

**Atomic and Molecular Absorption Spectrometry
for Pollution Monitoring**

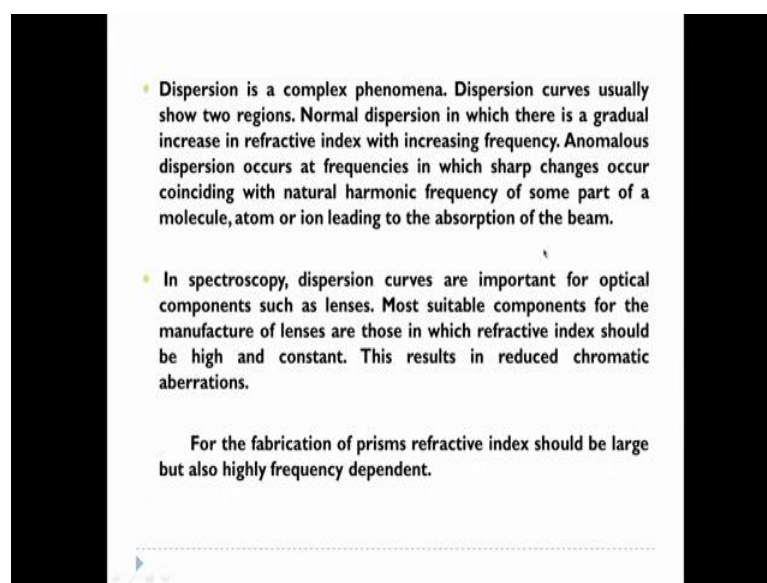
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Lecture – 06

Interaction of EM radiation with matter –II

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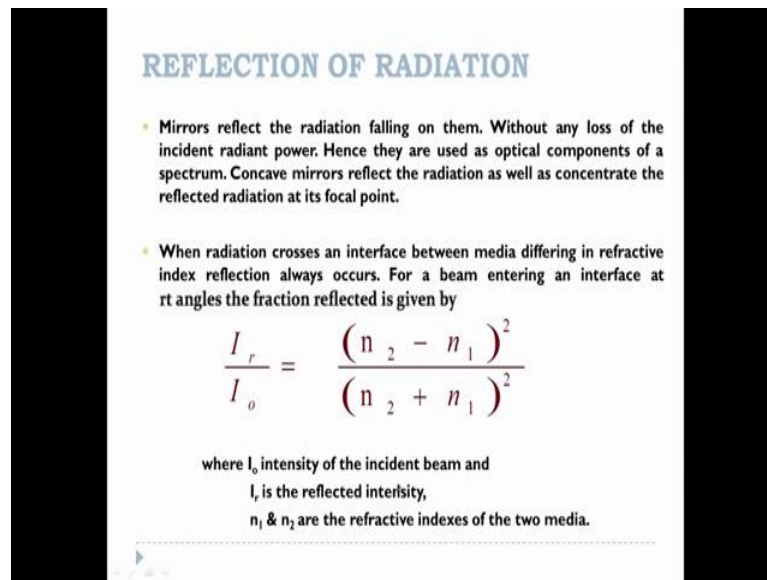


- Dispersion is a complex phenomena. Dispersion curves usually show two regions. Normal dispersion in which there is a gradual increase in refractive index with increasing frequency. Anomalous dispersion occurs at frequencies in which sharp changes occur coinciding with natural harmonic frequency of some part of a molecule, atom or ion leading to the absorption of the beam.
- In spectroscopy, dispersion curves are important for optical components such as lenses. Most suitable components for the manufacture of lenses are those in which refractive index should be high and constant. This results in reduced chromatic aberrations.

For the fabrication of prisms refractive index should be large but also highly frequency dependent.

So, most suitable components for the manufacture of lenses are those in which refractive index should not be should be high and it should be constant. So, this results in reduced chromatic aberrations; we will see what is chromatic aberrations later, but for the time being we can assume that most of the lenses and another thing are all basically used to produce parallel beam of electromagnetic radiation. So, the fabrication of prisms and lenses what we need is a high refractive index, but they should be highly frequency dependent also. So, the requirement of high frequency re dependency on refractive index is heavily on the selection of the lenses.

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REFLECTION OF RADIATION

- Mirrors reflect the radiation falling on them. Without any loss of the incident radiant power. Hence they are used as optical components of a spectrum. Concave mirrors reflect the radiation as well as concentrate the reflected radiation at its focal point.
- When radiation crosses an interface between media differing in refractive index reflection always occurs. For a beam entering an interface at rt angles the fraction reflected is given by

$$\frac{I_r}{I_o} = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2}$$

where I_o intensity of the incident beam and
 I_r is the reflected intensity,
 n_1 & n_2 are the refractive indexes of the two media.

So, another property of electromagnetic radiation is reflection of radiation. So, I think most of you are familiar with the reflection of radiation because the everyday we see ourselves in mirrors, mirrors do the job of reflection whenever you see yours you brush your teeth you go in front of a mirror look check your teeth etcetera it is just a reflection whenever you are in front of a camera you will be seeing the reflection of yourself, or a mirror you will see a reflection of yourself. So, the mirrors essentially represent the radiation falling on them they reflect the radiation. So, without any loss of instead incident radiant power, they are since there is no radiant power loss in mirrors they are used as optical components in a spectrum. The what do we need we need a concave mirror that reflect the radiation as well as concentrate the reflected radiation at its focal point.

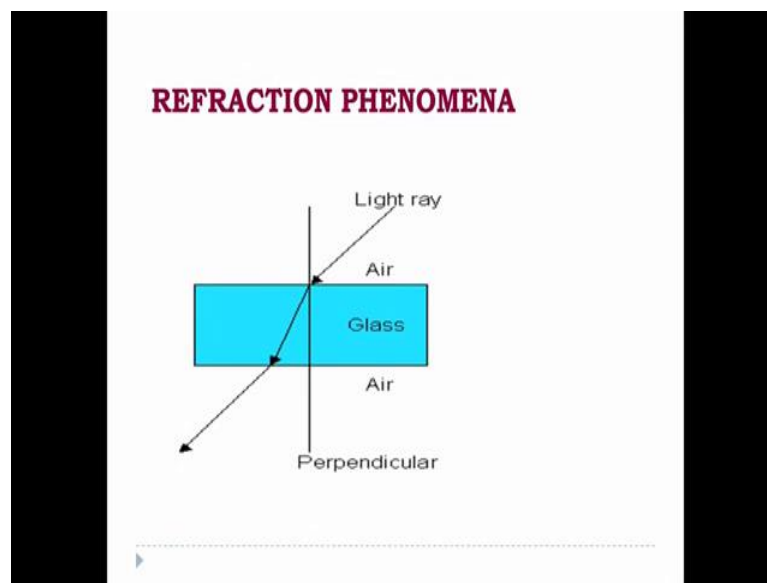
Now, these concave mirrors are available to you all over the world, you are very familiar with them and the concave mirrors basically are used in most of the cars the head light of a car they always concentration pass it through a concave mirror, so that the beam of the radiation in front of the car is properly illuminated with a parallel beam. And even on the side mirror of a driver the concave mirrors are used, because whenever you are parking it should be the visible what is available at the back.

So, again you need a parallel mirror concave mirror which shows you gives you a concentrated beam, and when radiation crosses an interface between the media; that

means, if I have a mirror radiation passes through the mirror, they ref differing it there will be a difference in the refractive index. So, the for a beam entering an interface that is a glass plate or whatever it is if it is interfacing the at right angles the fraction reflected is given by this equation intensity of the radiation reflected radiation divided by the intensity of the original radiation I_r by I_o is a question mark is a ratio of n_2 minus n_1 square divided by n_2 plus n_1 square where n_1 and n_2 are the refractive indexes of the 2 media.

Normally we have air and glass as the 2 refractive index I can have water and air and so many other possibilities are there, but in most of the spectroscopic instruments we have only the air and glass or air and lens etcetera. Glass is basically a transparent material on which a non reflective coating is provided at the back. So, the in such cases the reflection rules are govern governed by this previous equation this equation I_r by I_o is equal to n_2 minus n_1 divided by n_2 plus n_1 for both of them squared.

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So, this is how it looks refraction of phenomena and the there will be light path change here.

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- When radiation passes at an angle through the interface between two media having differing densities an abrupt change in the direction occurs. This is called as refraction owing to the changes in the velocity of the radiation in the two media.

The extent of refraction is given by Snells law

$$\frac{\sin \theta_1}{\sin \theta_2} = \frac{n_2}{n_1} = \frac{V_1}{V_2}$$

In vacuum $V_1 = c$ and n_1 is unity. Hence

$$(n_2)_{vac} = \frac{(\sin \theta_1)_{vac}}{\sin \theta_2}$$

Refractive indices of materials are measured with air as one medium and available in data bases.

And whenever radiation passes at an angle through the interface between 2 media just like what I had shown here it is coming at an angle, it is not coming from the top, but it is coming at an angle then it will not pass through the angle straight away so.

In such cases extent of refraction is given by n_2 by n_1 basically. So, the refractive indices different materials are measured with air as 1 medium, and they are all available in data basis for quartz, for glass, for metals, for aluminum like that.

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SCATTERING OF RADIATION

- Momentary absorption of radiant energy by atoms, ions, or molecules followed by reemission of the radiation in all directions is known as scattering. Particles having comparable dimensions to that of the incident radiation removes most of the reemitted radiation by destructive interference except those traveling in the original direction. A very small fraction of the radiation is transmitted at all angles from the original path & its intensity increases with particle size.
- Scattering by molecules or aggregates having smaller dimensions than the incident radiation is called Rayleigh scattering.
- Larger molecules scatter radiations in different quantities in different direction. This is called as Mie Scattering.
- When the scattered radiation is quantized like those occurring in vibrational energy level transitions in molecules as a consequence of polarization process, it is called as Raman Scattering.

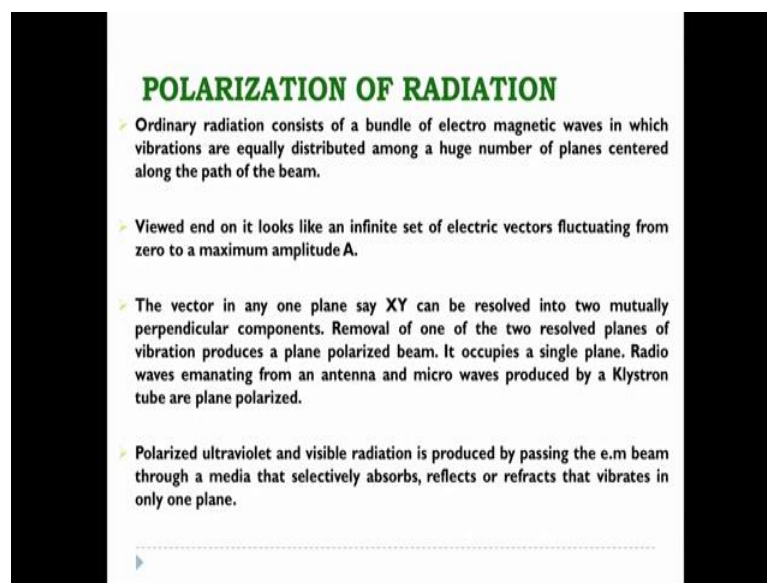
There will be lot of there will be lot of changes in the refractive index of the material this is another property of the electromagnetic radiation they always associated whenever electromagnetic radiation interacts with a given media. The media what we have already referred is it could be vacuum, it could be gas, it could be material, solid, liquid etcetera etcetera. Now I am going to talk to you another property of the radiation that is scattering of radiation; now what happens during scattering whenever again imagine I have a some amount of material radiation is passing through that material. So, the atoms are there, ions are there, molecule are there, all these things are in a state of constant movement constant vibrate dynamic equilibrium.

So, there will be part of the radiation is absorbed by the atoms or if the atoms are bigger by the molecules they represent, and if they are still bigger they could be particles like dust particles or it could be a liquid particles aerosols. So, many other solid and liquid particles are there, all these liquid particles and dust particles etcetera whenever they are in a given space of time and electromagnetic radiation is passing through them, there will be scattering the light will fall on the particle and then it will not pass through it will not follow a known path, it will be scattered in all directions that is known as scattering. In reflection it follows the same path in which it has gone and hit the material, in refraction it takes comes there takes a bend bent path and then again it comes out.

Whereas in scattering part of the energy is absorbed wavelength is changed, frequency is changed, and then it will be dispersed in all directions. So, the transmitted light will contain all kinds of radiations and it will be in all direction. So, that is what I have written here particles having comparable dimensions to that of the incident radiation; that means, comparable dimension to that of the incident radiation means particle size should be of the order of angstrom unit; that means, they would be in the form of atoms or molecules. So, if such is the case the emitted radiation may result in destructive interference except that travelling in the original direction. So, a very small fraction of the radiation is transmitted at all angles which I have already explained to you. So, scattering by molecules or aggregates having smaller dimensions than the incident radiation is known as Rayleigh's scattering; there are 2 kinds of scattering 1 is by molecules or aggregates having smaller dire dimension than the incident radiation that is known as Rayleigh, and different larger molecules scatter radiation in different quantity in different direction.

So, smaller once scattering by smaller particles is called the Rayleigh scattering, scattering by bigger particles is known as Mie, Mie is the name of the scientist. So, when the scattered radiations is quantized like those occurring in the vibrational energy level we call it Raman scattering. That is a very well-known scattering phenomena and what a Raman professor Raman said is the scattering occurs in in a quantized fashion. So, they can be used like any spectroscopy. So, that is how it is known as Raman spectroscopy. So, Raman scattering is also part of the electro interaction of the electromagnetic radiation with the material.

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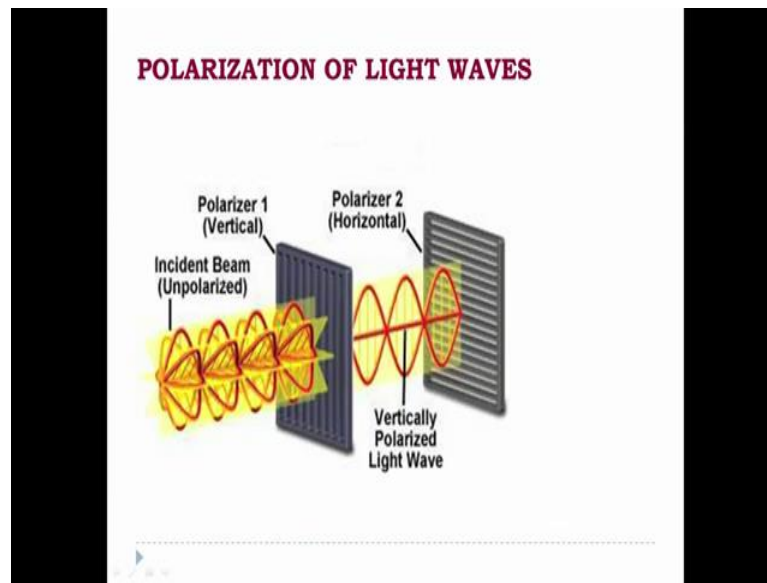


POLARIZATION OF RADIATION

- Ordinary radiation consists of a bundle of electro magnetic waves in which vibrations are equally distributed among a huge number of planes centered along the path of the beam.
- Viewed end on it looks like an infinite set of electric vectors fluctuating from zero to a maximum amplitude A .
- The vector in any one plane say XY can be resolved into two mutually perpendicular components. Removal of one of the two resolved planes of vibration produces a plane polarized beam. It occupies a single plane. Radio waves emanating from an antenna and micro waves produced by a Klystron tube are plane polarized.
- Polarized ultraviolet and visible radiation is produced by passing the e.m beam through a media that selectively absorbs, reflects or refracts that vibrates in only one plane.

So, another property of electromagnetic radiation, so far we had discussed reflection, refraction, and then scattering now we are discussing about polarization. So, what is polarization of a radiation? As I have already explained to you the radiation is a bundle of electromagnetic waves moving through a given space, and that bundle is usually associated with electromagnetic radiation. So, electromagnetic radiation if the particle is moving through like towards you, the electromagnetic radiation will be going like this and magnetic radiation will be going perpendicular to all the three will be going in the same direction.

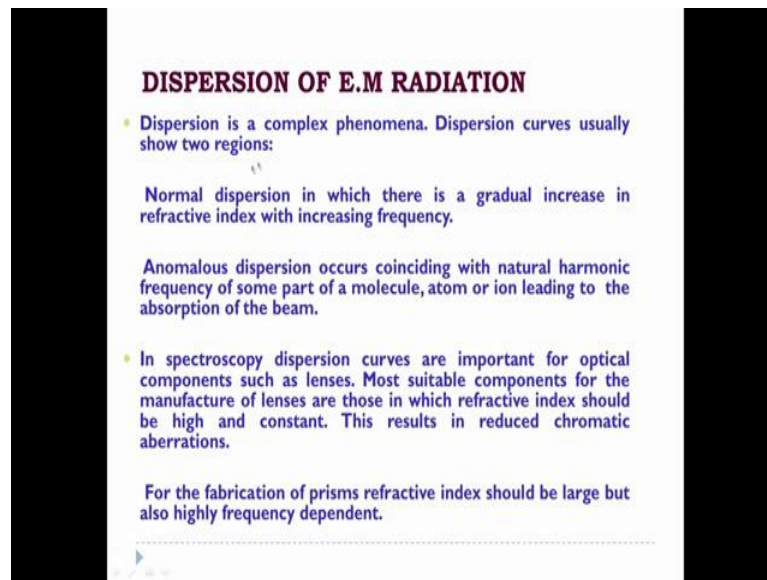
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So, viewed on end how does it look. So, it looks like this. So, here you can see that polarization of light the incident beam on the left side here, on the left side is a bundle of electro electric field and magnetic field radiation is going through the this end to this end. So, from this end it has it has all the electromagnetic part and the as well as the direction. Now I put 1 polarizer vertical polarizer what it will do is it will stop all the electrical vertical field 1 field. So, the out coming radiation out of this the electrical field is from the back side before that part polarizer there are 2 components here it is only 1 component.

Now, if I put one more component one more polarizer here I will have only the direction both electric field and magnetic field would be destroyed, they will not be there this known as polarization of light waves so; that means, it is separation of the electric and magnetic field from the radiation that is associated with each one, this is a very standard technique shown in almost all TV serials and others things all they got do is to use a polarizer which will permit the movement of the electro electric field cut off the electric field or magnetic field and that is how it works.

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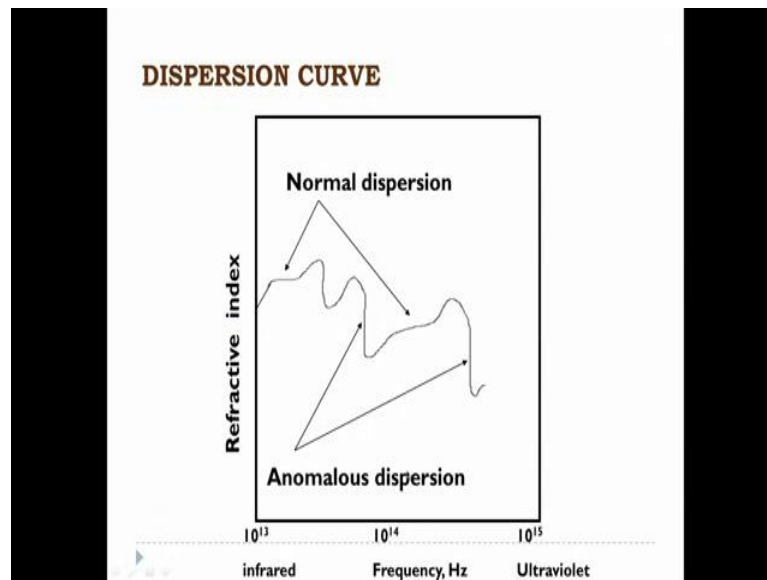
DISPERSION OF E.M RADIATION

- Dispersion is a complex phenomena. Dispersion curves usually show two regions:
 - Normal dispersion in which there is a gradual increase in refractive index with increasing frequency.
 - Anomalous dispersion occurs coinciding with natural harmonic frequency of some part of a molecule, atom or ion leading to the absorption of the beam.
- In spectroscopy dispersion curves are important for optical components such as lenses. Most suitable components for the manufacture of lenses are those in which refractive index should be high and constant. This results in reduced chromatic aberrations.

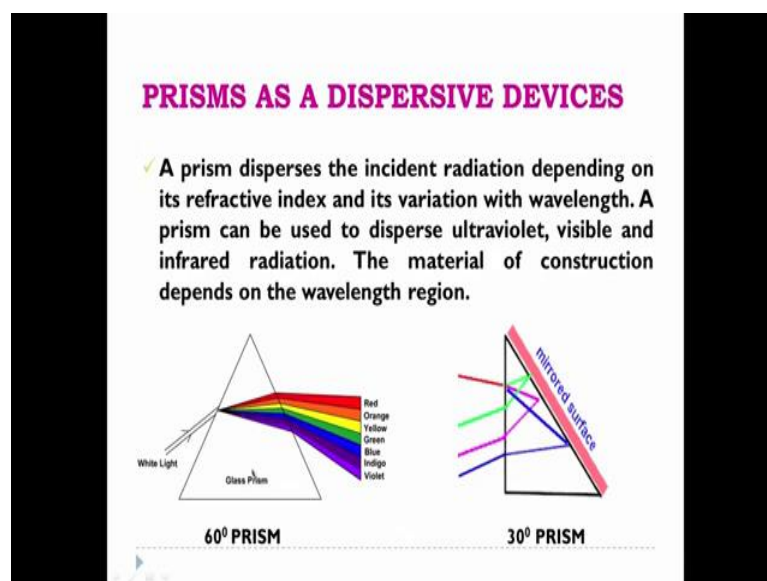
For the fabrication of prisms refractive index should be large but also highly frequency dependent.

So, dispersion is again another complex phenomena, a dispersion usually occurs in 2 reasons 1 is normal dispersion where there is gradual increase in the refractive index with increasing frequency, anomalous dispersion occurs coinciding with natural harmonic frequency of some part of the molecule or atom or ion leading to the absorption. So, in spectroscopy discuss dispersion curves are important for optical component such as lenses mirrors etcetera again these are very important concepts. Most suitable components for the manufacture of lens lenses are those in which refractive index should be very high and it should be constant, this results in reduced chromatograph chromatic aberrations for the fabrication of the prisms what we normally do is we take.

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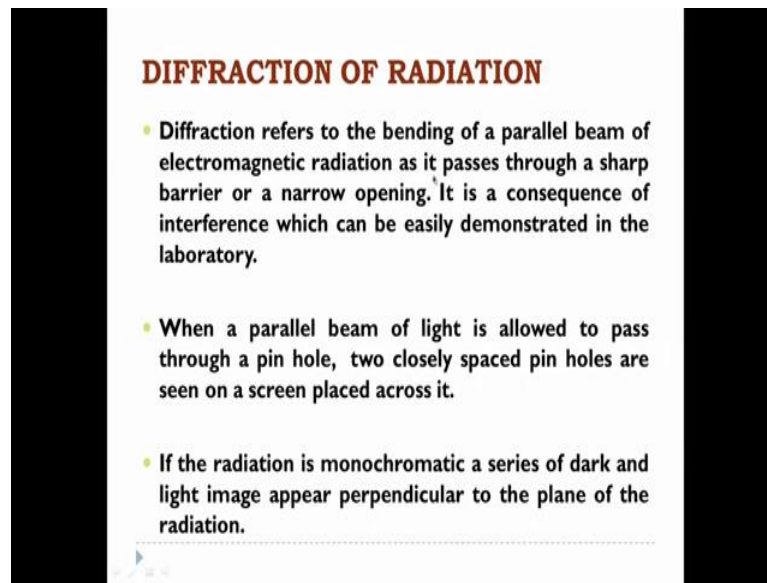
I have not shown you here this is a prism. So, this triangular glass material you must have seen prisms like this. So, for these prisms we use them as dispersive material devices while radiation is coming through here, and then it will pass through this it will have different components and each component will have different refractive index, and because of the this property they will exhibit you a white light coming entering at one end will give you red, orange, yellow, green on the other side of the frequency prism. We will come back to this what I wanted to show you is dispersion of electromagnetic

radiation, and lenses and prism are the most important components which for which high refractive dispersion characteristics are required.

So, I was talking about the normal dispersion and anomalous dispersion; normal dispersion is like this then a there is gradual change, but in anomalous this thing there will be a sudden change from this point to this point. So, this point to this point there is a sudden change, and here you can see that on the left x axis I have 10^3 to 10^{13} that is infrared 10^{14} frequency and 10^{15} is ultraviolet. So, from infrared to ultraviolet range there will be change in the refractive index therefore, the refractive same material what is used for infrared may not be useful for the ultraviolet and vice versa, and several other systems also what some material useful in the infrared a lens material.

For example if I use a glass for infrared, it would not be useful for ultraviolet glass also is not very useful for infrared. So, for visible light ordinary glass will be alright because it will not have change in the normal dispersion, but if I use the same glass for ultraviolet it will not allow any radiation to come out at all through the glass. So, a lens or prism to be used in a in an ultraviolet spectrophotometry cannot be used in the infrared. So, what is used in useful in visible range will may not be useful in the in ultraviolet range. So, for each different spectroscopic technique what we need is different materials which are suitable for the passing of the electromagnetic radiation with minimum side effects that is normal dispersion this that is the importance of this figure ok.

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DIFFRACTION OF RADIATION

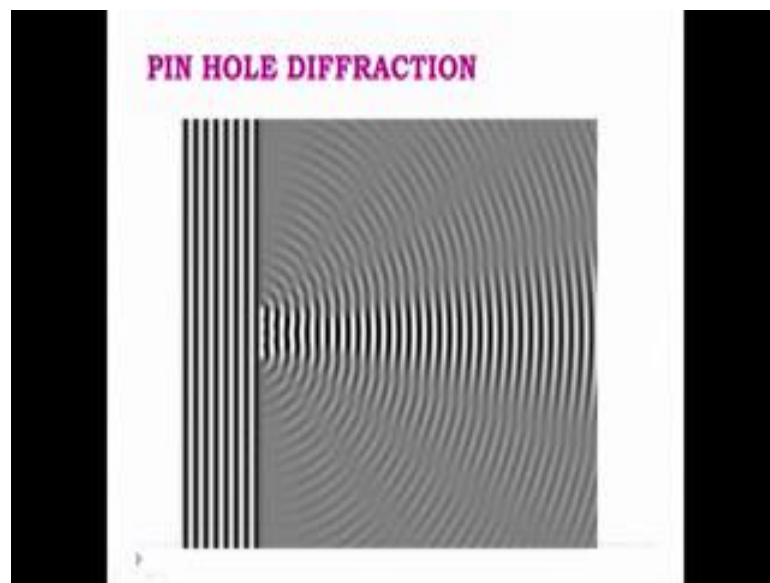
- Diffraction refers to the bending of a parallel beam of electromagnetic radiation as it passes through a sharp barrier or a narrow opening. It is a consequence of interference which can be easily demonstrated in the laboratory.
- When a parallel beam of light is allowed to pass through a pin hole, two closely spaced pin holes are seen on a screen placed across it.
- If the radiation is monochromatic a series of dark and light image appear perpendicular to the plane of the radiation.

So, diffraction is another aspect of interaction of radiation with electromagnetic radiation matter with electromagnetic radiation. So, what does diffraction refer? Diffraction refers to the bending of parallel beam electromagnetic radiation as it passes through a sharp barrier or a narrow opening; it is a consequence interference which can be easily demonstrated in the laboratory. What I do is I take 1 parallel beam of light I take 1 parallel beam of light coming through this through fingers like this and then I put a small pinhole put a screen in front of that, put a small hole in front of it like this so that the diffraction will occur.

So, whenever a parallel beam of light is allowed to pass through a small pinhole or 2 closely spaced pinholes. The through the pinhole all the radiation will be spreading and sometimes what happens when they are spreading through 1 pinhole another pinhole may be crisscrossing the electromagnetic radiation of the other coming from other pinhole. So, the interaction of these 2 radiations through the pinhole represent what is known as diffraction. So, there could be constructive interference or there could be destructive interference; whenever there is constructive interference high school physics I am teaching you constructive interference means you will see a string of bright and dark bright and spot bright spot dark spots like that, but if there is destructive interference you will not see any bright spot at all you will see only the dark spot.

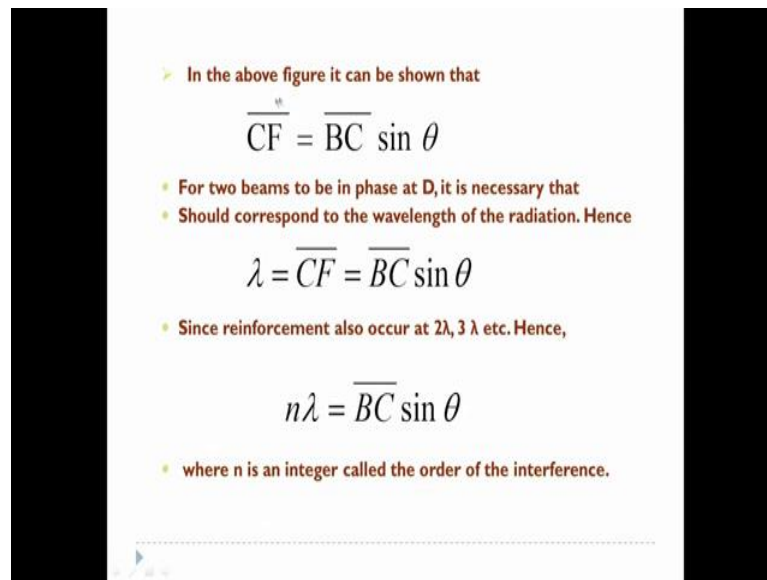
So, if the radiation is monochromatic again, what is the monochromatic radiation? A monochromatic radiation is the radiation having 1 frequency 1 wavelength, and 1 amount of single amount of energy. So, it may be a bundle of radiation, but all have the same wavelength. So, whenever I take monochromatic radiation and pass through a series of 2 pinholes etcetera, there will be a series of the dark and light images which appear perpendicular to the plane of radiation. So, that is diffraction.

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So, here is the representation of a electromagnetic radiation, here what I have is radiation coming through this there is a small pinhole here 1 2 3 4 in the center and the radiation is coming out like this you will see bright patch, black patch, bright patch, black patch like this as it spreads across you will see a bright patch all in the center, black path is at the this thing. So, all the black patches represent the destructive interference.

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➤ In the above figure it can be shown that

$$\overline{CF} = \overline{BC} \sin \theta$$

- For two beams to be in phase at D, it is necessary that
- Should correspond to the wavelength of the radiation. Hence

$$\lambda = \overline{CF} = \overline{BC} \sin \theta$$

- Since reinforcement also occur at $2\lambda, 3\lambda$ etc. Hence,

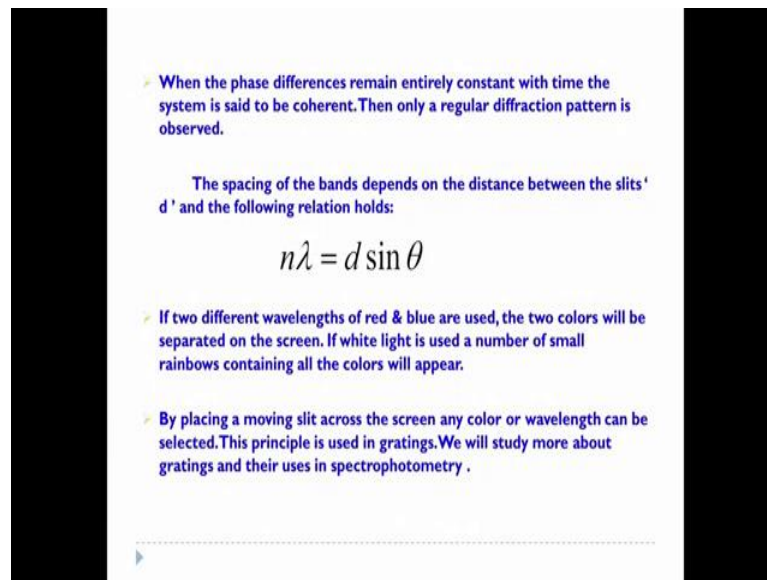
$$n\lambda = \overline{BC} \sin \theta$$

- where n is an integer called the order of the interference.

While the bright path represents constructive interference. So, the geometry geometrically I can say that it can you can see that the refractive index is a CF is given by B into sin theta for 2 beams to be in phase at d it is necessary that they should correspond to the wavelength of the radiation and that wavelength is given by CF here again that is BC into sin theta, and for reinforcement can also occur at 2 lambda, 3 lambda etcetera twice the wavelength are 3 times the wavelength that is known as order of diffraction first order diffraction, second order diffraction like that.

And in general what we have is any number dis interference or diffraction and that is given by n lambda is equal to BC sin theta BC can be related to the crystal structure that is 2 d sin theta, n lambda is equal 2 d sin theta this is a very important Bragg's equation.

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- When the phase differences remain entirely constant with time the system is said to be coherent. Then only a regular diffraction pattern is observed.

The spacing of the bands depends on the distance between the slits 'd' and the following relation holds:

$$n\lambda = d \sin \theta$$

- If two different wavelengths of red & blue are used, the two colors will be separated on the screen. If white light is used a number of small rainbows containing all the colors will appear.
- By placing a moving slit across the screen any color or wavelength can be selected. This principle is used in gratings. We will study more about gratings and their uses in spectrophotometry.

So, whenever the phase differences remain entirely constant with time, this system is said to be coherent then only a regular diffraction pattern is obtained. The spacing of the bands depends upon the distance between the slits that is mechanical slits, and the resulting equation is $n\lambda = d \sin \theta$ and if 2 different wavelengths are used the colours will be separated on the screen. So, if white light is used a number of small rainbows colours you will be obtaining on the other side. So, by placing a moving slit across the screen any colour or wavelength can be chosen for example, here in the next figure if I put a plate mechanical plate here with opening in the in this range, it will allow only red and keep all orange yellow etcetera green below; because there is only 1 slit and that slit will cover only the red region.

Now if I want orange I have to move the slit down stairs a little down and then I will be coming in the orange range you look at the same figure again you will still move still down you will see only the yellow colour. So, the same slit can be moved up and down to get red orange yellow green blue indigo violet etcetera.

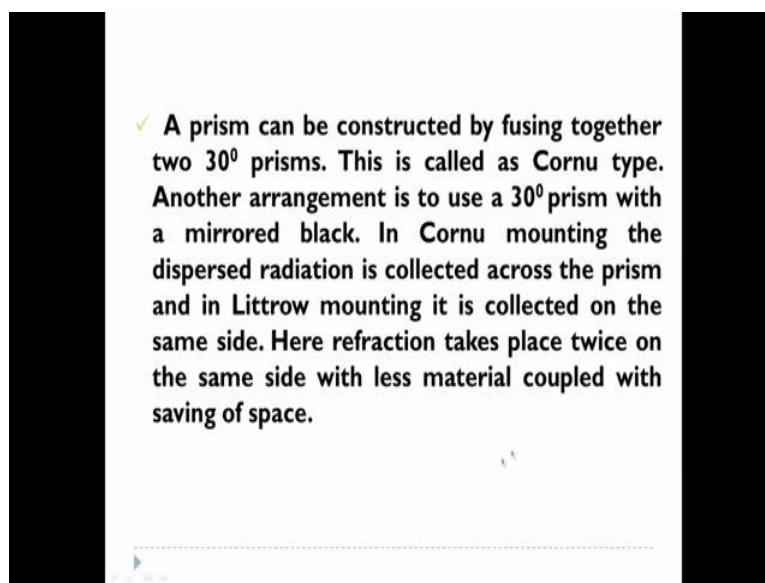
So, this is the beauty of prism and slits. So, the slits prisms as I need a prism has a dispersive unit, and after that I need a part as part of the instrument I need a slit. Now the prism basically this disperses incident radiation in different colours as you can see from this figure here is it not. So, the radiation how which what amount comes out as red, how much amount comes as blue etcetera it depends upon the prism material. And the a prism

can also be used to disperse ultraviolet visible and infrared radiation therefore, a prisms lenses, concave mirrors, gratings, diffraction gratings all these are part of the spectroscopic equipment in all tall equipment.

So, the material of construction depends on the wavelength region, this I already told you that what is useful in infrared may not be useful for visible range, what is useful for visible range need not be useful for ultraviolet range and vice versa. So, a prism and I can construct like this, I can take a prism like this and choose one more prism like this and then put it on the other side that you will get it here say that you will get a picture on the left side the that is 60 degree prism.

That means what I have done is I take a prism on the right side that is 30 degree join it opposite side, and I get what I get on the left side. So, if 30 degree prisms are join together I get a 60 degree prism and both are used in spectrophotometers.

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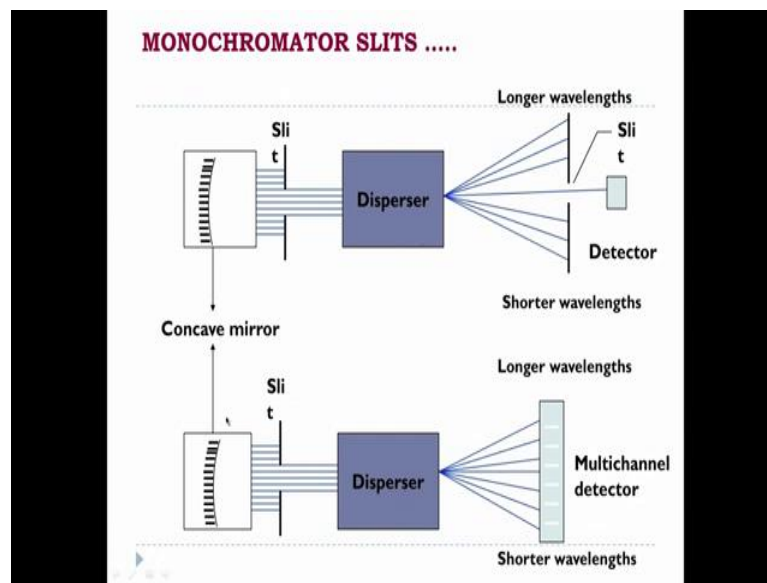


If I use 2 30 degree prisms like the previous 1 the like this on 60 it becomes a 60 degree prism this is known as (Refer Time: 25:50) mounting. So, in the (Refer Time: 25:56) mounting I have 2 30 degree mirrors join together at the vertical phase, but if I use only 1 prism like this and coated with a mirror surface on the other side. What it does is a radiation blue radiation you can see coming from this side reaches the mirror surface reflects back and then goes back. So, the distance actually travelled by a 30 degree mirror the mirrored mounting is exactly same as a 60 degree prism you understand the

difference basically a 60 degrees is 60 degree prism is 1 time pass 30 degree prism is it goes straight and then gets reflected on the same side. So, the distance between the 2 would be essentially same if I mirror one side of the prism.

So, the one side of the mirror prism that is 30 degree prism is known as s Littrow mounting. So, Littrow mounting is collected on the same side. So, here refraction takes place twice on the same side with less material I save the material as well as I save the space why because here I had to put a slit on the other side of the prism if I use a 60 degree prism whereas, if I use a 30 degree prism to collect the refracted light I had to put the slit on this side only and; that means, the instrument becomes a very small instrument compare to a 60 degree prism, it is the that is the advantage of a prism Littrow mounting and Cornu mounting.

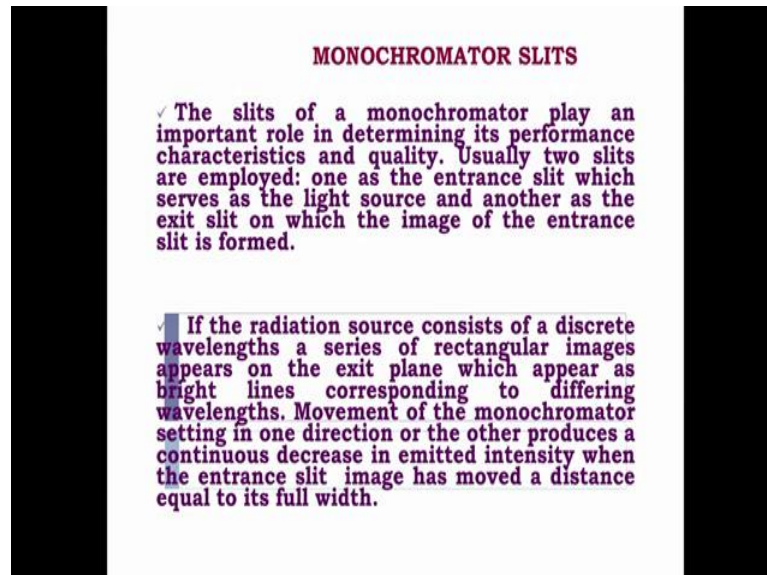
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So, here I have monochromatic slits, pictorial presentation, I have a mirror, I have concave mirror here I have slit here radiation us coming through this, I have a another mechanical slit and then it give me different kind of wavelengths and this is my slit and I can this slit, I can move the slit at different places to collect the top ray second ray third ray fifth ray fourth ray fifth ray like that, and for the longer wavelength I can use a multichannel, I can put take single plate with the multiple slits. So, it will collect 1 ray from here, another ray from here and another. So, multiple rays can be simultaneously

detected instead of making the one moment from the same slit. So, that is the multi that is known as multichannel detector I need a detector here to find out what is coming out.

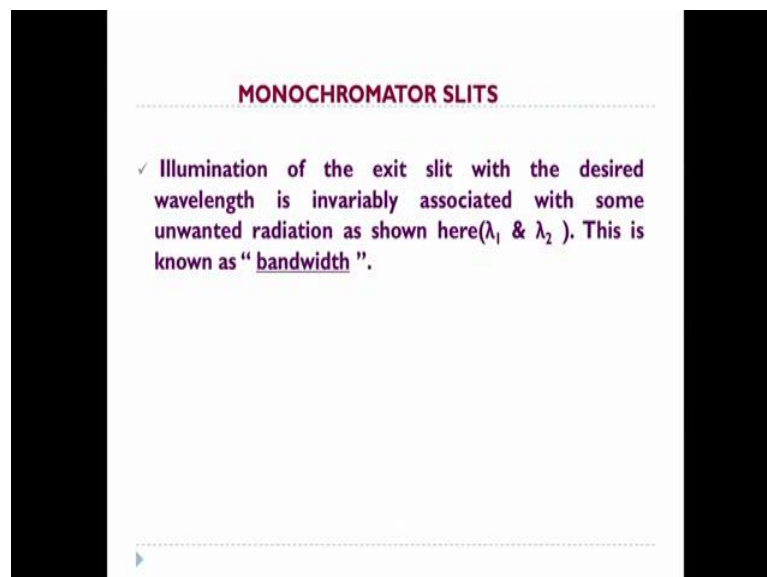
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MONOCHROMATOR SLITS

- ✓ The slits of a monochromator play an important role in determining its performance characteristics and quality. Usually two slits are employed: one as the entrance slit which serves as the light source and another as the exit slit on which the image of the entrance slit is formed.
- ✓ If the radiation source consists of a discrete wavelengths a series of rectangular images appears on the exit plane which appear as bright lines corresponding to differing wavelengths. Movement of the monochromator setting in one direction or the other produces a continuous decrease in emitted intensity when the entrance slit image has moved a distance equal to its full width.

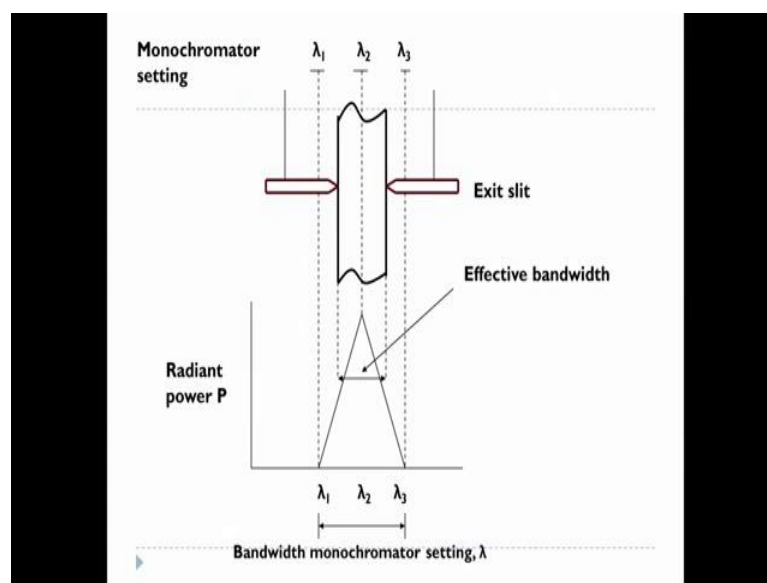
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MONOCHROMATOR SLITS

- ✓ Illumination of the exit slit with the desired wavelength is invariably associated with some unwanted radiation as shown here(λ_1 & λ_2). This is known as “ bandwidth ”.

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So, we have discussed about the monochromator slits, and in the monochromator slit what I have is part of the radiation is the peak wavelength that is λ_2 , and part of it is λ_1 , λ_3 and here I have an exit slit here I have a slit and effective bandwidth. So, this is radiant power. So, bandwidth monochromator setting if I take out any radiation coming out from a monochromator slit, a bunch of radiation comes out it is not a single wavelength even though the most of the radiations are parallel what comes out is a pure wavelength like this in the center, but also a little bit of other radiations corresponding to different wavelengths.

So, this is a practical difficulty whenever we are talking of monochromator slits and monochromatic monochromator designs you will never get a single wavelength output from any spectroscopic device, because the it is the inherent property of the slit if you can imagine something like this a basic radiation will be center radiation will be the what you want plus there will be some unwanted radiations corresponding to different wavelengths.

So, that how we select that out of that is the another aspect, but basically what comes out is a bunch of wavelength corresponding to the wavelength what you want, where slit is placed exactly, but also some unwanted extra radiation having slightly plus and minus wavelength on the of what you are choosing. So, that is what we mean here bandwidth. So, whenever we say I say I want 450 nanometer bandwidth wavelength, what I will be

getting is 420, 400 instead of 420 I will get maximum 420, but also I will get about 415 and 425 some amount of extra radiation. So, the whole range of wavelength corresponding from 425 to 415 with maximum at 420 is known as bandwidth. So, for good spectrophotometer what I need is a very small bandwidth small amount of wastage that is the important importance of the slit and slit management so.

We will continue our discussion after about 5 minutes.

Thank you.