity at early stage. In the gas tube remains only radiation polarized in the beam plane. The advantage of this arrangement is that the beam has no reflection losses, since only the transmitted polarized beam is traveling between the mirrors. The radiation out of these lasers is polarized as can be seen in Fig.20.15.



Brewster angle window at the end of gas laser
Fig. 20.15

(*iv*) Another application utilises the Brewster angle for transmitting a light beam into or out of an optical fibre without reflection losses.

20.6.2 POLARIZATION BY REFRACTION - PILE OF PLATES

When unpolarized light is incident at Brewster angle on a smooth glass surface, the reflected light is totally polarized, while the refracted light is partially polarized. If natural light is transmitted through a single plate, the transmitted beam is only partially polarized. If a stack of glass plates is used instead of a single plate, reflections from successive surfaces occur leading to the filtering of the s-component in the transmitted ray. Ultimately, the transmitted ray consists of p-component alone. It is found that a stack of about 15 glass plates is required for this purpose. The glass plates are supported in a tube of suitable size and inclined at an angle of about 33° to the axis of the tube, as shown in Fig.20.16. Such an arrangement is called a **pile of plates**. Unpolarized light enters the tube and is incident on the plates at Brewster angle and the transmitted light will be totally polarized parallel to the plane of incidence.

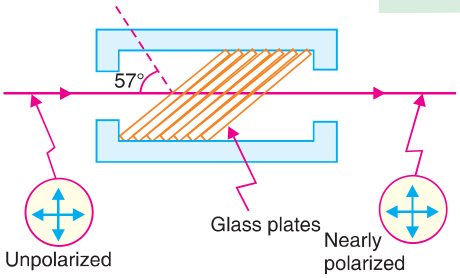


Fig. 20.16

20.6.3 POLARIZATION BY SCATTERING

If a narrow beam of natural light is incident on a transparent medium containing a suspension of ultramicroscopic particles, the light scattered is partially polarized. The incident light causes electrons in the scattering medium to vibrate. A vibrating electron emits most light in a direction perpendicular to its vibration and none along the direction of its vibration. The electric field of the emitted radiation is parallel to the direction of electron vibration. Hence light scattered through about 90° with respect to the incident direction is strongly polarized. The direction of vibration of E vector in the scattered light will be perpendicular to the plane defined by the direction of propagation and the direction of observation, *i.e.*, the plane of the paper, as illustrated in Fig.20.17.

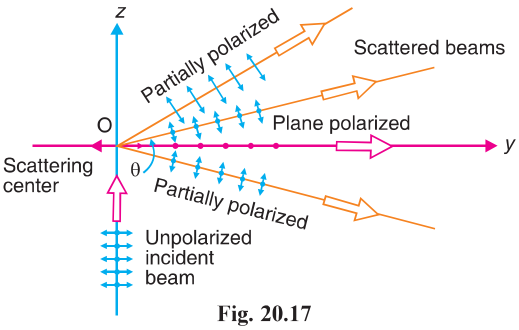


Fig. 20.17

The light from a blue sky is quite strongly polarised, particularly at 90° from the sun. It is not completely polarised because a significant amount of sunlight has undergone multiple-scattering, i.e. has been scattered more than once. Light scattered twice through a total angle of 90° would be less polarised than light scattered once.

20.6.4 POLARIZATION BY SELECTIVE ABSORPTION

A number of crystalline materials absorb more light in one incident plane than another, so that light progressing through the material become more and more polarized as they proceed. This difference in the absorption for the light rays is known as **selective absorption** or **dichroism**. Biot discovered this phenomenon in 1815. When natural light passes through a crystal such as tourmaline, it is split into two components, which are polarized in mutually perpendicular planes. The crystal absorbs light that is polarized in a direction parallel to a particular plane in the crystal but freely transmits the light component polarized in a direction perpendicular to that plane. If the crystal is of proper thickness, one of the components is totally absorbed and the other component emerging from the crystal is linearly polarized. Selective absorption is illustrated in Fig.20.18.

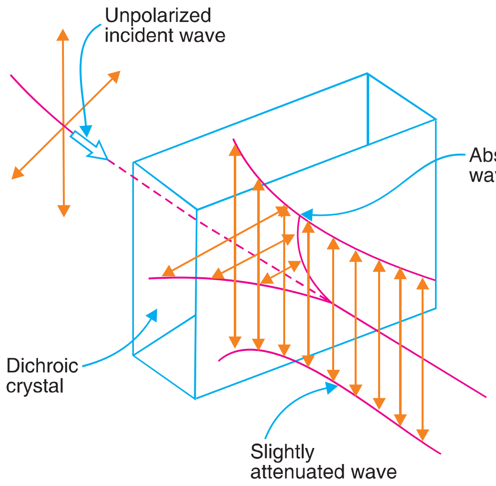


Fig. 20.18

20.6.5 POLARIZATION BY DOUBLE REFRACTION

When a beam of unpolarized light is incident on the surface of an anisotropic crystal such as calcite or quartz, it is found that it will separate into two rays (see Fig.20.19) that travel in different directions. This phenomenon is called **birefringence** or **double refraction**. The two rays are known as **ordinary ray** (**o-ray**) and **extraordinary ray** (**e-ray**), which are linearly polarized in mutually perpendicular directions. A single linearly polarized ray is obtained in practice through elimination of one of the two polarized rays.

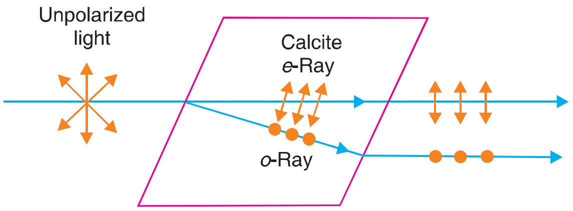


Fig. 20.19

20.7. POLAROID SHEETS

In 1928 E. H. Land invented Polaroid sheets, which utilize the phenomenon of selective absorption. The sheets are fabricated as follows. A clear plastic sheet of long chain molecules of PVA (polyvinyl alcohol) is heated and then stretched in a given direction to many times its original length. During the stretching process the PVA molecules become aligned along the direction of stretching. The sheet is then laminated to a rigid sheet of plastic to stabilise its size.It is then exposed to iodine vapour. The iodine atoms attach themselves to the straight long chain PVA molecules and consequently form long parallel conducting chains. The iodine atoms provide electrons, which can move easily along the aligned chains, but not perpendicular to them. When natural light is incident on the sheet, the electromagnetic vibrations that are in a direction parallel to the alignment of the iodine atoms are strongly absorbed because of the dissipative effects of the electron motion in the chains. Consequently, only those vibrations in a direction perpendicular to the direction of molecular chains are transmitted. Thus, the light transmitted through the polaroid sheet is polarized. A sheet fabricated according to this process is known as H-sheet.

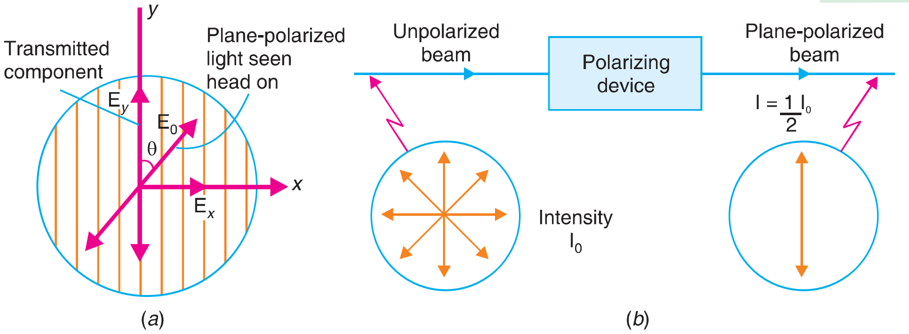
These sheet polarizers are inexpensive and can be made in large sizes. Polaroid sheets are widely used in sunglasses, camera filters etc to eliminate the unwanted glare from objects.

Polaroid sheets are extensively used for the production and detection of linearly polarized light.

20.8. POLARIZER AND ANALYZER

A *polarizer* is an optical element, which utilizes the phenomenon of selective absorption or double refraction, and transforms unpolarized light into polarized light. Plane polarized light is obtained by eliminating one of the two components in the unpolarized light. When natural light is incident on a polarizer, the E-field component that is parallel to the chains of iodine atoms induces current in the conducting chains and is therefore strongly absorbed. Consequently, the light transmitted contains only the component that is perpendicular to the direction of molecular chains. The direction of E-vector in the transmitted beam corresponds to the **transmission axis** of the Polaroid sheet.

Effect of polarizer on natural light



(*a*) Action of polarizer on linearly polarized wave
(*b*) The intensity of an unpolarized beam reduces to half after passing through a polarizer.

Fig. 20.20

Let us now understand the action of polarizer on the incident unpolarized light. Let us consider unpolarized light incident on a polarizer with the electric vector E_0 making an angle θ with respect to the *transmission axis* of the polarizer. The electric vector E_0 may be resolved into its component vectors lying parallel and perpendicular to the transmission axis of the polarizer (see Fig.20.20 *a*), that is E_y, parallel to the transmission axis and E_z, perpendicular to the transmission axis of the polarizer. The polarizer transmits the parallel component while blocking the perpendicular component. Thus, it is the parallel component E_y that is transmitted by the polarizer. But

$$E_y = E_0 \cos\theta \qquad \text{... (20.7)}$$

and hence, the intensity of the transmitted component is given by

$$I \propto E_y^2 = E_0^2 \cos^2\theta \qquad \text{... (20.8)}$$

In unpolarized light all the values of θ are equally probable. Therefore, the fraction of light transmitted through the polarizer equals the average value of $\cos^2\theta$.

$$\therefore \quad I = E_0(\cos^2\theta) = I_0(\cos^2\theta)$$

$$= \frac{I_0}{2\pi}\int_0^{2\pi}\cos^2\theta\, d\theta$$

$$= \frac{I_0}{2\pi}\int_0^{2\pi}\left(\frac{1+\cos 2\theta}{2}\right)d\theta$$

$$= \frac{I_0}{4\pi}\left[(\theta)_0^{2\pi} + \left\{\frac{\sin 2\theta}{2}\right\}_0^{2\pi}\right]$$

$$= \frac{I_0}{4\pi}(2\pi + 0)$$

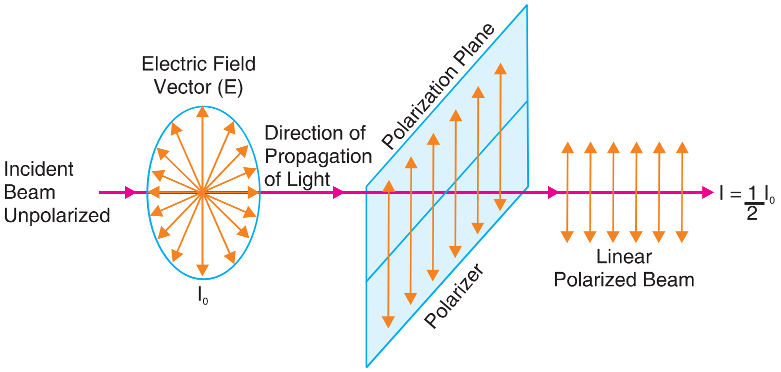
$$= \frac{1}{2}I_0$$

$$\therefore \quad I = \frac{1}{2}E_0^2 = \frac{1}{2}I_0 \qquad \text{... (20.9)}$$

Thus, **if unpolarized light of intensity I_0 is incident on a polarizer, the intensity of light transmitted through the polarizer is $I_0 / 2$.**

20.8.1 PRODUCTION OF LINEARLY POLARIZED LIGHT USING A POLARIZER

A polarizer is associated with a specific direction called the **transmission axis** of the polarizer. If natural light is incident on a polarizer, only those vibrations that are *parallel* to the transmission axis are allowed through the polarizer whereas the vibrations that are in perpendicular directions are totally blocked. Therefore, the transmitted light contains waves oscillating in the same plane, as illustrated in Fig.20.21. Thus, the transmitted beam is linearly polarized.



Production of linearly polarized light

Fig.20.21

According to equ.(20.9), *when unpolarized light of intensity I_0 is incident on a polarizer, the intensity of light transmitted by the polarizer is $I_0 / 2$.*

20.8.2 DETECTION OF LINEARLY POLARIZED LIGHT

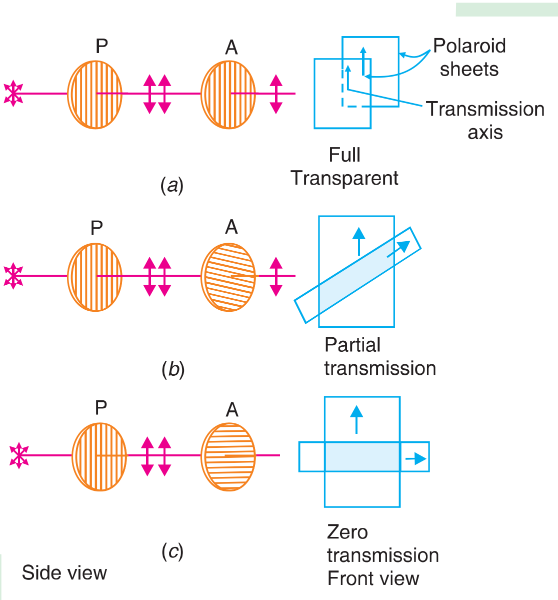


Fig. 20.22

An *analyzer* is an optical element, which is used to identify the plane of vibration of plane polarized light.

To examine light coming from some direction either after emission or reflection etc, we use a Polaroid sheet. The Polaroid sheet used to determine the plane of polarization of light is known as an **analyzer**. There is no difference between a polarizer and analyzer in fabrication but they differ in their roles. Both the polarizer and analyzer are characterized by a transmission axis.

When the transmission axis of the analyzer *A* is set up parallel to that of polarizer *P*, light transmitted by the polarizer, passes unhindered through the analyzer (Fig. 20.22 *a*).

If the transmission axes are set at an angle q, light is partially transmitted (Fig.20.22 *b*). As the angle rotates from 0 to 90 degrees, the amount of light that is transmitted decreases. When the axes are perpendicular to each other, the polarized light from P is extinguished by the analyzer A (Fig.20.22 *c*). The polarizer and analyzer are said to be **crossed** in this configuration.

When we rotate the axis of the analyzer with respect to that of the polarizer, we obtain two positions of maximum intensity and two positions of zero intensity in *one full rotation*. Conversely, if we obtain two positions of maximum intensity and two positions of zero intensity in one full rotation of the analyzer, we conclude that the light incident on the analyzer is plane-polarized light.

20.9. MALUS' LAW

The amount of light transmitted through a polarizer at an arbitrary angle [Fig.20.22 (*b*)] is given by **Malus's Law**.

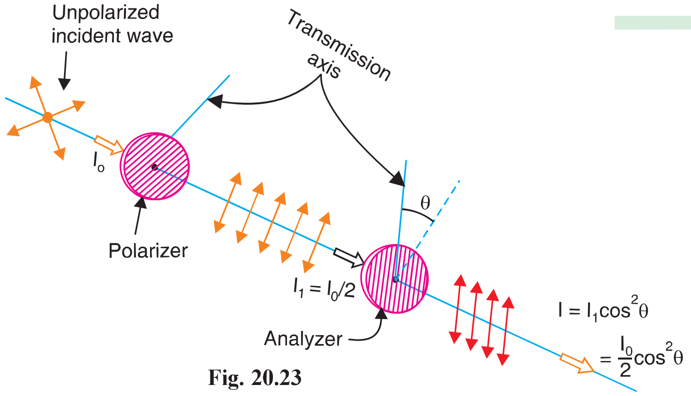


Fig. 20.23

In 1809 Malus found that the *intensity of polarized light transmitted through a polarizer is proportional to the square of cosine of the angle between the plane of polarization of the light and the transmisson axis of the polarizer.*

This statement is known as Malus' law.

If unpolarized light of intensity I_o is incident on a polarizer, plane polarized light of intensity $I_o/2$ is transmitted by it. Let us denote $I_o/2$ by I_1. Let this plane polarized light pass through an analyzer. The intensity of the light transmitted through the analyzer is given by

$$I \quad = \quad E_1^2 \cos^2 \theta = I_1 \cos^2 \theta = \frac{1}{2} I_0 \cos^2 \theta \qquad \text{... (20.10)}$$

Light transmitted through the analyzer at specific settings are as follows.

Case (*i*): If $\theta = 0°$	axes parallel	$I = I_1 = \frac{1}{2} I_0$
Case (*ii*): If $\theta = 90°$	axes perpendicular	$I = 0$
Case (*i*): If $\theta = 180°$	axes parallel	$I = I_1 = \frac{1}{2} I_0$
Case (*i*): If $\theta = 270°$	axes perpendicular	$I = 0$

Thus, we obtain two positions of maximum intensity and two positions of zero intensity when we rotate the axis of the analyzer with respect to that of the polarizer.

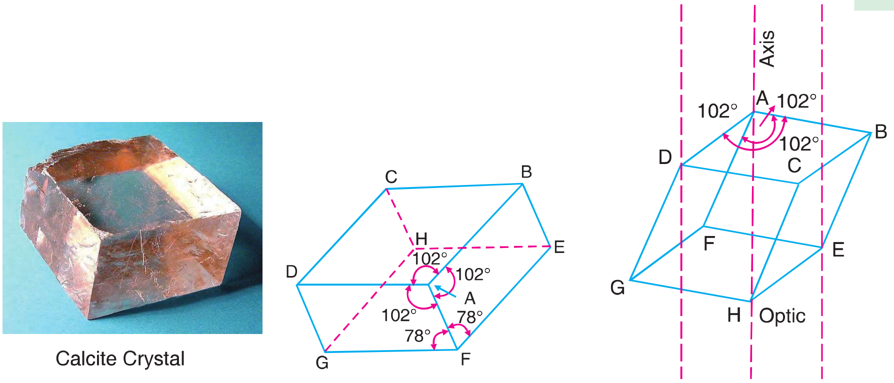
20.10. ANISOTROPIC CRYSTALS

When a light beam is incident on an *isotropic medium* such as a glass slab, it refracts as a single ray. An optically isotropic material is one in which the index of refraction is the same in all directions. Glass, water and air are examples of isotropic materials. The atoms in a crystal are arranged in a regular periodic manner. If the arrangement of atoms differ in different directions within a crystal, then the physical properties vary with the direction. The thermal conductivity, electrical conductivity, velocity of light and hence refractive index etc properties depend on the crystallographic direction along which the property is measured. Then we say that the crystal is **anisotropic**. In such anisotropic crystals the force of interaction between the electron cloud and the lattice is different in different crystallographic directions. The natural frequency of the electron cloud is likewise dependent on the direction in which the electrons are caused to vibrate by the incident light wave. This results in different velocities in different directions and the index of refraction is different in different directions within the crystal.

The anisotropic crystals are divided into two classes: uniaxial and biaxial crystals. In case of **uniaxial crystals**, one of the refracted rays is an ordinary ray and the other is an extraordinary ray. In **biaxial crystals** both the refracted rays are extraordinary rays. Calcite, tourmaline and quartz are examples of uniaxial crystals whereas mica, topaz and aragonite are examples of biaxial crystals.

20.10.1 CALCITE CRYSTAL

Calcite is a common naturally occurring substance. Both marble and limestone are made up of many small calcite crystals bonded together. A large crystal of calcite is colourless and transparent. It was at one time found in great quantities in Iceland and hence it is also known as **Iceland spar**. Naturally occurring calcite crystals (Fig.20.24*a*) has rhombohedral cleavage which means it breaks into blocks with parallelogram-shaped faces. It is bounded by six faces (Fig.20.24*b*), each of which is a parallelogram with angles equal to 101°55'and 78°5'. The rhombohedron has only two corners A and H where all the face angles are obtuse (101°55'). These two corners appear as the *blunt corners* of the crystal. At the rest of six corners there is one obtuse angle and two acute angles.



(*a*) (*b*) (*c*)

Fig. 20.24

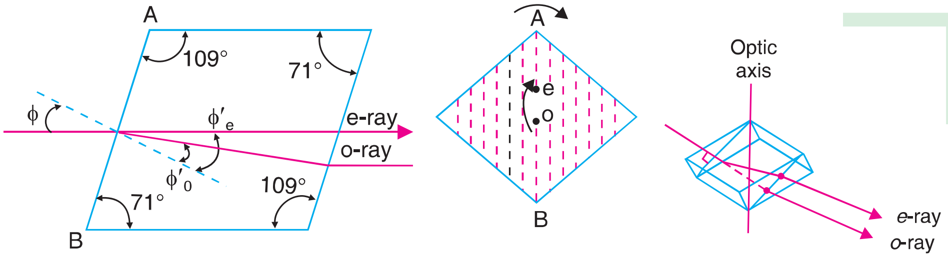
20.10.2 OPTIC AXIS

A line bisecting any one of the blunt corners (A or H) and making equal angles with each of the three edges meeting there, is the **optic axis** (see Fig.20.24 *c*). In fact any line parallel to this line is also an optic axis. Thus, the optic axis is a direction and not a specific line in the crystal. Hence an optic axis can be drawn through every point in the crystal, that is, any line parallel to the line above will also be the optic axis. It is to be noted that the optic axis is not obtained by joining the two blunt corners. Only in a special case, when the three edges of the crystal are equal, the line joining the two blunt corners A and H coincide with the crystallographic axis of the crystal and it gives the direction of the optic axis. The optic axis is actually the axis of symmetry of the crystal. A ray of light propagating along optic axis does not suffer double refraction, because the structure of the crystal is symmetric about that direction.

The optic axis is the direction in a uniaxial crystal along which the **e**-ray and the **o**-ray travel with the *same* speed and consequently double refraction *does not* take place along this direction. The corresponding refractive index is the refractive index for ordinary light, say μ_o.

20.10.3 PRINCIPAL SECTION

A plane containing the optic axis and perpendicular to a pair of opposite faces of the crystal is called the **principal section** of the crystal for that pair of faces (Fig.20.25 *a*). Thus, there are three principal sections passing through any point within the crystal, one corresponding to each pair of opposite faces. A principal section always cuts surfaces of calcite crystal in a parallelogram having angles 71° and 109° (see Fig.20.25 *b*). Fig.20.25 (*c*) shows a face of the crystal in which the end-view



(*a*) (*b*) (*c*)

Fig. 20.25

of the principal section AB (of Fig.20.25 b) is shown by the dotted line AB. The lines parallel to AB represent the end-views of other principal sections parallel to AB with in the crystal.

20.10.4 PRINCIPAL PLANE

Defining principal section is not enough to understand the directions of vibrations for the o-ray and e-rays. Hence, two more planes are defined as principal plane for the o-ray and the principal plane for the e-ray. The plane containing the optic axis and the o-ray is called the *principal plane of the o-ray* and the plane containing the optic axis and the e-ray is called the *principal plane of the e-ray*. The directions of vibrations in the o-ray and e-ray can be understood with reference to these planes. In general, the two principal planes do not coincide. Under the particular case, when the plane of incidence is the principal section of the crystal, then the principal planes of o- and e-rays and the principal section of the crystal coincide.

20.11. DOUBLE REFRACTION IN CALCITE CRYSTAL

Fig.20.25 (*a*) shows a principal section of calcite crystal. A ray of light is incident on the face AB of the crystal and it travels along the principal section. The ray is split into two rays, namely o-ray (fast ray) and e-ray (slow ray). The o-ray travels through the crystal without deviation while the e-ray is refracted at some angle. As the opposite faces of the crystal are parallel, the rays emerge out parallel to the incident ray. Within the crystal the o-ray *always* lies in the plane of incidence whereas e-ray does not lie in the plane of incidence. e- ray lies in the plane of incidence only when the plane of incidence is a principal section.

If a mark (dot or cross) is made on a paper and then the calcite crystal (AB face) is placed on it, two images are seen through the crystal, as illustrated in Fig.20.25 (*b*). The images are produced by the o-ray and e-ray. The intensities of the images are lesser than that of the original mark. The line joining them lies in the principal section. If now the crystal is rotated slowly about an axis passing through the o-image, the e-image moves round in a circle while the o-image remains stationary. It shows that the velocity of propagation of o-ray is the same in all directions, while that of e-ray changes with direction. O-ray obeys the laws of refraction and the e-ray does not follow the ordinary laws of refraction.

The e-ray and o-ray are linearly polarized. The e-ray has its vibrations (i.e., the optical vector) *parallel* to the principal section whereas the vibrations (optical vector) in o-ray are *perpendicular* to the principal section, as indicated in Fig.20.19. The vibration directions can be established by examining the rays through a polarizer. As the polarizer is held in the path of the rays and rotated slowly, the intensity of one of the images, say the o-image, increase while that of the e-image decreases. In one position, the intensity of the o-image will be a maximum while the e-image is extinguished. Further rotation through 90° from this particular position, causes the o-image to disappear and e-image intensity to become a maximum. It proves that the e- and o-rays are linearly polarized in mutually perpendicular directions.

The o-ray travels with the same velocity in all directions in the crystal whereas the e-ray travels with different velocities in different directions. Therefore, refractive index corresponding to o-ray is a constant and is designated by μ_o. The refractive index corresponding to e-ray varies and is denoted by μ_e. The difference between the refractive indices is known as the amount of double refraction or birefringence. Thus,

$$\Delta_\mu = \mu_e - \mu_o \qquad \text{... (20.11)}$$

20.11.1 HUYGENS' EXPLANATION OF DOUBLE REFRACTION

In order to explain the double refraction exhibited by anisotropic crystals, Huygens postulated that the incident light excites two separate wavelets within the crystal, one spherical wavelet associated with the ordinary waves and one ellipsoidal wavelet associated with the extraordinary waves. For example, the plane wavefront, in Fig.20.26, incident normally on the crystal surface generates spherical wavelets as well as ellipsoidal wavelets. The spherical wavelets propagate equally quickly in all directions. The wave surface corresponding to o-ray is therefore spherical. The tangent to these waves lies straight ahead and, by successive application of the principle, the plane wave propagates straight ahead with speed υ. The ellipsoidal wavelets propagate at different speeds in different directions. The wave surface corresponding to e-ray is therefore an ellipsoid of revolution about the optic axis. The common tangent to these ellipsoids after a little time is the new wavefront. The line from the point of generation of each ellipsoid to the tangent point on that ellipsoid is off at an angle and defines the direction of travel of the extraordinary wavefronts. The wavefronts are not perpendicular to their direction of travel.

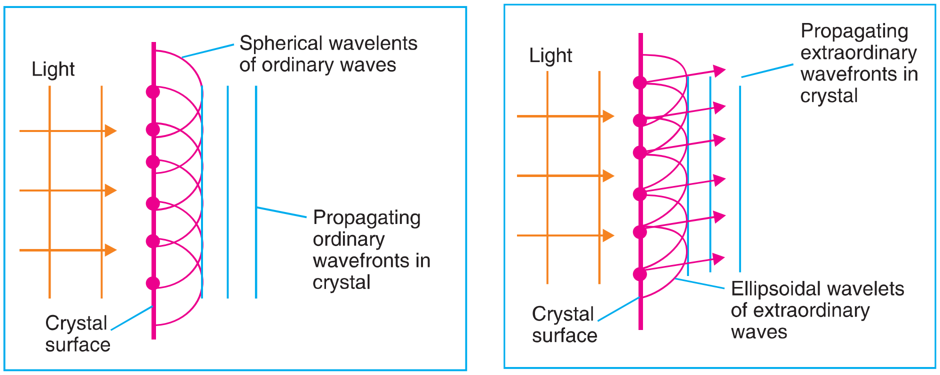


Fig. 20.26

The two wave surfaces touch each other at the two points where they are intersected by the optic axis. As light propagates through the crystal, the two wave surfaces travel in different directions in the crystal. Ultimately, two refracted rays emerge from the crystal.

20.11.2 ORDINARY AND EXTRA-ORDINARY RAYS

We now compare the properties of o- and e-rays:

(*i*) o-ray obeys the laws of refraction and the e-ray does not follow the ordinary laws of refraction.

(*ii*) Both o-ray and e-ray are plane polarized. They are polarized in mutually perpendicular planes. The electric vector of o-ray vibrates perpendicular to the principal section of o-ray while the vibrations of e-ray take place parallel to the principal section of e-ray.

(*iii*) O-ray travels with the same speed in all directions within the crystal. The e-ray travels with different speeds along different directions in the crystal. However, the speed of e-ray will be equal to that of o-ray along the optic axis direction.

(*iv*) Because o-ray travels with the same velocity in all directions, the refractive index corresponding to it has a constant value. On the other hand, the refractive index for e-ray varies from direction to direction. The principal refractive index for o-ray is defined as follows:

$$\mu_0 = \frac{c}{\upsilon_0} = \frac{\text{velocity of light in a vacuum}}{\text{velocity of o-ray in the crystal}} \quad \text{... (20.12)}$$

The principal refractive index for e-ray in ***positive crystals*** is defined as follows:

$$\mu_o = \frac{c}{(\upsilon_e)_{\min}} = \frac{\text{velocity of light in a vacuum}}{\text{minimum velocity of e-ray in the crystal}} \qquad \text{... (20.13)}$$

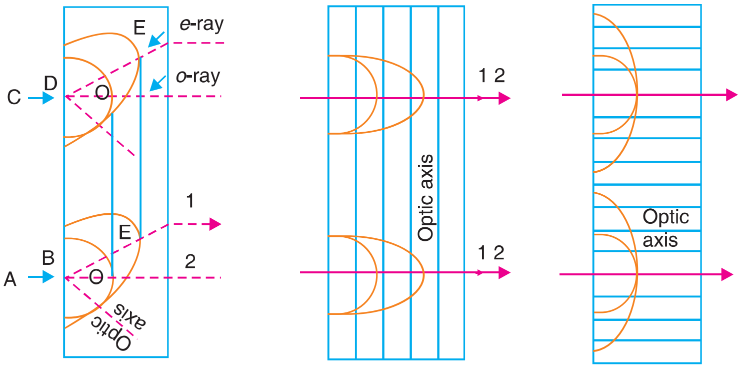
The principal refractive index for e-ray in ***negative crystals*** is defined as follows:

$$\mu_e = \frac{c}{(\upsilon_e)_{\max}} = \frac{\text{velocity of light in a vacuum}}{\text{maximum velocity of e-ray in the crystal}} \qquad \text{... (20.14)}$$

(*v*) When natural light is incident on an anisotropic crystal at an angle to the optic axis, it splits into o-and e-rays, which travel in *different directions* with *different velocities* (20.27 *a*).

When natural light is incident in a direction perpendicular to the optic axis, o-ray and e-ray propagate in the *same direction* in the crystal but with *different velocities*, as shown in Fig.20.27 (*b*). In a negative crystal e-ray leads o-ray and in case of a positive crystal o-ray leads e-ray.

When natural light is incident on the crystal in a direction parallel to the optic axis, it does not split into two rays. The o- and e- rays travel in the *same direction with the same velocity*, as shown in Fig.20.27 (*c*).



(*a*) (*b*) (*c*)

Fig. 20.27

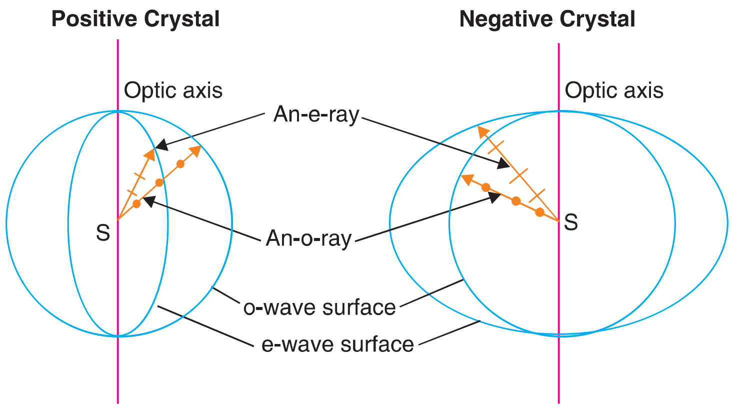
(*vi*) The distinction of o-ray and e-ray exists only within the crystal. Once they emerge from the crystal, they travel with the same velocity. The rays outside the crystal differ only in their direction of travel and plane of polarization. The designation of o- ray and e-ray has no meaning outside the crystal.

20.11.3 POSITIVE AND NEGATIVE CRYSTALS

Because of two different wave fronts, two different types of uniaxial crystals exist. In one type of crystals, the spherical wave front of o-ray is enclosed by the ellipsoidal wave front of e-ray. Such crystals are known as **negative crystals**. They are called negative crystals because the refractive index corresponding to the e-ray is less than that corresponding to o-ray. Calcite crystal is an example of negative type crystals. In the other case, the extraordinary wave front lies within the ordinary wave front and such crystals are called **positive crystals**. They are positive because the refractive index for the extraordinary ray is greater than that of o-ray. Quartz crystal is an example of positive crystals.

We compare here the characteristics of the positive and negative crystals.

(*i*) In positive uniaxial crystals, the ellipsoid of revolution corrrsponding to the e-ray is totally contained within the sphere corresponding to the o-ray.



(*a*) $\mu_e > \mu_0$ (*b*) $\mu_e < \mu_0$

Fig. 20.28

In negative uniaxial crystals, the ellipsoid of revolution for e-ray lies completely outside the sphere corresponding to o-ray. The two cases are depicted in Fig. 20.28.

(*ii*) In positive crystals the e-ray velocity has a maximum value along the optic axis and a minimum value in a direction perpendicular to the optic axis.

On the other hand, in negative crystals the velocity of e-ray has a minimum value parallel to the optic axis and a maximum value in a direction perpendicular to the optic axis.

(*iii*) In positive crystals, e-ray travels slower than o-ray in all directions except along the optic axis.

$\upsilon_e = \upsilon_o$ — parallel to optic axis
$\upsilon_e < \upsilon_o$ — other directions

In negative crystals, o-ray travels slower than e-ray in all directions except along the optic axis.

$\upsilon_e = \upsilon_o$ — parallel to optic axis
$\upsilon_e > \upsilon_o$ — other directions

(*iv*) In positive crystals the principal refractive index for e-ray is larger than the principal refractive index for o-ray.

$$\mu_e > \mu_o$$

In negative crystals the principal refractive index for o-ray is larger than the principal refractive index for e-ray.

$$\mu_e < \mu_o$$

(*v*) **Birefringence** or amount of double refraction of a crystal is defined as

$$\Delta\mu = \mu_e - \mu_o \qquad \text{... (20.15 } a\text{)}$$

As $\mu_e > \mu_o$ in these crystals, $\Delta\mu$ is a positive quantity for positive crystals.

$\Delta\mu$ is a negative quantity for negative crystals as $\mu_e < \mu_o$ in these crystals and the birefringence of a negative crystal is given by

$$\Delta\mu = \mu_o - \mu_e \qquad \text{... (20.15 } b\text{)}$$

20.12. NICOL PRISM

Nicol prism is a polarizing device fabricated from a double refracting crystal. It is similar to a Polaroid sheet in its action. A Nicol prism is made from calcite crystal. William Nicol designed it in 1820. A rhomb of calcite crystal about three times as long as it is thick, is obtained by cleavage from the original crystal. The ends of the rhombohedron are ground until they make an angle of 68°instead of 71° with the longitudinal edges. This piece is then cut into two along a plane perpendicular both to the principal axis and to the new end surfaces *AB* and *CD*. The two parts of the crystal are then cemented together with canada balsam, whose refractive index lies between the refractive indices of calcite for the o-ray and e-ray. μ_o=1.66, μ_e=1.486 and $\mu_{\text{canada balsam}}$=1.55. The position of the optic axis is as shown in Fig.20.29. The refractive index for e-ray depends upon the direction in which e-ray is propagating in the crystal. The difference between the refractive index between o-ray and that for e-ray goes on increasing with the angle between the two rays in the crystal. When this angle is 90°, the difference is a maximum. Thus, for a fixed value for μ_o, the μ_e has its maximum or minimum value in perpendicular direction. In the above μ_e = 1.486 represents the minimum value.

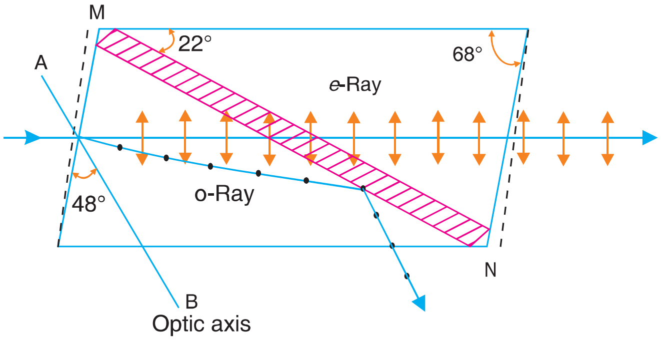


Fig. 20.29

Unpolarized light is made to fall on the crystal as shown in Fig.20.29 at an angle of about 15°. The ray after entering the crystal suffers double refraction and splits up into o-ray and e-ray. The two rays with their directions of vibrations are as shown in the Fig.20.29. The values of the refractive indices and the angles of incidence at the canada balsam layer are such that the e-ray is transmitted while the o-ray is internally reflected. The face where the o-ray is incident is blackened so that the o-ray is completely absorbed. Then we get only the plane-polarized e-ray coming out of the Nicol. Thus, the Nicol works as a polarizer.

For studying the optical properties of transparent substances, two Nicols are used - one as a polarizer and the other as an analyzer.

When two Nicol prisms P and A are placed adjacent to each other as shown in Fig.20.30, one of them acts as a polarizer and the other acts as an analyser. If unpolarized ray of light is incident on the Nicol prism P, a linearly polarized e-ray emerges from P with its vibration direction lying in the principal section of P. The state of the polarization of the light emerging from polarizer P can be examined with another polarizer A, which for convenience is called an analyser. Let now this ray be incident on the second Nicol prism A, whose principal section is parallel to that to P. The vibration direction of the ray will be in the principal section of A and hence it is transmitted unhindered through the analyser A.

If the Nicol prism A is gradually rotated, the intensity of the e-ray decreases in accordance with Malus law. When its principal section becomes perpendicular to that of the Nicol prism reversed, and its return path is blocked by the polarizer. Light generated by the display passes through the polarizer and hence is seen without the background reflecting light.

7. Photoelasticity: Photoelasticity is an experimental method to determine stress distribution in various engineering components. The method is mostly used in cases where mathematical methods become quite cumbersome. Photoelasticity is especially useful for the study of objects with irregular boundaries and stress concentrations, such as pieces of machinery with notches or curves, structural components with slits or holes, and materials with cracks.

Principle: The method is based on the property of double refraction, which is exhibited by photoelastic materials on the application of stress. Double refraction or birefringence is a property by virtue of which a ray of light passing through a birefringent material splits into two beams (e- and o-rays). The two beams travel along the same path in the material and their speed at each point in the material is directly related to the state of stress at that point. Because the velocities of light propagation are different in each direction, there occurs a phase shifting of the light waves. Therefore, light emerges out of the component as two beams vibrting out of phase with one another and when they are combined, produce interference pattern.

The stressed component is examined under monochromatic polarized light in a polariscope. The polarizer in the polariscope produces polarized light. When the analyzer in the polariscope recombines the waves, interference pattern is observed. Regions of stress where the wave phases cancel appear dark, and regions of stress where the wave phases add appear bright. Therefore, in models of complex stress distribution, bright and dark fringe patterns (isochromatic fringes) are projected from the model. As these fringes are related to the stresses, the magnitude and direction of stresses at any point can be determined by examination of the fringe pattern. When the component is unloaded, the photoelastic fringe pattern disappears.

When white light is used in place of monochromatic light, coloured fringes are observed. White light is often used for demonstration, and monochromatic light is used for precise measurements.

The above method is suitable when the component is transparent. In the case of opaque components, a thin sheet of photoelastic material is suitably bonded to the surface of the component. When the component is loaded, the surface strain in the component is transmitted to the photoelastic sheet producing stress in it. The resulting fringe pattern is observed by illuminating the component with polarized light and viewing it through an analyzer. More commonly, a transparent scale model of the part is made out of a material, which is optically sensitive to stress such as epoxy, glyptol or polyester resins. The model is then subjected to the forces that the actual component would experience in use. The birefringence varies from point to point over the surface of the model. When viewed with crossed polarizers, a complicated fringe pattern is seen which provides a visual means of observing overall stress characteristics of an object. The patterns can be projected on a screen or photographic film.

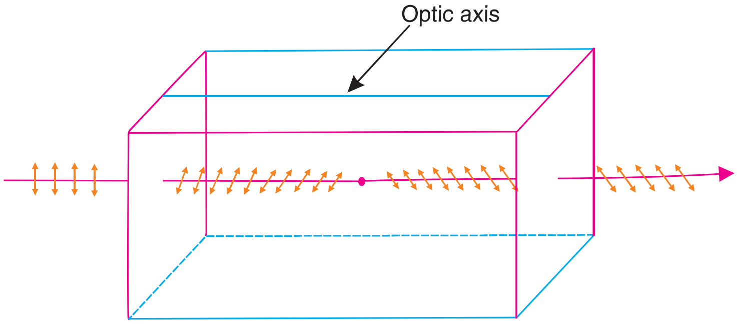
20.27. OPTICAL ACTIVITY

Certain crystals and solutions possess a natural ability to rotate the plane of polarization about the direction of propagation. It is known as *optical activity*. In case of crystals this ability arises due to the twisted arrangement of atomic layers with respect to one another. In liquids and solutions the optical activity is due to certain structural symmetry in their molecules. The optical activity found in bigger organic molecules provides a number of clues which help us understand biological activity.

Many crystalline materials exhibit birefringence naturally, without application of any voltage. The birefringence is present all the time. Examples of such crystals are quartz and calcite. There are also a number of crystals that are not birefringent naturally but in which application of a voltage or magnetic field induces birefringence. The induced optical activity leads to the ability to control light beams in a variety of ways and is the basis of a number of applications such as light-beam modulators, Q-switches, and deflectors.

20.28. OPTICAL ROTATION

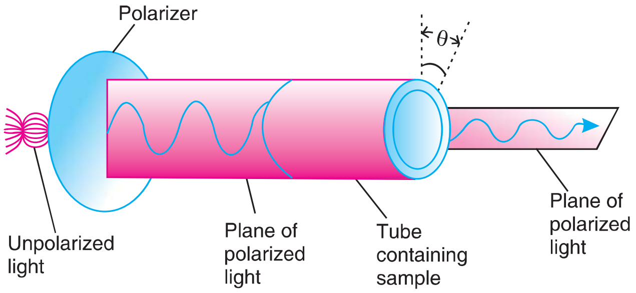
When a beam of plane polarized light propagates through a quartz crystal along the optic axis, the plane of polarization steadily turns about the direction of the beam. The optical rotation can be detected as follows. If two polaroid sheets or Nicol prisms are held in crossed configuration and if a beam of unpolarized light is viewed through them, the field of view appears to be completely dark. Now let a quartz crystal, cut with its faces perpendicular to the optic axis, be inserted between the polarizers such that light is incident normally on the crystal. The field of view now appears lit up indicating that the light is not cut off by the analyzer. In order to cut off the transmitted light, we find that the analyzer is to be rotated through a certain angle. The experiment establishes that the plane polarized light produced by the polarizer remains plane polarized while passing through the quartz crystal but the plane of polarization is rotated through an angle. This angle is the angle through which the analyzer is rotated in order to cut off the light totally. The optical rotation, i.e., rotation of the plane of polarized light is shown in Fig.20.65(*a*).



(*a*) Optically active crystal

Fig. 20.65

The ability to rotate the plane of polarization of plane polarized light by certain substance is called **optical activity**. Substances, which have the ability to rotate the plane of the polarized light passing through them, are called ***optically active*** substances. Quartz and cinnabar are examples of optically active crystals while aqueous solutions of sugar, tartaric acid are optically active solutions.



(*b*) Optically active solution

Rotation of the plane-polarized light. The plane is rotated by an angle after the light passes through an optically (*a*) active crystal or (*b*) solution.

Fig. 20.65

Optically active substances are classified into two types.

(*i*) **Dextrorotatory substances**: Substances which rotate the plane of polarization of the light toward the right are known as right-handed or dextrorotatory .

(*ii*) **Laevorotatory substances**: Substances which rotate the plane of polarization of the light toward the left are known as left-handed or laevorotatory .

20.29. SPECIFIC ROTATION

A measure of the optically activity of a sample is the rotation produced for a 1 mm slab for a solid, or a 100 mm path length for a liquid. This measure is called the *specific rotation*. Liquids usually rotate the light much less than solids. Solutions of solids will obviously show an effect that depends on the concentration of active material and, to a small extent, both on temperature and the solvent.

If an optically active material is kept between two crossed polarizers, the field of view becomes bright. In order to get darkness once again, the analyzer has to be rotated through an angle. The angle through which the analyzer is rotated equals the angle through which the plane of polarization is rotated by the optically active substance. This angle depends on

(*a*) The thickness of the substance,

(*b*) Density of the material or concentration of the solution,

(*c*) Wavelength of light, and

(*d*) The temperature.

The amount of rotation θ caused by crystalline materials is given by

$$\theta = \alpha l \qquad \text{... (20.55)}$$

where α is called the **rotational constant**.

In solutions the amount of rotation θ is given by

$$\theta = s\,c\,l \qquad \text{... (20.56)}$$

where c is the concentration and s is called the **specific rotation**.

The specific rotation for a given wavelength of light at a given temperature is defined conventionally as the rotation produced by one decimetre long column of the solution containing 1 gm of optically active material per c.c .of solution.

$$[S]_\lambda^t = \frac{\theta}{l \times C} = \frac{\text{Rotation in degrees}}{\text{Length in decimetres} \times \text{conc. in gm/c.c.}} = \frac{10\theta}{l(cm)C} \qquad \text{... (20.57)}$$

20.30. FRESNEL'S EXPLANATION

A linearly polarised light can be considered as a resultant of two circularly polarised vibrations rotating in opposite directions with the same angular velocity. Fresnel assumed that plane-polarised light on entering a crystal along the optic axis is resolved into two circularly polarised vibrations rotating in opposite directions with the same angular frequency. In an optically inactive crystal like calcite, the two circularly polarised vibrations travel with the same angular velocity. On the other hand, in an optically active crystal like quartz, the two circularly polarised vibrations travel with the different angular velocities.

Fig.20.66 (a) shows plane polarized light entering a calcite crystal along the optic axis AB and split up into two circular motions rotating in opposite directions. They are represented by OL and OR. OL is the circularly polarised vector rotating in the anticlockwise direction and OR is the circularly polarised vector rotating in the clockwise direction. If OL and OR start simultaneously from OA and rotate with the same angular velocity, then at any subsequent time, the resultant of OL and OR will lie along OA. Hence on emerging from the crystal, the two circular waves combine to

Introduction 1

One of the most exciting scientific investigations has been the attempt to understand the basic units of matter and how they are held together. For a chemical physicist, the basic units of matter are the atoms and the molecules. For understanding the atomic and molecular structure and the nature of chemical bonding, one requires a thorough knowledge of the methods of quantum mechanics and the different types of spectroscopic techniques. Spectroscopy is the measurement and interpretation of absorption and emission of electromagnetic radiation when atoms or molecules or ions move from one energy level to another. It has become an indispensable tool to present day chemists and physicists because of the availability of sophisticated instrumentation techniques.

In this introductory chapter, some of the very basic concepts which we require for understanding the different branches of molecular spectroscopy are discussed.

1.1 ELECTROMAGNETIC SPECTRUM

Electromagnetic theory, developed by Clark Maxwell, suggests that an alternating current in a circuit radiates energy in the form of waves having oscillating electric and magnetic fields in planes perpendicular to the direction of propagation. As these radiations possess electric and magnetic fields, they are called electromagnetic radiations. They travel with the velocity of light (c) and can be treated in terms of frequency (ν) of the oscillating electric and magnetic fields. The frequency, wavelength (λ) and velocity of these radiations are connected by the relation

$$c = \nu\lambda \tag{1.1}$$

and the energy associated with the wave is given by

$$E = h\nu = \frac{hc}{\lambda} \tag{1.2}$$

where h is the Planck's constant and is equal to 6.626×10^{-34} Js.

The names of the different regions along with the order of the range of frequencies and wavelengths are summarised in Table 1.1. The regions from radio frequency to gamma rays together is called the electromagnetic spectrum. The different regions are primarily based on the experimental techniques used in the generation, dispersion or detection of the radiation. In fact, the name 'visible region' is based on the detection system. It occupies only a very small region of the electromagnetic spectrum.

The commonly used units for wavelength are metre (m), centimetre (cm), micrometre (μm), nanometre (nm) and Angstrom (Å). They are related as given below:

$$1\ \text{Å} = 10^{-1}\ \text{nm} = 10^{-4}\ \mu\text{m} = 10^{-8}\ \text{cm} = 10^{-10}\ \text{m}$$

In molecular spectroscopy, very often instead of frequency (ν), wavenumber ($\bar{\nu}$) is used.

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

It is usually expressed in cm^{-1} or m^{-1}

$$\text{cm}^{-1} = 100\ \text{m}^{-1}$$

Table 1.1 Regions of Electromagnetic Spectrum

ν (Hz)	λ (m)	*Regions*
	— 10^{-12}	
— 10^{20}		Gamma rays
	— 10^{-11}	
— 10^{19}		
	— 10^{-10}	
— 10^{18}		X-rays
	— 10^{-9}	
— 10^{17}		
	— 10^{-8}	Vacuum Ultraviolet
— 10^{16}		
	— 10^{-7}	
— 10^{15}		Ultraviolet
		Visible
	— 10^{-6}	
— 10^{14}		Near infrared
	— 10^{-5}	
— 10^{13}		
	— 10^{-4}	
— 10^{12}		
	— 10^{-3}	Far infrared
— 10^{11}		
	— 10^{-2}	
— 10^{10}		
	— 10^{-1}	Microwaves
— 10^{9}		
	— 1	
— 10^{8}		
	— 10	Radio frequency
— 10^{7}		
	— 100	
— 10^{6}		

1.2 TYPES OF MOLECULAR ENERGIES

Molecules (gas and liquid phase) possess different types of energies. They are:

(i) The translational energy (E_t) due to the translational motion of the molecule

(ii) The electronic energy (E_e) since the electrons associated with each atom or bond are in continuous motion

(iii) The vibrational energy (E_v) due to the periodic displacement of its atom from their equilibrium position

(iv) The rotational energy (E_r) by virtue of bodily rotation about its centre of gravity.

For a fluid in a container, the space available for the translational motion is large compared to the molecular dimensions and therefore E_t is not quantized. The electrons in a molecule are confined to a part or to the whole volume of the molecule. In the case of vibrational motion, the atoms can undergo only small displacements because of the restoring forces of the bonds. A rotating molecule can move utmost in the volume occupied by it. Therefore, one expects significant quantum restriction on the electronic, vibrational and rotational energies of a molecule and we shall be considering only those at least in the case of liquids and gases.

According to Born and Oppenheimer, the various forms of energies of a molecule are independent of each other. Hence, leaving the traslational contribution, the total energy E and wave function ψ are given by

$$E_{\text{total}} = E_e + E_v + E_r \qquad \text{and} \qquad \psi = \psi_e\ \psi_v\ \psi_r \tag{1.3}$$

where ψ_e, ψ_v, and ψ_r are the electronic, vibrational and rotational wave functions. The quantized levels of these energies for a diatomic molecule are shown in Figure 1.1. The rotational, vibrational and electronic energy separations are of the order of 1–300 cm^{-1}, 300–4000 cm^{-1}, and 10^6 cm^{-1} respectively.

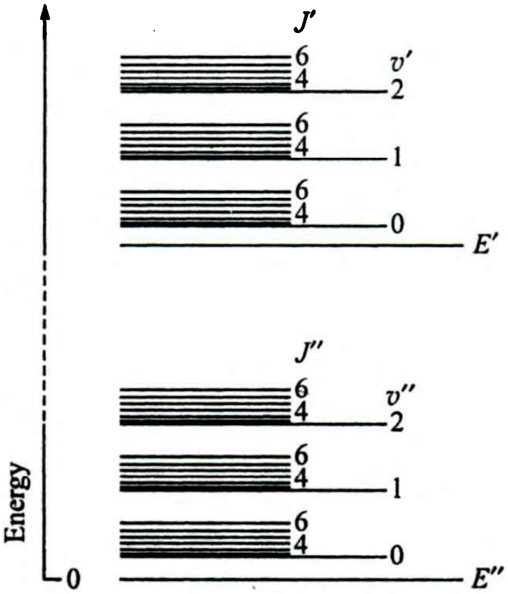


Figure 1.1 Quantized energy levels of a diatomic molecule: E'', E'—electronic levels; J'', J'—rotational levels; v'', v'—vibrational levels.

1.3 DIFFERENT SPECTROSCOPIC METHODS—AN OVERVIEW

An understanding of the different physical and chemical processes in molecular systems requires a fairly detailed knowledge of their internal structure. The advancements in the spectroscopy of different regions of the electromagnetic spectrum have provided valuable informations for the investigation of molecular structure. Most of the experimental methods depend upon the study of interaction between electromagnetic radiation and the molecular system. The nature of the information required decides the selection of the particular spectroscopic technique. For the understanding of molecular spectroscopy, the study of the spectra of atoms is essential as it gives a solid foundation for spectroscopy.

A spectral line is exhibited when a molecule absorbs radiation of energy $h\nu$ and goes to an excited state, or a molecule in an excited state emits a quantum of energy $h\nu$ and drops to a lower level. Transitions between electronic energy levels give the spectrum in the visible or ultraviolet region and is referred to as electronic spectra. Vibrational spectra are due to transitions between vibrational levels within the same electronic level which fall in the infrared region. Transitions between rotational levels within the same vibrational level give the spectra in the far infrared or microwave region and is referred to as rotational spectra. In addition to these, a nucleus or electron can give interaction energies when placed in a magnetic field. These give respectively, Nuclear Magnetic Resonance (NMR) and the Electron Spin Resonance (ESR) spectroscopy. Table 1.2 summarises the different spectroscopies associated with the different regions of the electromagnetic spectrum.

Table 1.2 Spectral Regions and Associated Absorption Phenomena

Frequency region (Hz)	*Spectral region*	*Absorption phenomena*
$10^6 - 3 \times 10^8$	Radio frequency (NMR)	Nuclear Zeeman transitions
$10^9 - 4 \times 10^{10}$	Microwave (ESR)	Electron spin reversal
$10^{10} - 3 \times 10^{12}$	Microwave	Rotational transitions
$3 \times 10^{12} - 3 \times 10^{14}$	Infrared	Vibrational transitions
$4.2 \times 10^{14} - 7.5 \times 10^{14}$	Visible	Valence electron transitions
$7.5 \times 10^{14} - 3 \times 10^{16}$	Ultraviolet	Valence electron transitions
$10^{17} - 10^{19}$	X-rays	Innercore electron transitions

Emission and absorption are the two general areas of spectroscopy. The general experimental method for obtaining an emission spectrum is shown in Figure 1.2. In absorption spectroscopy, depending on the region there are two types of spectrometers—ordinary absorption spectrometer (Figure 1.3) and resonance absorption spectrometer (Figure 1.4). In the first type, the radiation is allowed to pass through the sample and the difference in the intensity level of the incident and emergent beam is measured. In a resonance

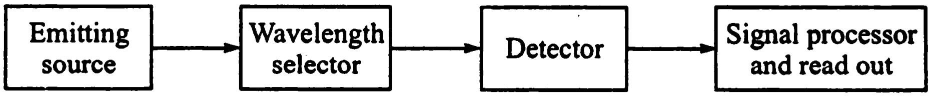


Figure 1.2 Components of an emission spectrometer.

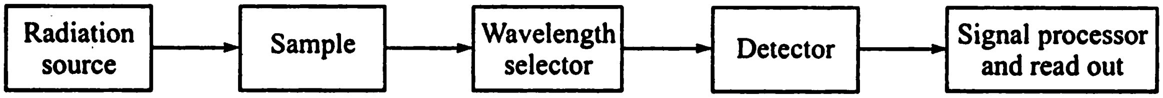
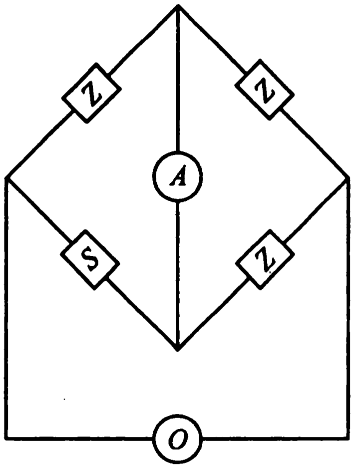


Figure 1.3 Components of an absorption spectrometer.



Z—Variable impedance elements for balancing
A—Current detector
S—Sample coil
O—Variable frequency oscillator

Figure 1.4 Components of a resonance spectrometer.

spectrometer, the absorption is detected as a current or voltage unbalance when the energy of the incident radiation equals the energy separation between the two levels involved. This type is usually employed in spectrometers below the microwave region. Another type of absorption experiment of fundamental significance is the Fourier transform spectroscopy which is illustrated in Figure 1.5.

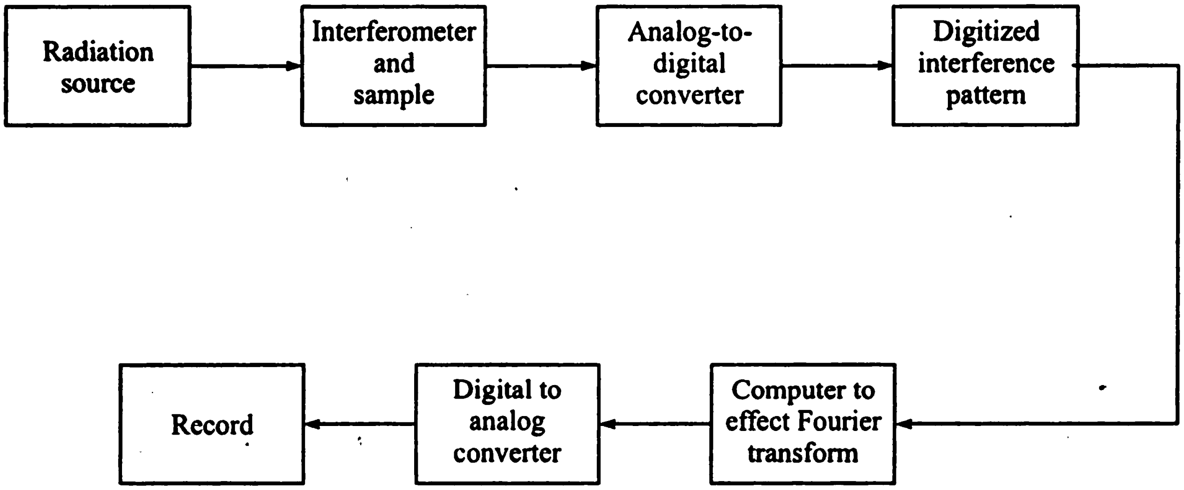


Figure 1.5 Fourier transform spectrometer.

In addition to emission and absorption, the following important phenomena are also possible when radiation of frequency ν_0 interacts with matter giving radiation of frequency ν:

(i) Fluorescence ($\nu < \nu_0$)
(ii) Phosphorescence ($\nu < \nu_0$)

(iii) Rayleigh scattering ($\nu = \nu_0$)
(iv) Raman scattering ($\nu = \nu_0 \pm \nu_m$).

Fluorescence results when an atomic or molecular system is excited into an upper state by absorption of radiation of energy $h\nu_0$ and then decaying back to a lower state in a time less than 10^{-5} s. If the emitted radiation is of energy $h\nu_0$, it is called **resonance fluorescence.**

Phosphoresence is a phenomenon similar to fluorescence, but results when the molecule loses energy by means of a nonradiative transition and ends up in a metastable state from which it makes a delayed re-emission. It continues even after the removal of the exciting source. The energy level representation of these two processes are shown in Figure 1.6.

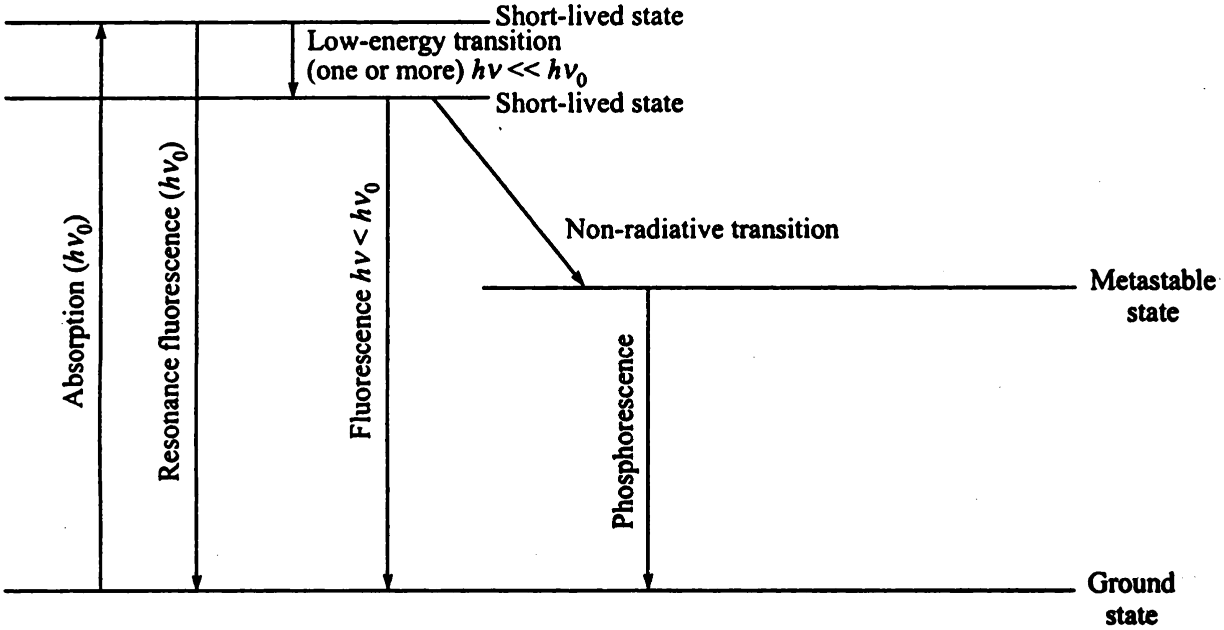


Figure 1.6 Energy level diagram for fluorescence and phosphorescence.

Rayleigh and Raman scatterings result when light from a monochromatic source is allowed to be scattered by a solid or a collection of molecules. Most of the scattered radiations have the same energy (elastic scattering—Rayleigh scattering). However, a few (1 in 10^6) undergo inelastic scattering. These inelastically scattered photons have frequencies lower and higher than the incident frequency. The scattered photons have frequency shifts characteristic of the vibrational or rotational energies of the molecule/solid. This phenomenon is called **Raman effect**.

1.4 SPECTRAL LINE WIDTH

Width of a spectral line is usually defined by the Full Width at Half Maximum (FWHM). Theoretically, energy levels of isolated molecules are discrete and therefore one expects spectral lines of infinite sharpness. However, experimental absorption and emission lines appear with finite width. Broadening of spectral lines depends on the experimental conditions and wavelength region. The important factors that contribute to broadening are natural linewidth, collision broadening, Doppler broadening and saturation broadening.

1.4.1 Natural Line Width

This arises because the energy levels of atomic and molecular systems are not precisely determined. The energy spread ΔE is related to the uncertainty in the lifetime Δt by the relation (Chapter 2)

$$\Delta E \cdot \Delta t \approx \frac{h}{2\pi} \tag{1.4a}$$

The corresponding frequency spread $\Delta \nu$ is given by

$$\Delta E = h \Delta \nu \tag{1.4b}$$

Combining, Eqs. (1.4a) and (1.4b)

$$\Delta \nu \simeq \frac{1}{2\pi \Delta t} \tag{1.5}$$

That is, longer a molecule remains in a particular energy level, more precisely the energy is defined.

The uncertainty in the lifetime Δt of a state can reasonably be taken as the lifetime τ of the molecule/atom in that state. The ground state of a system is more sharply defined because Δt will be extremely large. However, the excited state energy is not sharply defined as its lifetime is much less than the lifetime of the ground state. Assuming that the energy of the ground state is known precisely, a transition from the excited state to the ground state will have an uncertainty in frequency given by

$$\Delta \nu = \frac{1}{2\pi\tau} \tag{1.6}$$

where τ is the lifetime of the upper state. Typical value for τ of an excited electronic state $\approx 10^{-8}$ s which leads to an uncertainty in frequency $\Delta \nu \approx 10^{8}$ Hz. This is extremely small compared with the frequency of radiations (10^{14}–10^{16} Hz) used to excite transitions between electronic energy levels. In such cases, the natural line width is very small. The situation is different for a transition from an excited electron spin state to the ground state. The lifetime τ of an electron spin state $\approx 10^{-8}$ s which leads to $\Delta \nu \approx 10^{8}$ Hz. This is of the order of the frequency (10^{8}–10^{9} Hz) used for exciting the transition.

1.4.2 Collision or Pressure Broadening

Collision between molecules perturbs the different energies of a molecular or atomic system. This causes a broadening of the energy levels. Collision in liquids are more pronounced than in gases. Hence, spectral line in gases are usually sharper than those in liquids. Since the collision rate is dependent on pressure, this is also known as pressure broadening. If each collision results in a transition between two states there is a line broadening $\Delta \nu$ of the transition which is given by

$$\Delta \nu = \frac{1}{2\pi\tau} \tag{1.7}$$

where τ is the mean time between collisions. Like natural line broadening this line broadening is homogeneous and produces a Lorentian line shape.

1.4.3 Doppler Broadening

The random motions of atoms or molecules in liquids and gases cause the absorption and emission frequencies to show a Doppler shift. For an individual atom or molecule, the Doppler shifted absorption frequency is given by

$$\nu = \nu_0\left(1 \pm \frac{v}{c}\right)$$

where ± sign relates to motion of the molecule towards or away the exciting radiation source, ν_0 is the absorption frequency of the stationary atom and v is the component of the molecular velocity along the light propagation direction. The usual Maxwell velocity distribution gives a Gaussian line shape function with a line broadening

$$\Delta\nu_D = \frac{\nu_0}{c}\left(\frac{2kT\,ln2}{m}\right)^{1/2} \tag{1.8}$$

where m is the mass of the atom or molecule, k is the Boltzmann constant and T is the absolute temperature. The broadening is inhomogeneous since the different atoms or molecules in a particular sample behave in different ways.

1.4.4 Saturation or Power Broadening

When light radiation passes through an absorbing medium, the energy absorbed depends on the length of the medium, incident flux and the absorption coefficient of the medium. Consider a transition from state m to state n of a system. Let N_m and N_n be the number density of the two states at equilibrium. From simple considerations it can be shown that when g_nN_m approaches g_mN_n, the rate of absorption approaches zero. Here g_m and g_n are the degeneracy of the two states. This phenomenon is called **saturation**. When the population ratio N_n/N_m approaches unity the possibility for saturation is more. Consequently, saturation is more common in rotational spectroscopy as the separation between energy levels is very small. In higher energy regions of the spectrum, extremely high power of a source may also result in saturation.

Thus, the overall lineshape exhibited by any particular transition will contain contributions from number of sources. Spectra of large molecules are further complicated by the overlap of frequencies leading to a spectrum with broad lines. Such broad absorptions are the norm in spectra recorded in the condensed phase. Doppler broadening is often the single most important factor limiting the resolution of spectra.

1.4.5 Reduction of Line Broadening

Except at very low frequencies, collision broadening can be reduced considerably by working at sufficiently low pressure.

Effusive beam method

Effusive beam of atoms or molecules or ions is produced by allowing a high pressure beam to pass through a narrow slit on the source side before entering a low pressure region. The beam may be further collimated by placing a baffle with a hole in the path of the beam (Figure 1.7). Beyond the baffle a well-collimated molecular beam is obtained. Such beams will have sufficiently long mean free path to allow one to neglect collisions even if the pressure is not too low. If observation is made perpendicular to the direction of the beam, the velocity component in that direction will be negligible and the Doppler broadening will be reduced considerably.

Another very powerful technique is the spectra of molecules in supersonic jets which is discussed in detail in Section 15.4.

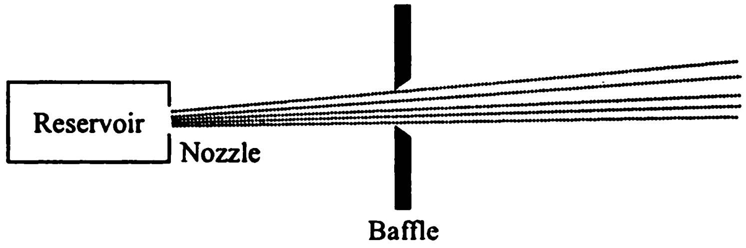


Figure 1.7 Collimated, molecular beam with reduced transverse velocity components.

1.5 ABSORPTION AND EMISSION OF RADIATION

The various energy states of a molecule form a series of energy levels. If a system has number of molecules, they are distributed among the various levels as per the Boltzmann distribution law. There are three ways by which a molecule can change its energy state.

1.5.1 Absorption

Consider a system of atoms or molecules having two energy levels, a ground level of energy E_1 (state 1) and an excited level of energy E_2 (state 2). When we allow electromagnetic radiation of frequency ν, where $h\nu = E_2 - E_1$, to interact with the system, some of the atoms or molecules absorb radiation and make transitions from state 1 to state 2. This absorption of radiation of appropriate frequency by a system is called **induced absorption** or **simply absorption**. Symbolically, absorption is represented as:

$$\text{Atom} + \text{Photon} \longrightarrow \text{Atom}^*$$

The asterisk indicates an excited state. Figure 1.8 illustrates this absorption process.

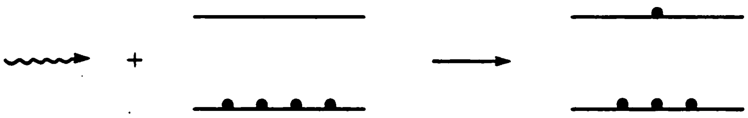


Figure 1.8 The absorption process.

1.5.2 Spontaneous Emission

Atoms or molecules in the excited state can spontaneously emit a photon of energy $h\nu = E_2 - E_1$ and come to the lower state as represented in Figure 1.9. This process of emission of a photon without the influence of an external agency is called **spontaneous emission** which is represented as:

$$\text{Atom}^* \longrightarrow \text{Atom} + \text{Photon}$$

Photons emitted by spontaneous emission will not be in phase and are said to be incoherent. Light from an ordinary light source is incoherent.

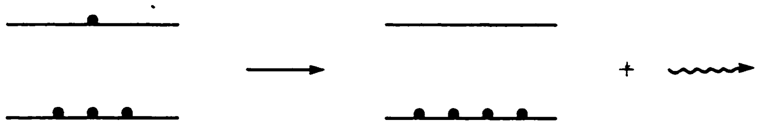


Figure 1.9 Spontaneous emission.

1.5.3 Stimulated Emission

In **stimulated emission** or **induced emission**, a molecule in the upper state may be stimulated to release a quantum of energy $h\nu = E_2 - E_1$ by the presence of another quantum of equivalent energy $h\nu$ as in Figure 1.10. Symbolically,

$$\text{Atom}^* + \text{Photon} \longrightarrow \text{Atom} + 2\ \text{Photons}$$

These two photons will be in phase and will move in the same direction. That is the output will be completely coherent. The stimulated emission process suggested by Einstein in 1917 is of fundamental importance in the development of lasers.

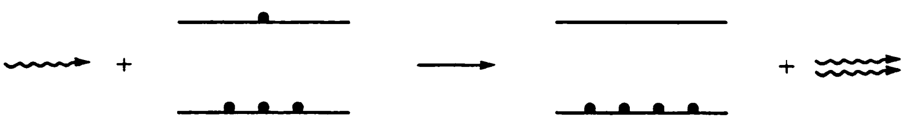


Figure 1.10 Stimulated emission.

1.6 EINSTEIN'S COEFFICIENTS

In any process of absorption or emission, two energy states are involved. Consider a two level system with n_1 atoms in level 1 (ground state) and n_2 atoms in level 2 (excited state). The distribution of atoms in the two levels is given by the Boltzmann distribution:

$$\frac{n_2}{n_1} = \frac{\exp(-E_2/kT)}{\exp(-E_1/kT)} = \exp[-(E_2 - E_1)/kT] = \exp(-h\nu/kT) \tag{1.9}$$

where k is the Boltzmann constant and ν is the frequency corresponding to the energy difference $E_2 - E_1$.

Let us assume that the system of atoms or molecules is in thermal equilibrium with radiation of density u_ν. The rate of absorption would depend on the density of radiation u_ν and the number of atoms present in the lower state.

$$\text{The rate of absorption} = B_{12} n_1 u_\nu \tag{1.10}$$

where the constant of proportionality B_{12} is simply the probability per unit time for absorption. It is usually expressed in units of $\mathrm{N^{-1}m^2s^{-2}}$. Next consider transition from state 2 to state

1. As already discussed, atoms or molecules can come from the upper state to the lower state by spontaneous and stimulated emissions.

$$\text{The rate of spontaneous emission} = A_{21}n_2 \tag{1.11}$$

where A_{21} is the probability per unit time for spontaneous emission. The unit of the constant A is s^{-1}

$$\text{The rate of stimulated emission} = B_{21}n_2u_\nu \tag{1.12}$$

where B_{21} is the probability per unit time for stimulated emission. Under equilibrium the rate of absorption must be equal to the net rate of emissions. That is

$$B_{12}n_1u_\nu = A_{21}n_2 + B_{21}n_2u_\nu$$

$$u_\nu = \frac{A_{21}n_2}{B_{12}n_1 - B_{21}n_2} = \frac{A_{21}n_2}{B_{21}n_2\left(\frac{B_{12}}{B_{21}}\frac{n_1}{n_2} - 1\right)} \tag{1.13}$$

Substituting the value of n_1/n_2 from Eq. (1.9)

$$u_\nu = \frac{A_{21}}{B_{21}\left(\frac{B_{12}}{B_{21}}e^{h\nu/kT} - 1\right)} \tag{1.14}$$

The energy density u_ν given by Planck's radiation law is

$$u_\nu = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT} - 1} \tag{1.15}$$

Comparing the two expressions for u_ν, we get

$$\frac{B_{12}}{B_{21}} = 1 \quad \text{or} \quad B_{12} = B_{21} = B \tag{1.16}$$

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3} \tag{1.17}$$

These two relations are called **Einstein's relations** and the coefficients A and B are called **Einstein's A and B coefficients**. From Eqs (1.11) and (1.12)

$$\frac{\text{Spontaneous emission rate}}{\text{Stimulated emission rate}} = \frac{A_{21}}{B_{21}u_\nu} = e^{h\nu/kT} - 1 \tag{1.18}$$

where Eqs. (1.15) and (1.17) have also been used. If $h\nu << kT$,

$$e^{h\nu/kT} - 1 \approx h\nu/kT << 1$$

the number of stimulated emission per second far exceeds the number of spontaneous emissions per second which is valid in the microwave region. If $h\nu >> kT$ the spontaneous transitions far exceed the number of stimulated emissions which is applicable in the visible and ultraviolet regions.

8.6 ROTATIONAL ENERGY LEVELS

Molecular rotational spectra are in the microwave region

Molecular energy states arise from the rotation of a molecule as a whole, from the vibrations of its atoms relative to one another, and from changes in its electronic configuration:

1 *Rotational states* are separated by quite small energy intervals (10^{-3} eV is typical). The spectra that arise from transitions between these states are in the microwave region with wavelengths of 0.1 mm to 1 cm. The absorption by water molecules of rotational energy from microwaves underlies the operation of microwave ovens.
2 *Vibrational states* are separated by somewhat larger energy intervals (0.1 eV is typical). Vibrational spectra are in the infrared region with wavelengths of 1 μm to 0.1 mm.
3 *Molecular electronic states* have the highest energies, with typical separations between the energy levels of outer electrons of several eV. The corresponding spectra are in the visible and ultraviolet regions.

A detailed picture of a particular molecule can often be obtained from its spectrum, including bond lengths, force constants, and bond angles. For simplicity the treatment here will cover only diatomic molecules, but the main ideas apply to more complicated ones as well.

The lowest energy levels of a diatomic molecule arise from rotation about its center of mass. We may picture such a molecule as consisting of atoms of masses m_1 and m_2 a distance R apart, as in Fig. 8.16. The moment of inertia of this molecule about an axis passing through its center of mass and perpendicular to a line joining the atoms is

$$I = m_1 r_1^2 + m_2 r_2^2 \tag{8.3}$$

where r_1 and r_2 are the distances of atoms 1 and 2, respectively, from the center of mass. From the definition of center of mass,

$$m_1 r_1 = m_2 r_2 \tag{8.4}$$

Hence the moment of inertia may be written

Moment of inertia

$$I = \frac{m_1 m_2}{m_1 + m_2}(r_1 + r_2)^2 = m'R^2 \tag{8.5}$$

Here

Reduced mass

$$m' = \frac{m_1 m_2}{m_1 + m_2} \tag{8.6}$$

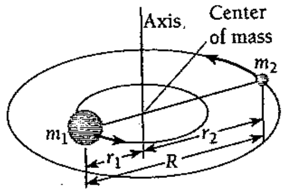


Figure 8.16 A diatomic molecule can rotate about its center of mass.

is the **reduced mass** of the molecule. Equation (8.5) states that the rotation of a diatomic molecule is equivalent to the rotation of a single particle of mass m' about an axis located a distance R away.

The angular momentum **L** of the molecule has the magnitude

$$L = I\omega \tag{8.7}$$

where ω is its angular velocity. Angular momentum is always quantized in nature, as we know. If we denote the **rotational quantum number** by J, we have here

Angular momentum

$$L = \sqrt{J(J+1)}\hbar \qquad J = 0, 1, 2, 3, \ldots \tag{8.8}$$

The energy of a rotating molecule is $\frac{1}{2}I\omega^2$, and so its energy levels are specified by

Rotational energy levels

$$E_J = \frac{1}{2}I\omega^2 = \frac{L^2}{2I}$$

$$= \frac{J(J+1)\hbar^2}{2I} \tag{8.9}$$

Rotations about the Bond Axis

We have been considering only rotation about an axis perpendicular to the bond axis of a diatomic molecules, as in Fig 8.16—end-over-end rotations. What about rotations about the axis of symmetry itself?

Such rotations can be neglected because the mass of an atom is located almost entirely in its nucleus, whose radius is only $\sim 10^{-4}$ of the radius of the atom itself. The main contribution to the moment of inertia of a diatomic molecule about its bond axis therefore comes from its electrons, which are concentrated in a region whose radius about the axis is roughly half the bond length R but whose total mass is only about $\frac{1}{4000}$ of the total molecular mass. Since the allowed rotational energy levels are proportional to $1/I$, rotation about the symmetry axis must involve energies $\sim 10^4$ times the E_J values for end-over-end rotations. Hence energies of at least several eV would be involved in any rotation about the symmetry axis of a diatomic molecule. Bond energies are also of this order of magnitude, so the molecule would be likely to dissociate in any environment in which such a rotation could be excited.

Example 8.1

The carbon monoxide (CO) molecule has a bond length R of 0.113 nm and the masses of the ^{12}C and ^{16}O atoms are respectively 1.99×10^{-26} kg and 2.66×10^{-26} kg. Find (*a*) the energy and (*b*) the angular velocity of the CO molecule when it is in its lowest rotational state.

Solution

(*a*) The reduced mass m' of the CO molecule is

$$m' = \frac{m_1 m_2}{m_1 + m_2} = \left[\frac{(1.99)(2.66)}{1.99 + 2.66}\right] \times 10^{-26}\,\text{kg}$$

$$= 1.14 \times 10^{-26}\,\text{kg}$$

and its moment of inertia I is

$$\begin{aligned} I = m'R^2 &= (1.14 \times 10^{-26}\ \text{kg})(1.13 \times 10^{-10}\ \text{m})^2 \\ &= 1.46 \times 10^{-46}\ \text{kg} \cdot \text{m}^2 \end{aligned}$$

The lowest rotational energy level corresponds to $J = 1$, and for this level in CO

$$\begin{aligned} E_{J=1} &= \frac{J(J+1)\hbar^2}{2I} = \frac{\hbar^2}{I} = \frac{(1.054 \times 10^{-34}\ \text{J} \cdot \text{s})^2}{1.46 \times 10^{-46}\ \text{kg} \cdot \text{m}^2} \\ &= 7.61 \times 10^{-23}\ \text{J} = 4.76 \times 10^{-4}\ \text{eV} \end{aligned}$$

This is not a lot of energy, and at room temperature, when $kT \approx 2.6 \times 10^{-2}$ eV, nearly all the molecules in a sample of CO are in excited rotational states.

(*b*) The angular velocity of the CO molecule when $J = 1$ is

$$\begin{aligned} \omega &= \sqrt{\frac{2E}{I}} = \sqrt{\frac{(2)(7.61 \times 10^{-23}\ \text{J})}{1.46 \times 10^{-46}\ \text{kg} \cdot \text{m}^2}} \\ &= 3.23 \times 10^{11}\ \text{rad/s} \end{aligned}$$

Rotational Spectra

Rotational spectra arise from transitions between rotational energy states. Only molecules that have electric dipole moments can absorb or emit electromagnetic photons in such transitions. For this reason nonpolar diatomic molecules such as H_2 and symmetric polyatomic molecules such as CO_2 (O=C=O) and CH_4 (Fig. 8.13) do not exhibit rotational spectra. Transitions between rotational states in molecules like H_2, CO_2, and CH_4 can take place during collisions, however.

Even in molecules with permanent dipole moments, not all transitions between rotational states involve radiation. As in the case of atomic spectra, certain selection rules summarize the conditions for a radiative transition between rotational states to be possible. For a rigid diatomic molecule the selection rule for rotational transitions is

Selection rule

$$\Delta J = \pm 1 \tag{8.10}$$

In practice, rotational spectra are always obtained in absorption, so that each transition that is found involves a change from some initial state of quantum number J to the next higher state of quantum number $J + 1$. In the case of a rigid molecule, the frequency of the absorbed photon is

Rotational spectra

$$\begin{aligned} \nu_{J \rightarrow J+1} &= \frac{\Delta E}{h} = \frac{E_{J+1} - E_J}{h} \\ &= \frac{\hbar}{2\pi I}(J + 1) \end{aligned} \tag{8.11}$$

where I is the moment of inertia for end-over-end rotations. The spectrum of a rigid molecule therefore consists of equally spaced lines, as in Fig. 8.17. The frequency of each line can be measured, and the transition it corresponds to can often be found from the sequence of lines. From these data the moment of inertia of the molecule can be calculated. Alternatively, the frequencies of any two successive lines may be used to determine I if the lowest-frequency lines in a particular spectral sequence are not recorded

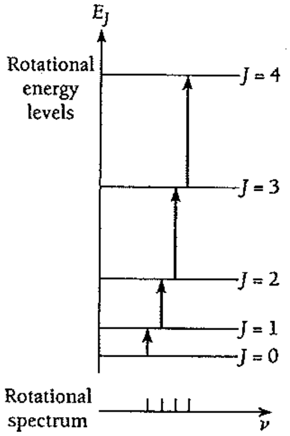


Figure 8.17 Energy levels and spectrum of molecular rotation.

Example 8.2

In CO the $J = 0 \rightarrow J = 1$ absorption line occurs at a frequency of 1.15×10^{11} Hz. What is the bond length of the CO molecule?

Solution

First we find the moment of inertia of this molecule from Eq. (8.11):

$$I_{CO} = \frac{\hbar}{2\pi\nu}(J + 1) = \frac{1.054 \times 10^{-34}\,\mathrm{J \cdot s}}{(2\pi)(1.15 \times 10^{11}\,\mathrm{s^{-1}})} = 1.46 \times 10^{-46}\,\mathrm{kg \cdot m^2}$$

In Example 8.1 we saw that the reduced mass of the CO molecule is $m' = 1.14 \times 10^{-26}$ kg. From Eq. (8.5), $I = m'R^2$, we obtain

$$R_{CO} = \sqrt{\frac{I}{m'}} = \sqrt{\frac{1.46 \times 10^{-46}\,\mathrm{kg \cdot m^2}}{1.14 \times 10^{-26}\,\mathrm{kg}}} = 1.13 \times 10^{-10}\,\mathrm{m} = 0.113\,\mathrm{nm}$$

This is the way in which the bond length for CO quoted earlier was determined.

8.7 VIBRATIONAL ENERGY LEVELS

A molecule may have many different modes of vibration

When sufficiently excited, a molecule can vibrate as well as rotate. Figure 8.18 shows how the potential energy of a diatomic molecule varies with the internuclear distance R. Near the minimum of this curve, which corresponds to the normal configuration of the molecule, the shape of the curve is very nearly a parabola. In this region, then,

Parabolic approximation
$$U = U_0 + \frac{1}{2}k(R - R_0)^2 \qquad (8.12)$$

where R_0 is the equilibrium separation of the atoms.

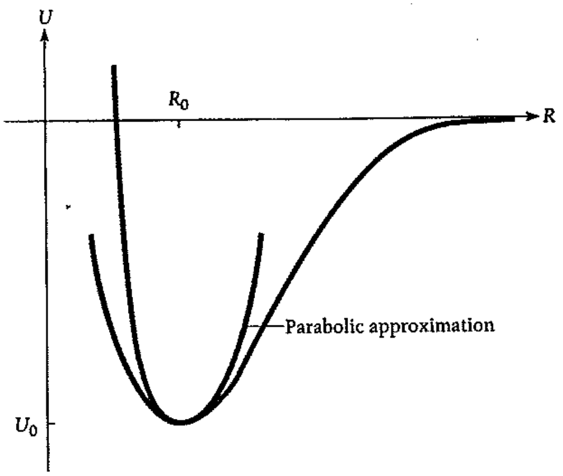


Figure 8.18 The potential energy of a diatomic molecule as a function of internuclear distance.

The interatomic force that gives rise to this potential energy is given by differentiating U:

$$F = -\frac{dU}{dR} = -k(R - R_0) \tag{8.13}$$

The force is just the restoring force that a stretched or compressed spring exerts—a Hooke's law force—and, as with a spring, a molecule suitably excited can undergo simple harmonic oscillations.

Classically, the frequency of a vibrating body of mass m connected to a spring of force constant k is

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \tag{8.14}$$

What we have in the case of a diatomic molecule is the somewhat different situation of two bodies of masses m_1 and m_2 joined by a spring, as in Fig. 8.19. In the absence

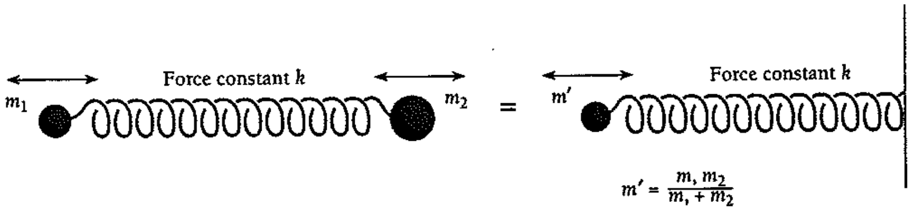


Figure 8.19 A two-body oscillator behaves like an ordinary harmonic oscillator with the same spring constant but with the reduced mass m'.

of external forces the linear momentum of the system remains constant, and the oscillations of the bodies therefore cannot effect the motion of their center of mass. For this reason m_1 and m_2 vibrate back and forth relative to their center of mass in opposite directions, and both reach the extremes of their respective motions at the same times. The frequency of oscillation of such a two-body oscillator is given by Eq. (8.14) with the reduced mass m' of Eq. (8.6) substituted for m:

Two-body oscillator

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m'}} \tag{8.15}$$

When the harmonic-oscillator problem is solved quantum mechanically (see Sec. 5.11), the energy of the oscillator turns out to be restricted to the values

Harmonic oscillator

$$E_v = (v + \tfrac{1}{2})h\nu_0 \tag{8.16}$$

where v, the **vibrational quantum number**, may have the values

Vibrational quantum number

$$v = 0, 1, 2, 3, \ldots$$

The lowest vibrational state ($v = 0$) has the zero-point energy $\frac{1}{2}h\nu_0$, not the classical value of 0. This result is in accord with the uncertainty principle, because if the oscillating particle were stationary, the uncertainty in its position would be $\Delta x = 0$ and its momentum uncertainty would then have to be infinite—and a particle with $E = 0$ cannot have an infinitely uncertain momentum. In view of Eq. (8.15) the vibrational energy levels of a diatomic molecule are specified by

Vibrational energy levels

$$E_v = (v + \tfrac{1}{2})\hbar\sqrt{\frac{k}{m'}} \tag{8.17}$$

The higher vibrational states of a molecule do not obey Eq. (8.16) because the parabolic approximation to its potential-energy curve becomes less and less valid with increasing energy. As a result, the spacing between adjacent energy levels of high v is less than the spacing between adjacent levels of low v, which is shown in Fig. 8.20.

Gerhard Herzberg (1904–1999) was born in Hamburg, Germany, and received his doctorate from the Technical University of Darmstadt in 1928. The rise to power of the Nazis led Herzberg to leave Germany in 1935 for Canada, where he joined the University of Saskatchewan. From 1945 to 1948 he was at Yerkes Observatory in Wisconsin, and after that he directed the Division of Pure Physics of Canada's National Research Council in Ottawa until he retired in 1969. Herzberg was a pioneer in using spectra to determine molecular structures, and also did important work in analyzing the spectra of stars, interstellar gas, comets, and planetary atmospheres. His books under the general title *Molecular Spectra and Molecular Structure* are classics in the field. He received the Nobel Prize in chemistry in 1971.

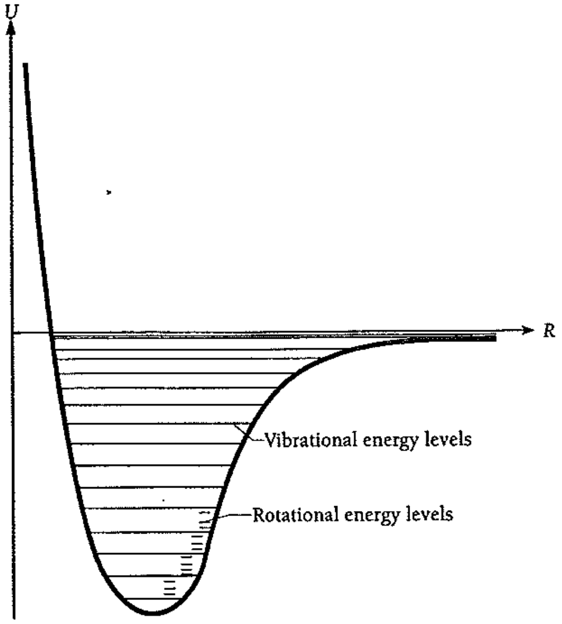


Figure 8.20 The potential energy of a diatomic molecule as a function of interatomic distance, showing vibrational and rotational energy levels.

This diagram also shows the fine structure in the vibrational levels caused by the simultaneous excitation of rotational levels.

Vibrational Spectra

The selection rule for transitions between vibrational states is

Selection rule $$\Delta v = \pm 1 \qquad (8.18)$$

in the harmonic-oscillator approximation. This rule is easy to understand. An oscillating dipole whose frequency is ν_0 can absorb or emit only electromagnetic radiation of the same frequency and all quanta of frequency ν_0 have the energy $h\nu_0$. The oscillating dipole accordingly can only absorb $\Delta E = h\nu_0$ at a time, in which case its energy increases from $(v + \frac{1}{2})h\nu_0$ to $(v + \frac{1}{2} + 1)h\nu_0$. It can also emit only $\Delta E = h\nu_0$ at a time, in which case its energy decreases from $(v + \frac{1}{2})h\nu_0$ to $(v + \frac{1}{2} - 1)h\nu_0$. Hence the selection rule $\Delta v = \pm 1$.

Example **8.3**

When CO is dissolved in liquid carbon tetrachloride, infrared radiation of frequency 6.42×10^{13} Hz is absorbed. Carbon tetrachloride by itself is transparent at this frequency, so the absorption must be due to the CO. (*a*) What is the force constant of the bond in the CO molecule? (*b*) What is the spacing between its vibrational energy levels?

Solution

(*a*) As we know, the reduced mass of the CO molecule is $m' = 1.14 \times 10^{-26}$ kg. From Eq. (8.15), $\nu_0 = (1/2\pi)\sqrt{k/m'}$, the force constant is

$$\begin{aligned} k &= 4\pi^2\nu_0^2 m' = (4\pi^2)(6.42 \times 10^{13}\ \text{Hz})^2(1.14 \times 10^{-26}\ \text{kg}) \\ &= 1.86 \times 10^3\ \text{N/m} \end{aligned}$$

This is about 10 lb/in.

(*b*) The separation ΔE between the vibrational levels in CO is

$$\begin{aligned} \Delta E = E_{v+1} - E_v = h\nu_0 &= (6.63 \times 10^{-34}\ \text{J} \cdot \text{s})(6.42 \times 10^{13}\ \text{Hz}) \\ &= 4.26 \times 10^{-20}\ \text{J} = 0.266\ \text{eV} \end{aligned}$$

This is considerably more than the spacing between its rotational energy levels. Because $\Delta E > kT$ for vibrational states in a sample at room temperature, most of the molecules in such a sample exist in the $v = 0$ state with only their zero-point energies. This situation is very different from that characteristic of rotational states, where the much smaller energies mean that the majority of the molecules in a room-temperature sample are excited to higher states.

A complex molecule may have many different modes of vibration. Some of these modes involve the entire molecule (Figs. 8.21 and 8.22), but others ("local modes") involve only groups of atoms whose vibrations occur more or less independently of the rest of the molecule. Thus the —OH group has a characteristic vibrational frequency of 1.1×10^{14} Hz and the —NH_2 group has a frequency of 1.0×10^{14} Hz.

The characteristic vibrational frequency of a carbon-carbon group depends upon the number of bonds between the C atoms: the >C—C< group vibrates at about 3.3×10^{13} Hz, the >C=C< group vibrates at about 5.0×10^{13} Hz, and the —C≡C— group vibrates at about 6.7×10^{13} Hz. (As we would expect, the more carbon-carbon bonds, the larger the force constant k and the higher the frequency.) In each case the frequency does not depend strongly on the particular molecule or the location in the molecule of the group, which makes vibrational spectra a valuable tool in determining molecular structures.

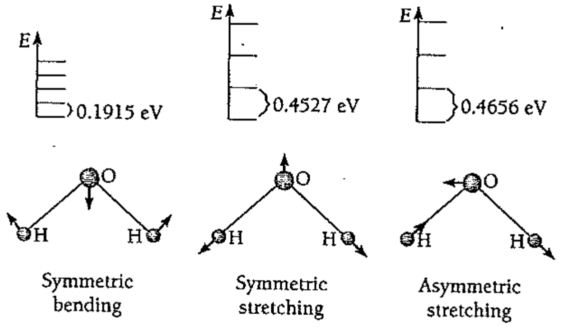


Figure 8.21 The normal modes of vibration of the H_2O molecule and the energy levels of each mode. More energy is needed to stretch the molecule than to bend it, which is generally true.

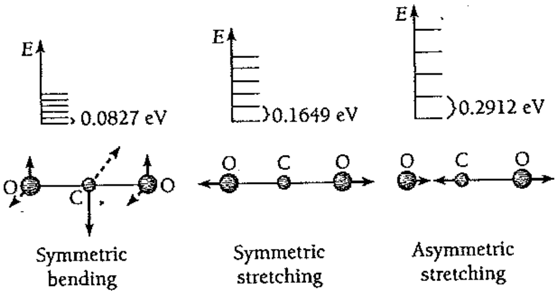
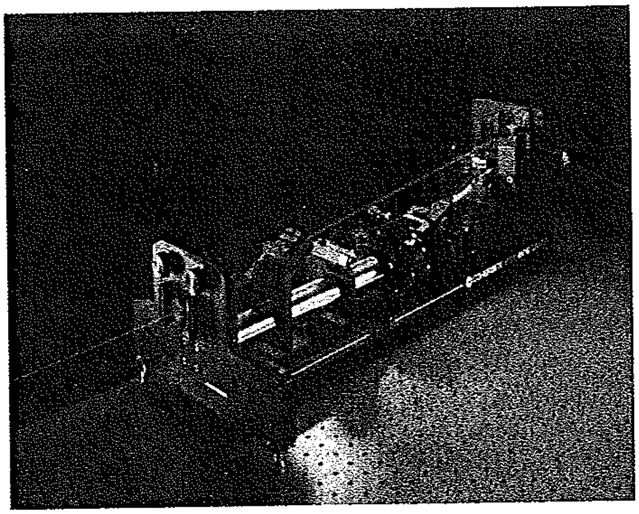


Figure 8.22 The normal modes of vibration of the CO_2 molecule and the energy levels of each mode The symmetric bending mode can occur in two perpendicular planes. In this molecule the O atoms are negatively charged and the C atom is positively charged. The symmetric streching mode cannot be initiated by the absorption of a photon because the overall charge distribution in the molecule does not change in this mode. In the other modes of vibration, however, the charge distribution does change and the molecule can absorb photons of appropriate wavelength (4.26 μm and 15.00 μm for the asymmetric stretching and symmetric bending modes, respectively). The absorption of infrared radiation from the earth by atmospheric CO_2 molecules is partly responsible for the greenhouse effect (see Fig. 9.8), and the increase in the CO_2 content of the atmosphere due to the burning of fossil fuels seems to be the chief cause of the global warming trend now under way. Other molecules in the atmosphere, such as H_2O and CH_4 (methane), also contribute to the greenhouse effect, but N_2 and O_2 do not because, since their overall charge distributions do not change when they vibrate, they do not absorb infrared radiation.

An example is thioacetic acid, whose structure might conceivably be either CH_3CO—SH or CH_3CS—OH. The infrared absorption spectrum of thioacetic acid contains lines at frequencies equal to the vibrational frequencies of the $>$C=O and and —SH groups, but no lines corresponding to the $>$C=S or —OH groups. The first alternative is evidently the correct one.



This tunable dye laser emits light with wavelengths from 370 to 900 nm, which includes the entire visible spectrum. The bandwidth can be as narrow as 500 kHz.

Vibration-Rotation Spectra

Pure vibrational spectra are observed only in liquids where interactions between adjacent molecules inhibit rotation. Because the excitation energies involved in molecular rotation are much smaller than those involved in vibration, the freely moving molecules in a gas or vapor nearly always are rotating, regardless of their vibrational state. The spectra of such molecules do not show isolated lines corresponding to each vibrational transition, but instead a large number of closely spaced lines due to transitions between the various rotational states of one vibrational level and the rotational states of the other. In spectra obtained using a spectrometer with inadequate resolution, the lines appear as a broad streak called a vibration-rotation band.

Tunable Dye Lasers

The existence of bands of extremely closely spaced lines in molecular spectra underlies the operation of the **tunable dye laser.** Such a laser uses an organic dye whose molecules are "pumped" to excited states by light from another laser. The dye then fluoresces in a broad emission band. From this band, light of the desired wavelength λ can be selected for laser amplification with the help of a pair of facing mirrors, one of them partly transparent. The separation of the mirrors is set to an integral multiple of $\lambda/2$. As in the case of the lasers discussed in Sec. 4.9, the trapped laser light forms an optical standing wave that emerges through the partly transparent mirror. A dye laser of this kind can be tuned to a precision of better than one part in a million by adjusting the spacing of the mirrors.

8.8 ELECTRONIC SPECTRA OF MOLECULES

How fluorescence and phosphorescence occur

The energies of rotation and vibration in a molecule are due to the motion of its atomic nuclei, which contain virtually all the molecule's mass. The molecule's electrons also can be excited to higher energy levels than those corresponding to its ground state. However, the spacing of these levels is much greater than the spacing of rotational or vibrational levels.

Electronic transitions involve radiation in the visible or ultraviolet parts of the spectrum. Each transition appears as a series of closely spaced lines, called a band, due to the presence of different rotational and vibrational states in each electronic state (Fig. 8.23). All molecules exhibit electronic spectra, since a dipole moment change always accompanies a change in the electronic configuration of a molecule. Therefore homonuclear molecules, such as H_2 and N_2, which have neither rotational nor

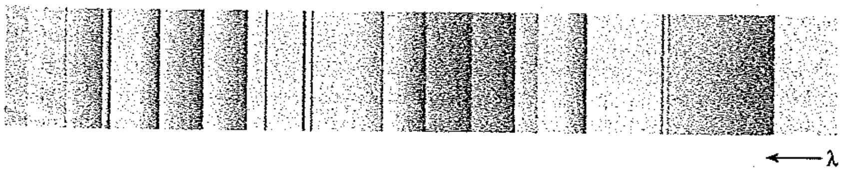
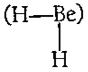


Figure 8.23 A portion of the band spectrum of PN.

vibrational spectra because they lack permanent dipole moments, nevertheless have electronic spectra whose rotational and vibrational fine structures enable moments of inertia and bond force constants to be found.

Electronic excitation in a polyatomic molecule often leads to a change in the molecule's shape, which can be determined from the rotational fine structure in its band spectrum. The origin of such changes lies in the different characters of the wave functions of electrons in different states, which lead to correspondingly different bond geometries. For example, the molecule beryllium hydride, BeH_2, is linear (H—Be—H) in one state and bent  $(\mathrm{H{-}\underset{\underset{H}{|}}{Be}})$ in another.

Fluorescence

A molecule in an excited electronic state can lose energy and return to its ground state in various ways. The molecule may, of course, simply emit a photon of the same frequency as that of the photon it absorbed, thereby returning to the ground state in a single step. Another possibility is **fluorescence.** Here the molecule gives up some of its vibrational energy in collisions with other molecules, so that the downward radiative transition originates from a lower vibrational level in the upper electronic state (Fig. 8.24). Fluorescent radiation is therefore of lower frequency than that of the absorbed radiation.

Fluorescence excited by ultraviolet light has many applications, for instance to help identify minerals and biochemical compounds. Fabric "brighteners" that are sometimes

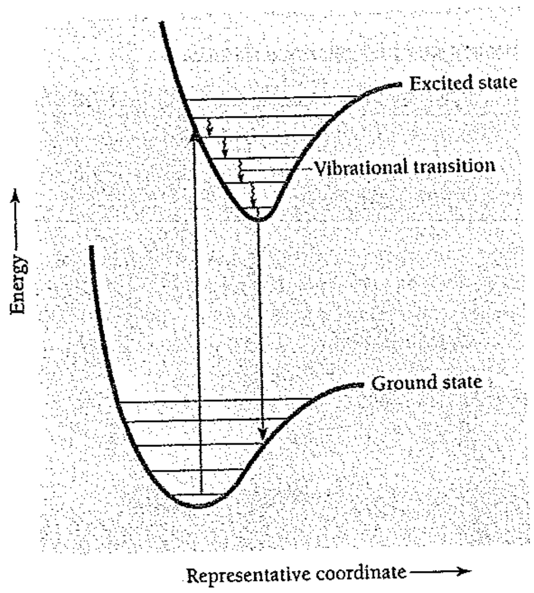


Figure 8.24 The origin of fluorescence. The emitted radiation is lower in frequency than the absorbed radiation.

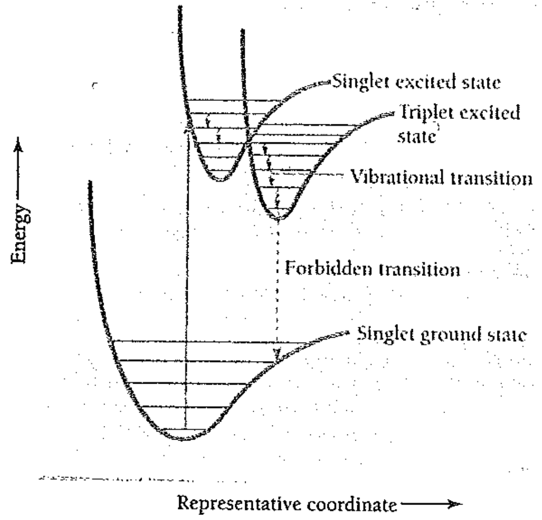


Figure 8.25 The origin of phosphorescence. The final transition is delayed because it violates the selection rules for electronic transitions.

added to detergents absorb ultraviolet radiation in daylight and then fluoresce blue light. In a **fluorescent lamp**, a mixture of mercury vapor and an inert gas such as argon inside a glass tube gives off ultraviolet radiation when an electric current is passed through it. The inside of the tube is coated with a fluorescent material called a phosphor that emits visible light when excited by the ultraviolet radiation. The process is much more efficient than using a current to heat a filament to incandescence, as in ordinary light bulbs.

Phosphorescence

In molecular spectra, radiative transitions between electronic states of different total spin are prohibited. Figure 8.25 shows a situation in which the molecule in its singlet (total spin quantum number $S = 0$) ground state absorbs a photon and is raised to a singlet excited state. In collisions the molecule can undergo radiationless transitions to a lower vibrational level that may happen to have about the same energy as one of the levels in the triplet ($S = 1$) excited state. There is then a certain probability for a shift to the triplet state to occur. Further collisions in the triplet state bring the molecule's energy below that of the crossover point, so that it is now trapped in the triplet state and ultimately reaches the $v = 0$ level.

A radiative transition from a triplet to a singlet state is "forbidden" by the selection rules, which really means not that it is impossible but that it has only a small likelihood of occurring. Such transitions accordingly have long half-lives, and the resulting **phosphorescent radiation** may be emitted minutes or even hours after the initial absorption.

Raman Scattering 8

8.1 INTRODUCTION

Photons can interact with molecules of matter in number of ways. When they strike a solid or collection of molecules, most of them are scattered elastically (Rayleigh scattering). But a few (1 in 10^6) undergo inelastic scattering. These inelastically scattered photons have frequencies lower and higher than the incident frequency. This phenomenon, predicted in 1923 by Smekel and observed by Sir C.V. Raman in 1928, is referred to as Raman scattering. The lines on the low and high frequency sides of the Rayleigh line are called **Stokes and anti-Stokes lines** respectively. The scattered photons have frequency shifts ($10 - 4{,}000\ \text{cm}^{-1}$) characteristic of the vibrational or rotational energies of the molecule. These weak lines of modified frequencies are generally referred to as the **Raman spectrum** and the frequency shift from the exciting line as **Raman shift.**

8.2 THEORY OF RAMAN SCATTERING

8.2.1 Classical Theory

An insight into the phenomenon of Raman scattering is possible on the basis of classical considerations. When a molecule is placed in an electric field, polarization of the medium takes place as the negatively-charged electron cloud is being attracted towards the positive pole and the positively-charged nuclei being attracted towards the negative pole. The polarization P so induced is proportional to the applied electric field **E**. That is,

$$\mathbf{P} = \alpha \mathbf{E} \tag{8.1}$$

The constant of proportionality α is the polarizability of the molecule. In general, it is a tensor with nine components.

When radiation of frequency ν_0 is allowed to fall on molecules, each molecule experiences a varying electric field

$$E = E_0 \cos 2\pi \nu_0 t \tag{8.2}$$

For simplicity let us consider the vibrational motion of the molecule. Q be the normal coordinate associated with a particular mode of vibration of frequency ν_m of the molecule. In the harmonic approximation, Q can be written as

$$Q = Q_0 \cos 2\pi \nu_m t \tag{8.3}$$

The polarizability α can be expressed as a Taylor series in the normal coordinate Q as

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial Q}\right)_0 Q + \ldots \tag{8.4}$$

Neglecting higher order terms and substituting Eqs. (8.2), (8.3) and (8.4) in Eq. (8.1)

$$P = \left[\alpha_0 + \left(\frac{\partial \alpha}{\partial Q}\right)_0 Q_0 \cos 2\pi \nu_m t\right] E_0 \cos 2\pi \nu_0 t$$

$$= \alpha_0 E_0 \cos 2\pi \nu_0 t + \left(\frac{\partial \alpha}{\partial Q}\right)_0 Q_0 E_0 \cos 2\pi \nu_0 t \cos 2\pi \nu_m t$$

Using the trigonometric relation

$$2 \cos \theta \cos \phi = \cos (\theta + \phi) + \cos (\theta - \phi)$$

the above equation can be written as

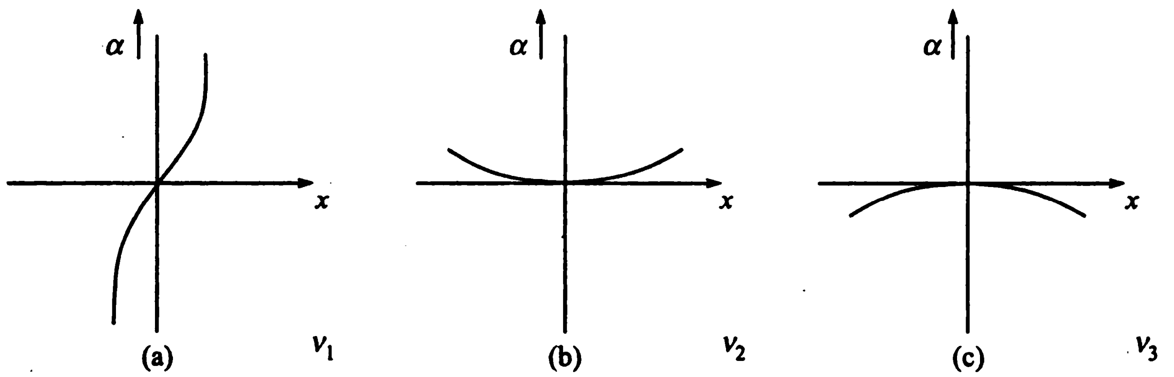
$$P = \alpha_0 E_0 \cos 2\pi \nu_0 t + \frac{1}{2}\left(\frac{\partial \alpha}{\partial Q}\right)_0 Q_0 E_0 [\cos 2\pi(\nu_0 + \nu_m)t + \cos 2\pi(\nu_0 - \nu_m)t] \tag{8.5}$$

The polarization thus induced contains the three distinct frequency components

(i) $\nu = \nu_0$	**Rayleigh line**
(ii) $\nu = \nu_0 - \nu_m$	**Raman Stokes line**
(iii) $\nu = \nu_0 + \nu_m$	**Raman anti-Stokes line**

It may be noted that if $(\partial \alpha / \partial Q)_0$ is zero, no Raman line will be observed. Thus, we get the important rule that a molecular vibration will be Raman-active only if it causes a change in a component of the polarizability.

A change in polarizability means a change either in magnitude or in direction. This is illustrated for the normal modes of the linear triatomic molecule CO_2 in Figure 8.1. The polarizability is plotted with respect to the displacement coordinate x. For the ν_1 and ν_3 modes, x is a measure of the extension or compression of the bond. For the ν_2 mode, x measures the displacement of the bond angle from its equilibrium value. For small



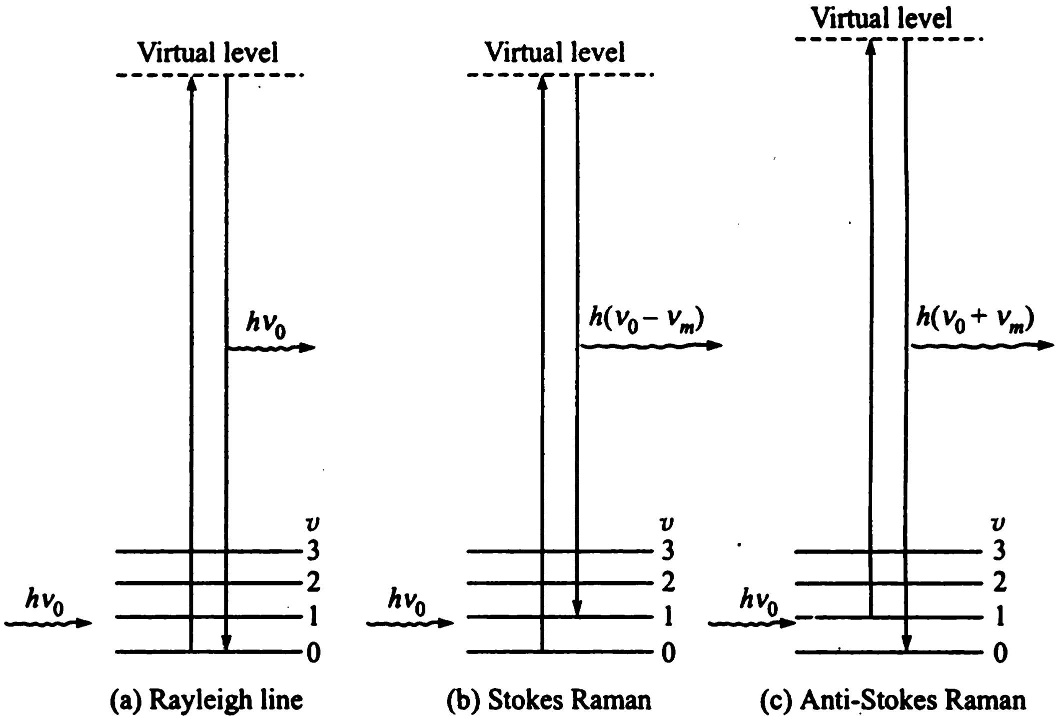
(a) ν_1 (b) ν_2 (c) ν_3

Figure 8.1 Variation of the polarizability α with the displacement coordinate x during the normal modes in CO_2 molecule.

displacement from the equilibrium position, the curve is almost flat in both ν_2 and ν_3 modes leading to zero value for $(\partial\alpha/\partial x)$. Hence, they are Raman-inactive. However, ν_1 is Raman-active since a small displacement changes the polarizability appreciably. Though the classical theory correctly describes the frequencies $\nu_0 \pm \nu_m$ of the Raman lines, it fails to give the correct intensities. Only a quantum mechanical theory would be able to predict the intensities.

8.2.2 Quantum Theory

In the quantum picture, radiation has both particle and wave nature. In explaining Raman scattering, incident radiation of frequency ν_0 is considered as a stream of particles (photons) undergoing collision with molecules. If the collision is perfectly elastic, there will not be any exchange of energy between the photons and the molecule. However, there will be exchange of energy between the two if the collision is inelastic. The molecule can gain or lose energy equal to the energy difference ΔE between any two of its allowed states. If the molecule gains energy, the scattered photons will have frequency $\nu_0 - \nu_m$ where $\nu_m = \Delta E/h$ **(Stokes line)**. On the other hand if it loses energy the scattered photon will have frequency $\nu_0 + \nu_m$ **(anti-Stokes line)**. The different processes giving rise to Rayleigh, Stokes and anti-Stokes lines are illustrated in Figure 8.2.



(a) Rayleigh line (b) Stokes Raman (c) Anti-Stokes Raman

Figure 8.2 Energy level diagram showing Rayleigh and Raman lines. v = 0, 1, 2, 3, ... are the vibrational levels of the ground electronic state.

When a system interacts with a radiation of frequency ν_0, it may make an upward transition to a virtual state of the system (A virtual state is not one of the stationary states of the molecule. It corresponds to a combined state of the molecule and radiation. Such a state will not be there when only one of them alone is there). Most of the molecules of the system return to the original state from the virtual state giving the Rayleigh scattering. However, a very small fraction returns to states of higher and lower energies giving rise to Stokes and anti-Stokes lines respectively. If the virtual state of the system coincides with a real state of the system, it will lead to **resonance Raman effect**. It may be pointed out here that the annihilation of the incident photon and the creation of the scattered photon are simultaneous.

The intensity of a spectral line depends on number of factors, the most important being the initial population of the state from which the transition originates. The Stokes line originating from $v = 0$ and the anti-Stokes from $v = 1$ give the same Raman shift ν_m. Based on Boltzmann distribution for the population in states, the intensity ratio of Stokes to anti-Stokes is given by

$$\frac{I_s}{I_{a.s}} = \exp\frac{h\nu_m}{kT} \tag{8.6}$$

where k is the Boltzmann constant and T is the temperature in Kelvin. A more rigorous theory, taking other factors into account, gives

$$\frac{I_s}{I_{a.s}} = \frac{(\nu_0 - \nu_m)^4}{(\nu_0 + \nu_m)^4} \exp\frac{h\nu_m}{kT} \tag{8.7}$$

Anti-Stokes lines have much less intensity than Stokes lines as evident from Eq. (8.7).

8.3 ROTATIONAL RAMAN SPECTRA

8.3.1 Linear Molecules

Rotational energy changes in molecules can be studied with the help of Raman scattering. As Raman spectrometer is not that sensitive to detect small energy contributions, the rotational energy levels of a linear molecule can be written as (Eq. 6.8)

$$\varepsilon_J = BJ(J + 1)\,\text{cm}^{-1}, \qquad J = 0, 1, 2, 3, \ldots \tag{8.8}$$

A quantum mechanical treatment leads to the rotational selection rule

$$\Delta J = 0, \pm 2$$

$\Delta J = 0$ corresponds to the trivial Rayleigh scattering. If the usual practice of defining ΔJ as J in the upper state minus J in the lower state is followed, $\Delta J = -2$ may be ignored since for a pure rotational change the upper state J must necessarily be greater than the lower state J. Then restricting only to $\Delta J = J' - J'' = +2$ (S-branch), from Eq. (8.8) we have

$$\begin{aligned}\bar{\nu} = \varepsilon_{J'=J+2} - \varepsilon_{J''=J} &= BJ'(J' + 1) - BJ''(J'' + 1)\\ &= B(4J + 6), \qquad J = 0, 1, 2, \ldots\end{aligned}$$

During collision, if the molecule gains rotational energy from the photon, it gives rise to a series of lines on the low frequency side of the exciting line. Such spectral lines are the Stokes lines. Raman spectra deals with the displacement of each Raman line from the exciting line $\bar{\nu}_0$. Hence, we may write for Stokes lines

$$\bar{\nu} = \bar{\nu}_0 - B(4J + 6)\,\text{cm}^{-1} \qquad J = 0, 1, 2, 3, \ldots \tag{8.9a}$$

During collision, if the molecule gives energy to the photon, the *S* branch lines appear on the high frequency side of the exciting line. These are the anti-Stokes lines and their frequencies are given by

$$\bar{\nu} = \bar{\nu}_0 + B(4J + 6)\,\text{cm}^{-1} \qquad J = 0, 1, 2, 3, \ldots \tag{8.9b}$$

Combining Eqs. (8.9a) and (8.9b)

$$\bar{\nu} = \bar{\nu}_0 \pm B(4J + 6)\,\text{cm}^{-1}, \qquad J = 0, 1, 2, \ldots \tag{8.10}$$

Here, the positive sign refers to anti-Stokes line and negative sign to Stokes lines.

Figure 8.3 shows schematically the allowed transitions and the rotational Raman spectrum exhibited by a linear molecule. The Raman shift of the first Stokes or anti-Stokes line from the exciting line is $6B\,\text{cm}^{-1}$. The separation between successive lines on either side of the exciting line is $4B\,\text{cm}^{-1}$. The Stokes and anti-Stokes lines appear with considerable intensity as all the rotational levels belong to $v = 0$ vibrational state which makes all the levels reasonably populated. Molecules having larger moment of inertia may not give a well resolved rotational spectrum as *B* will be very small for such systems. However, for diatomic and other light linear molecules the spectrum will normally be resolved and a measurement of the separation allows the determination of *B* which in turn gives the interatomic distances.

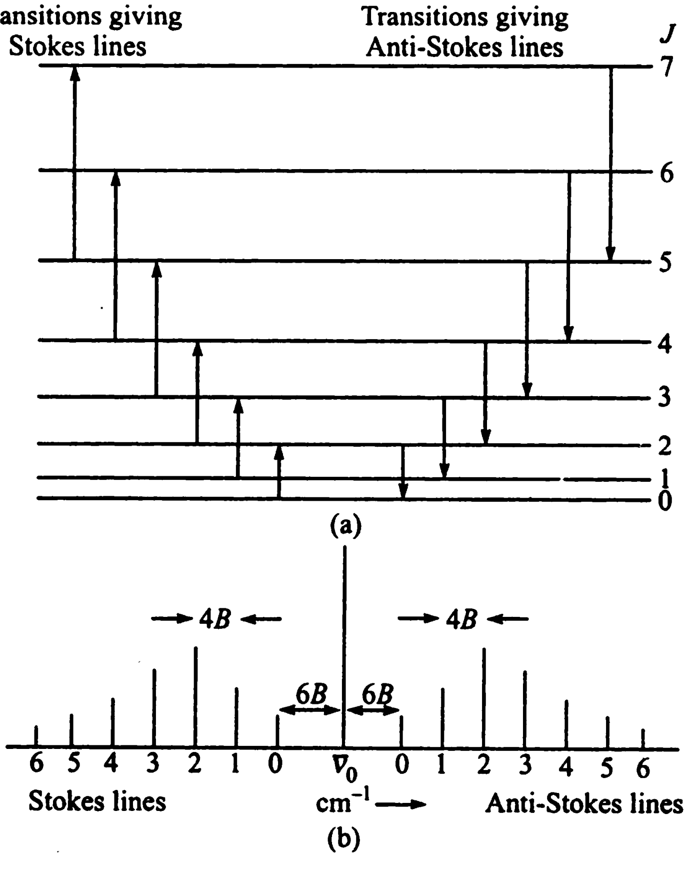


Figure 8.3 (a) The allowed transitions between rotational energy levels of a linear molecule. (b) The predicted rotational Raman spectrum. The spectral lines are numbered according to their lower *J* values.

We have already seen that homonuclear diatomic molecules do not give an infrared or microwave spectrum (Sections 6.2, 7.3). However, such molecules give pure rotational Raman spectra since the polarizability changes during the rotational motion. Therefore, Raman spectroscopy may be used as a method for obtaining molecular parameters of homonuclear diatomic molecules. Another interesting feature observed is the effect of nuclear spin on the spectra of molecules having centre of symmetry as in infrared spectra. As already discussed (Section 7.11), levels with even J values are empty in molecules like O_2 and CO_2 (nuclear spin of oxygen zero), and therefore, transitions labelled 0, 2, 4, ... in Fig. 8.3(b) will be absent. Consequently, a spacing of $8B$ between consecutive lines is observed instead of $4B$. In the case of molecules made up of nuclei with nonzero spin (H_2, $H{-}C \equiv C{-}H$) and having a centre of symmetry, the spectral lines show an alternation of intensities (Section 7.11.2).

8.3.2 Symmetric Top Molecules

In symmetric top molecules, the rotation about the top axis does not produce a change in the polarizability whereas end over end rotation produces a change. The rotational energy levels of a symmetric top molecule is given by

$$\varepsilon_{J,K} = BJ(J+1) + (A-B)K^2\,\text{cm}^{-1} \qquad J = 0, 1, 2, \ldots, \quad K = 0, \pm 1, \pm 2, \ldots \pm J \tag{8.11}$$

The selection rules are

$$\Delta K = 0, \qquad \Delta J = 0, \pm 1, \pm 2 \qquad (\text{for } K = 0 \text{ states, } \Delta J = \pm 2 \text{ only}) \tag{8.12}$$

Again, $\Delta J = 0$ corresponds to Rayleigh scattering. As K represents the angular momentum about the top axis, $\Delta K = 0$ implies that rotations about the top axis are Raman inactive. Since $K = 0$ for the ground state, it is governed by the selection rule $\Delta J = \pm 2$ only. For $J = 1, 2, 3, \ldots$, K will have values other than zero and $\Delta J = \pm 1$ transitions are allowed.

We shall next consider the frequencies of the transitions. Restricting ourselves again to $\Delta J = J' - J'' = 1$

$$\begin{aligned} \varepsilon_{J+1,K} - \varepsilon_{J,K} &= B(J+1)(J+2) + (A-B)K^2 - BJ(J+1) - (A-B)K^2 \\ &= 2B\,(J+1)\,\text{cm}^{-1}, \qquad J = 1, 2, 3, \ldots \end{aligned}$$

When the molecules gain rotational energy from the photon we get Stokes lines of frequencies

$$\bar{\nu} = \bar{\nu}_0 - 2B(J+1)\,\text{cm}^{-1}, \qquad J = 1, 2, 3, \ldots$$

and when molecule loses energy to photon we get anti-Stokes lines of frequencies

$$\bar{\nu} = \bar{\nu}_0 + 2B(J+1)\,\text{cm}^{-1}, \qquad J = 1, 2, 3, \ldots$$

Hence, for $\Delta J = +1$ (R branch), we have the frequencies of anti-Stokes and Stokes lines as

$$\bar{\nu}_R = \bar{\nu}_0 \pm 2B(J+1)\,\text{cm}^{-1}, \qquad J = 1, 2, 3, \ldots \tag{8.13}$$

where the subscript R stands for R branch. The R branch lines appear at $4B$, $6B$, $8B$, $10B$, ... cm^{-1} from the exciting line. Similar calculations for $\Delta J = +2$ (S-branch) leads to anti-Stokes and Stokes lines of frequencies

$$\bar{\nu}_s = \bar{\nu}_0 \pm B(4J+6)\,\text{cm}^{-1}, \qquad J = 0, 1, 2, 3, \ldots \tag{8.14}$$