Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) for Pollution Monitoring

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Lecture – 08
Interaction of EM radiation with matter-I

So, so far, we have been discussing about the nature of Electromagnetic Radiation. Now, we will study about the typical properties of the electromagnetic radiation that is transmission, diffraction, refraction etcetera.

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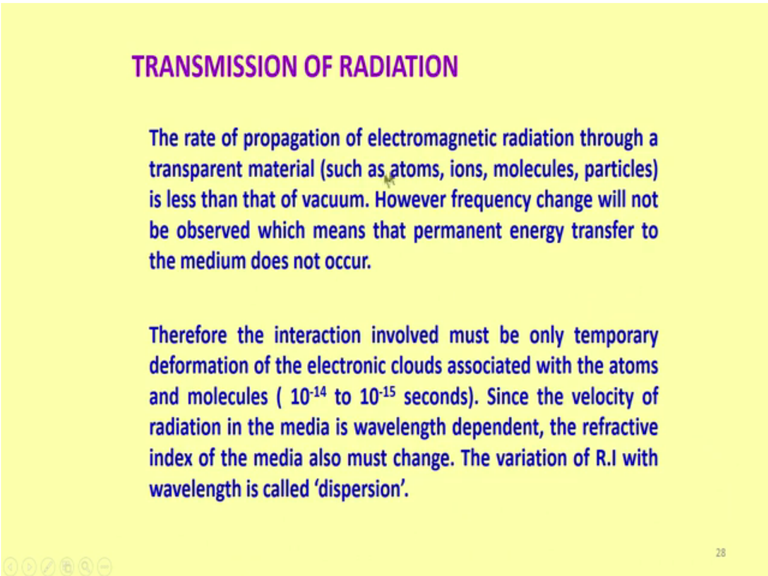

All these things are important as far as the instrumentation is concerned. That is why I spend lot of time in all my courses to teach about the electromagnetic radiation. So that, whenever any instrument will never be stand alone without reflection, refraction, mirrors concave mirrors and then diffraction, grating and prisms etcetera. So, it is important for us to understand a little bit about the Transmission of the Radiation. So, what we will do is the, spend a little time regarding the different properties of the transmission of the electromagnetic radiation. So, the rate of propagation of the electromagnetic radiation through a transparent material, it can be atoms, ions, molecules, gases, particles etcetera. ok.

So, the rate of propagation is less than that of the vacuum. Why? because the in vacuum there is nothing to stop whereas, any group of any type of matter that is atoms, ions, molecules they offer some kind of resistance for the flow of the electromagnetic radiation. So, there will may be some type of interaction also. So, the there will not be any change in the frequency, but the permanent energy transferred to the medium does not occur. So, this is very important concept again.

So, whenever I pass the electromagnetic radiation through these things, there will not be any permanent energy transferred to the matter. Therefore, the interaction involved must be only temporary deformation of the electronic cloud associated with the atoms and molecules. So, the time frame during which such interactions occur is of the order of about 10 raise to minus 14 to 10 raise to minus 15 seconds. Since the velocity of the radiation in the media is a wavelength dependent, the refractive index also must change. So, the variation of refractive index with wavelength, we call it 'dispersion' ok.

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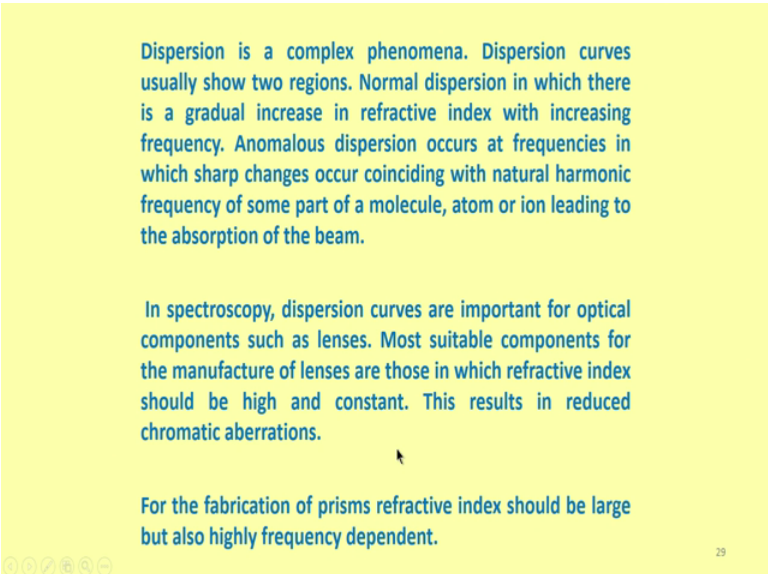

So, what is a Dispersion? Dispersion is basically a very complex phenomenon. It occur dispersion occurs usually show 2 reasons. One is in which the normal dispersion that is there is a gradual increase in the refractive index of the material as the as the electromagnetic radiation passes through the matter, another is anomalous dispersion, that is it occurs at frequency at which sharp changes occur coinciding with the natural harmonic frequency of some sort part of a molecule or atom or ion a leading to the absorption of electromagnetic beam.

So in spectroscopy, dispersion curves are important again. For optical components such as lenses, most suitable components for the manufacture of lenses are those in which the refractive index should be high and constant. This results in reduced chromatic aberrations. So, you please look up what is a chromatic aberration. Again it is the second year physics portions. So, far the fabrication of prisms, refractive index should be large and it also should be high frequency dependent. So if I want to make prisms refractive, I must chose a material whose refractive index is large, but it must also be highly frequency dependent. What are the materials through which we make prisms? One is glass, quartz, sodium chloride, crystals, etcetera.

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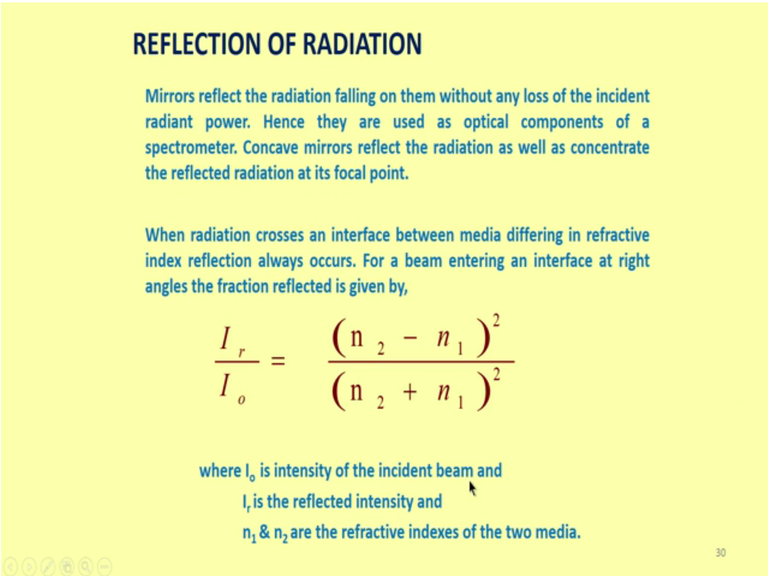

So, another type of material is Reflection of the Radiation. So, normally mirrors reflect the radiation falling on them without any loss of the incident radiation power. You take a beam of radiation, pass it through a mirror, mirror will just reflect the light. So, they are used as optical components of a spectrometer. Concave mirrors reflect the radiation as well as concentrate the reflected radiation at it is focal point. I think most of you must be familiar with the car, side mirror of a car which are supposed to be sort of concave mirrors.

So, apart from such uses, concave mirrors are also used in spectroscopic instruments. So, when radiations crosses an interface between the media differing in reflective index of reflection, it always occurs for a beam entering an interface as right angles. The reflected light is given by I r by I 0, that is n 2 minus n 1 whole square divided by n 2 plus n 1 whole square where I 0 and I r are the reflected intensity of the incident beam and reflected beam and n 1 and n 2 are the refractive index of the 2 media.

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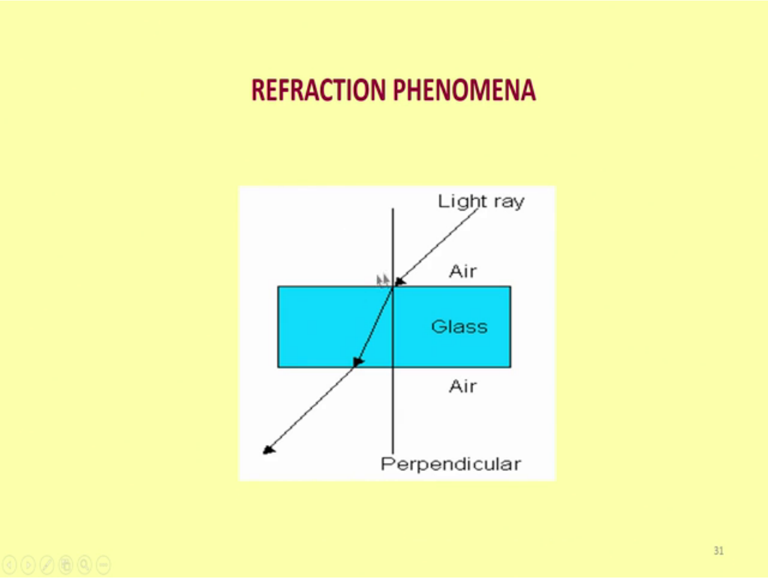

I think the picture becomes clear instead of me showing you the slide; if I show you this picture.

So, here the light beam is coming falling, light beam is falling, there is a glass here, there is air above the light above the glass and there is air below the glass. So what I am doing is, taking a light ray passing through the glass and then in the glass there will be refraction of the electromagnetic beam. Again this is second year p u physics syllabus.

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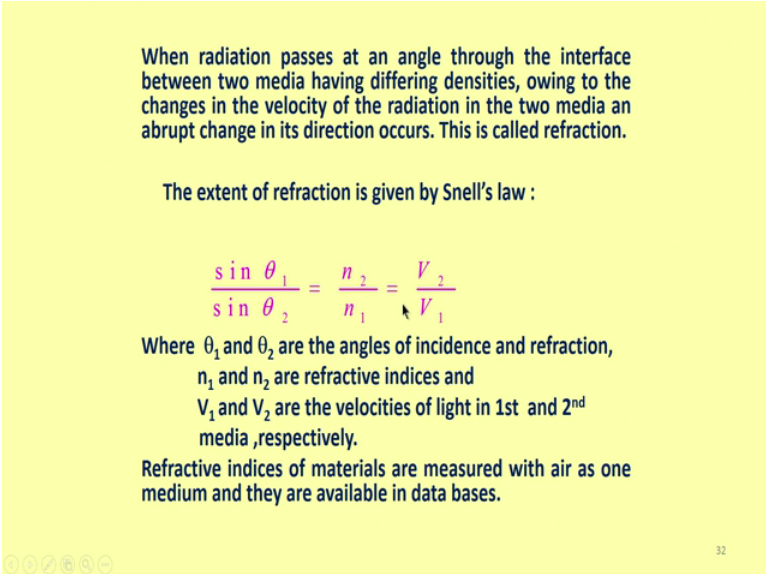

So, when radiation passes at an angle through the interface between the 2 media having different densities, owing to changes in each velocity of the radiation in the 2 media an abrupt change in the direction occurs. This is known as refraction. This is a definition of refraction. So, the extent of refraction is given by Snell's law; again second year p u subject; sin theta 1 by sin theta 2 would be equal to the ratio of the refractive index n 1 and n 2 and v 1 and v 2 are the velocities of the light in the first and second media. That is in the previous case it was air and glass.

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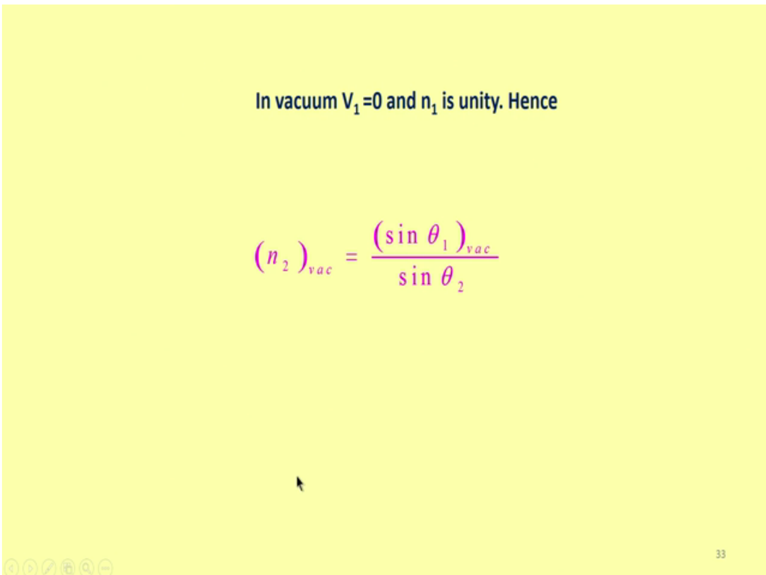

So, in vacuum v 1 is equal to 0 and n 1 is unity. So, we can write instead of n 2 by n 1 n, n 1 is unity. So, n 2 by n 1 is 1, you will be nothing but sin theta 1 in the vacuum divided by sin theta 2.

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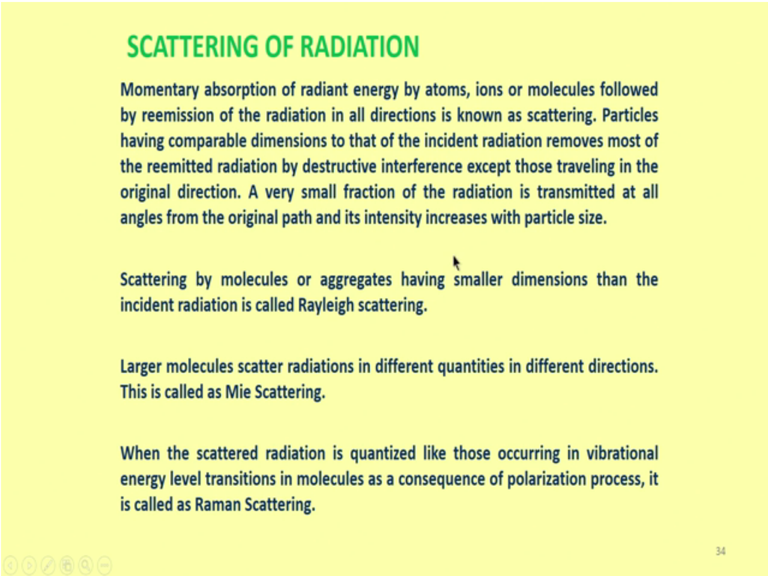

So, now we come to the another property of the electromagnetic radiation that is with matter. So, the whenever I take electromagnetic radiation and pass it through the matter atoms, molecules, ions, gases whatever it is so, momentary absorption of radiation radiant energy by atoms, ions, molecules followed by any emission of the radiation in all direction is known as scattering. You take the material, take the radiation make it fall on the matter; it will scatter all over. So, it is identified or un defined moment of the photons. So, particles having comparable dimensions to that of the incident radiation, removes most of the emitted radiation by destructive interference except those traveling in the originals direction. So, a very small portion of the radiation is transmitted at all angles from the original path and the it is intensity increase with particle size.

So, scattering by molecules or a aggregates having smaller dimensions than the incident radiation is known as Rayleigh scattering. There are couple of definitions here that is scattering by molecules having smaller dimension than the incident radiation you can see. You can imagine the radiation having certain magnitude, wavelength. So, wavelength is the photon, you can call it roughly the size of the photon.

So, the particles having a smaller than that wavelength, they scatter the radiation that is known as Rayleigh scattering. Sometimes the molecules scatter a larger molecules scatter radiation in different quantities in different directions; this is called as Mie scattering. So, when the scatter radiation is quantized like those occurring in vibrational energy level length and rotational energy levels transitions in molecules. As a consequence of the polarization process it is known as Raman scattering. So, as you know professor Raman is a Nobel orate.

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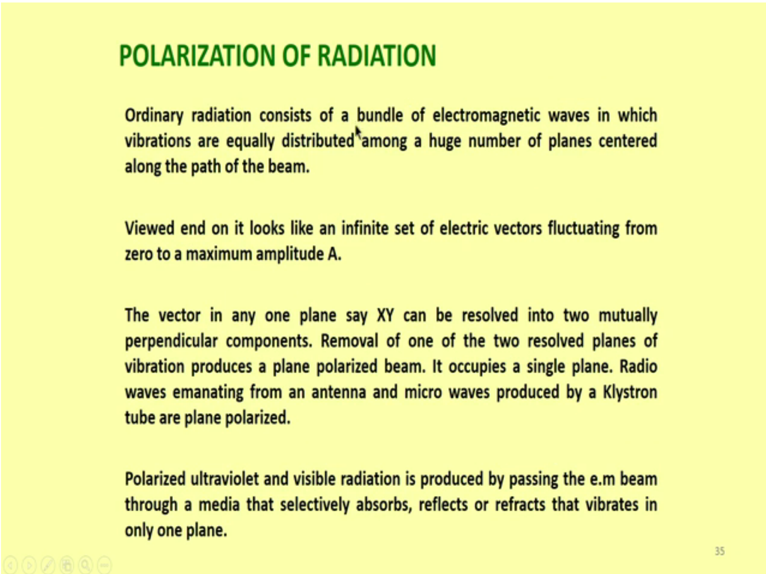

And Raman scattering is a very famous techniques, spectroscopic technique. So, now we talk about polarization of the radiation, ordinary radiation consists of a bundle of electromagnetic radiation in which vibrations are equally distributed among a huge number of planes centered along the path.

So, viewed end on it looks like an infinite set of electric vectors fluctuating from 0 to maximum amplitude. It is a fairly complex structure. If you want to take a look at the non-polarized radiation, you will be surprised to see how a the electromagnetic radiation looks so chaotic. So, the vector in any of one plane say x y can be resolved into 2 mutually perpendicular components that we know already, electric field and magnetic field. So, the removal of one of the 2 resolved planes of vibration produces a plane polarized beam.

So, this occupies a single plane. Radio waves emanating from a ninety 9 microwave produced by Klystron tube or plane polarized. So, polarized ultra violet and visible radiation is produced by passing the electromagnetic radiation through a media that selectively absorbs reflects or refracts that vibrates in only 1 plane. That is how we produce a the a plane polarized lights.

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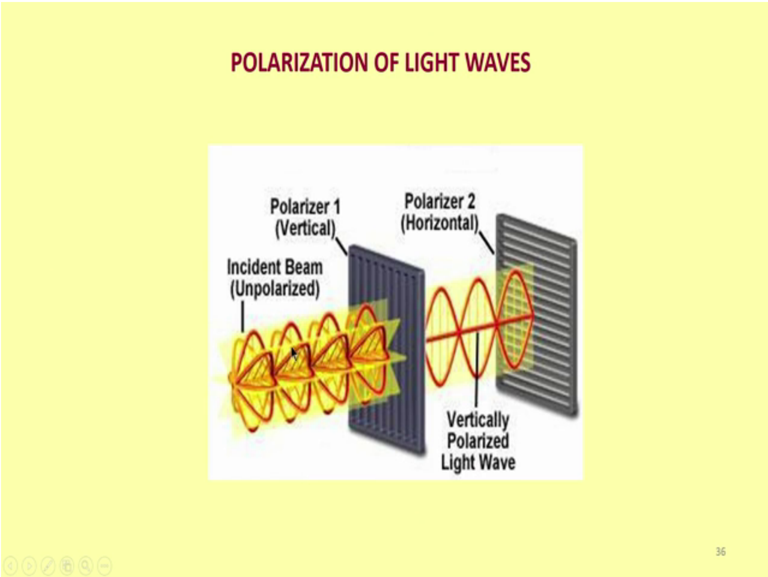

So, you can see here, in this figure I have electromagnetic radiation going like this through this from left to right and incident beam; this is un polarized.

You can see that it is a very complex structure containing both electric and magnetic fields. Here I have put a polarizer that is, a material that removes a electric field or magnetic field. So, I can put one is vertical another is horizontal. So, this removes vertical polarizer, vertical components and I can the output would be like this. I can even put a horizontal polarizer. So, I can get another type of polarized light.

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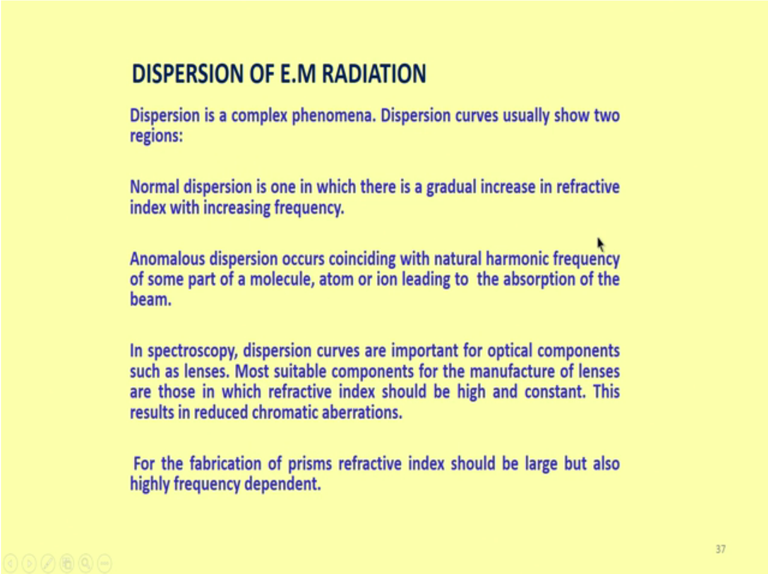

Again the polarization is a concept which is very important with respect to spectroscopy. So, regarding dispersion, I just wanted to show you that the normal dispersion, as I told you that it increase the refractive index.

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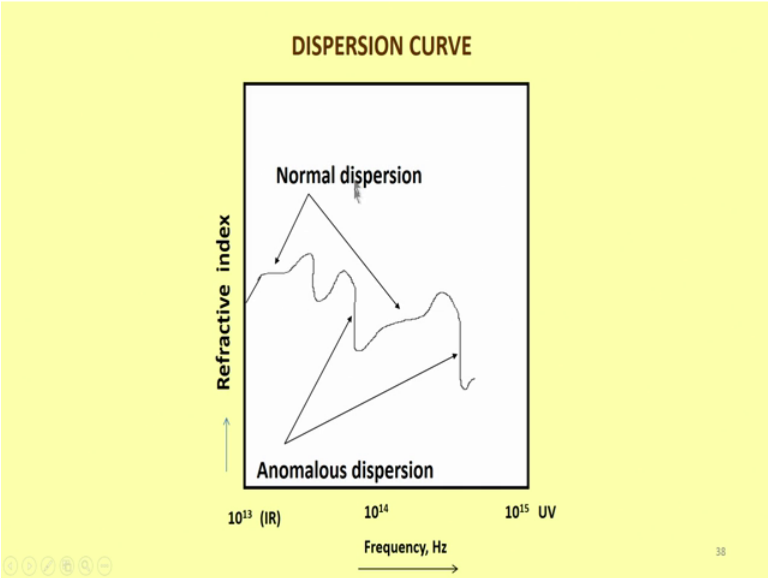

So, that it keeps on increasing like this, but you can see that it keeps on increasing but at some stage Anomalous dispersion, here in this range it keeps on falling. So, this is Anomalous dispersion. So, just to refresh your memory with respect to this, because these are important concepts of optical components of a spectroscope.

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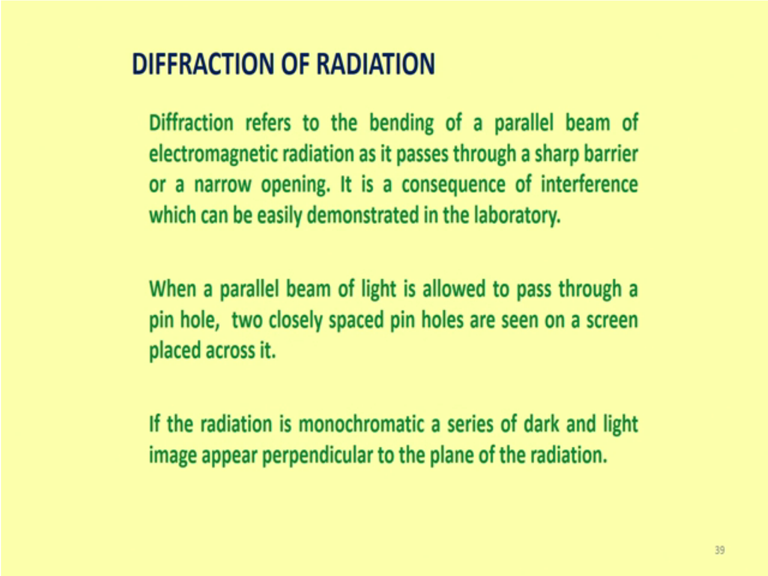

So, Diffraction! Now we will discuss about the Diffraction. A Diffraction refers to the bending of a parallel beam of a electro magnetic radiation as it passes through a sharp barrier or a narrow opening. As it passes through a sharp barrier or an narrow opening, it is a consequence of the interface which can be easily demonstrated in the laboratory. When a parallel beam of light is allowed to pass through a pin hole, 2 closely space pin holes are seen on a screen across the screen placed across that. So, if the radiation is monochromatic radiation that is having a single wavelength, a series of dark and light images appear perpendicular to the plane of the radiation.

Now, instead of explain to you in theory, I prefer to show you this figure now.

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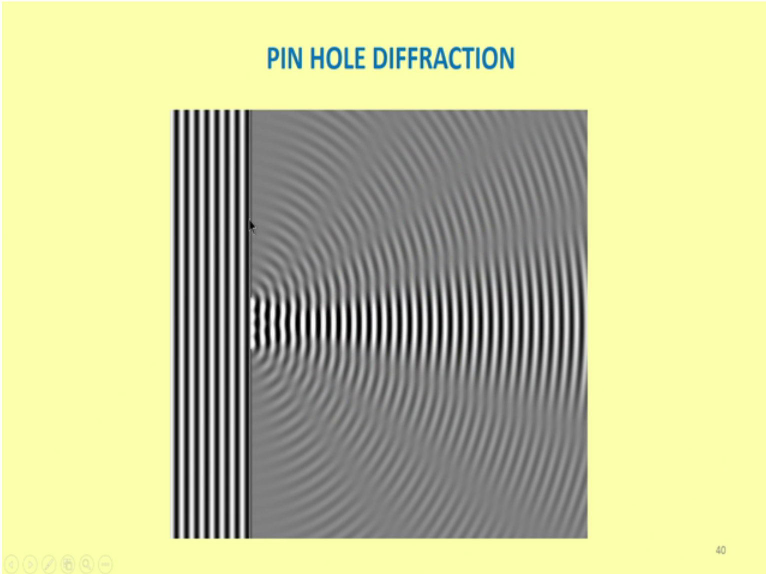

See here, I have this is known as a Pin Hole. So, radiation is coming like this and I have a Pin Hole here. And whatever rays are bending, I can see you can see that there is constructive interface as well as destructive interface; dark and white patches. This is known as pin hole diffraction. So, if I have 2 pin holes, again there will be much more complicated pictures.

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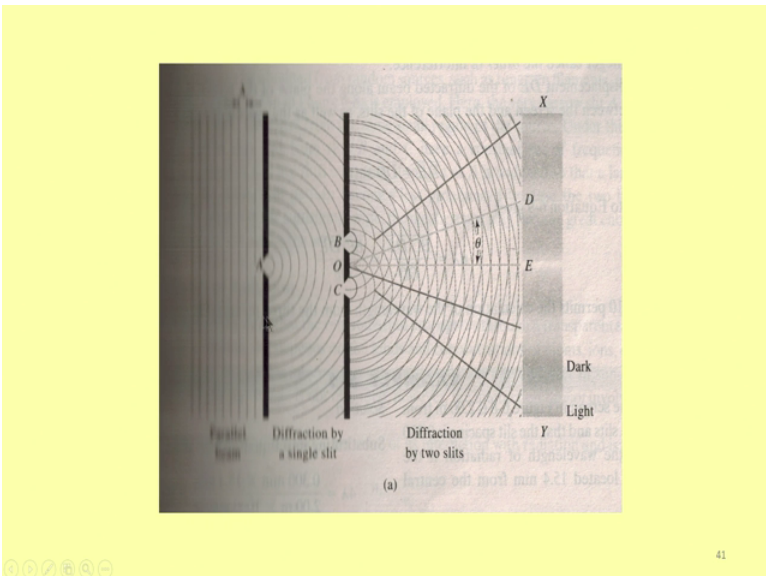

So, this is how diffraction by single slit, this is one single slit, this are double slits, 2 small slits.

So, the there will be you can, this figure is fairly simple. Only thing is you have to spend the little time to understand. So, this is the angle theta and this is D, E, O, B, C, etcetera. Now I am going to do a little derivation with respect to this. The same thing what I did here I am going to draw the figures O, B, C, D, E, etcetera.

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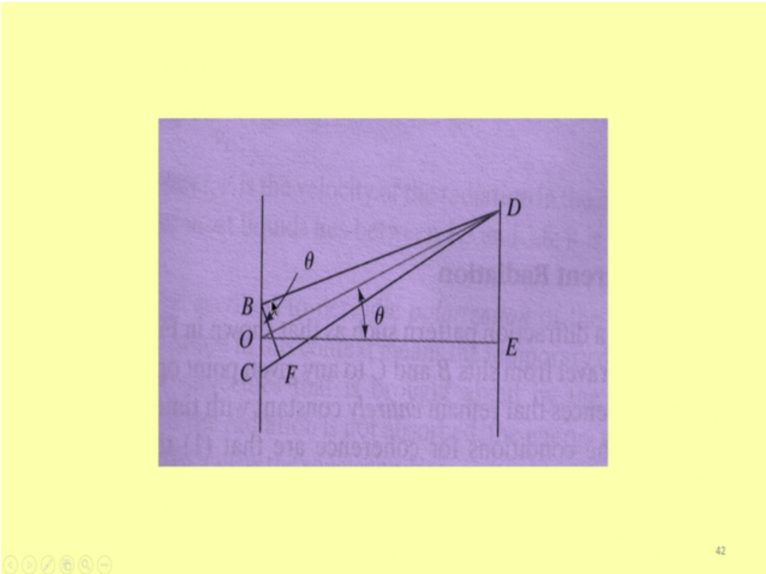

When I do that, I have a angle through which this electromagnetic radiation falls and then OBC, etcetera.

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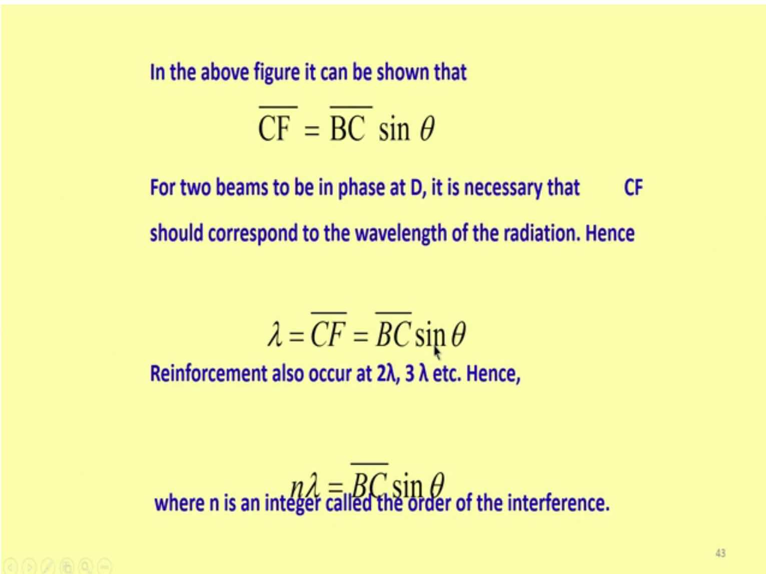

In this figure CF, this is CF. CF is nothing but BC into sin theta. That is BC multiplied by sin theta whereas theta is the angle of deflection.

So, for 2 beams to be in face at the, it is necessary that should correspond CF should correspond to the wavelength of the radiation. So, lambda is nothing but CF that is wavelength and that is nothing but BC into sin theta, reinforcement also occurs at 2 lambda, 3 lambda, etcetera; hence n lambda is equal to BC sin theta. We can say instead of 2, 3 etcetera, we write n lambda where n is the integer called as the order of interference ok.

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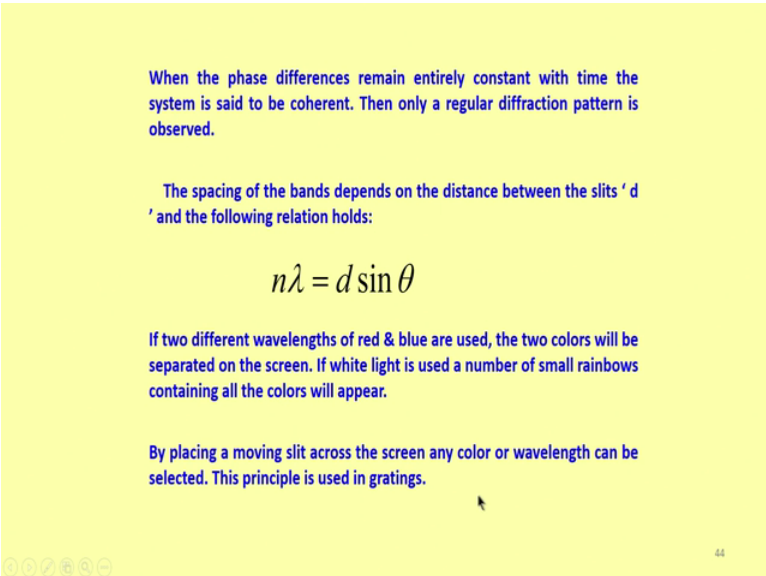

So, when the phase difference is remain entirely constant with time, the system is set to be coherent. Then only a small regular diffraction pattern is observed. The spacing of the bands depends on the distance between the slits d and the following relation holds, n lambda is equal to d sin theta. So, if 2 different wavelengths of red and blue are used the 2 colors will be separated on the screen. If white light is used, a number of small rainbow that containing all the colors will appear. So, by placing a moving slit across the screen, any color or wavelength, color means wavelength it can be selected.

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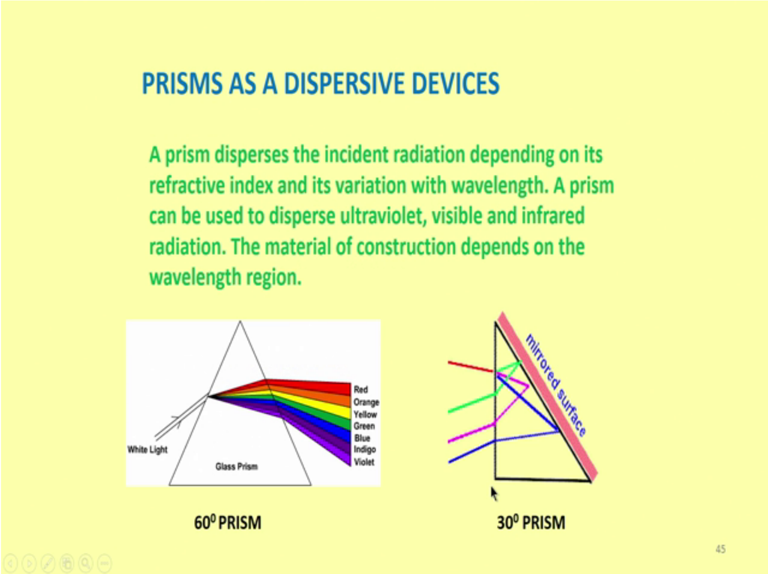

This principle is used in the gratings. Most of the spectroscopic techniques contain used gratings.

So, I want to spend some time with you regarding thee gratings also. Now apart from gratings, we also use prisms. So, what is a prism do? A prism resolves the incoming radiation into it is components. So, what happens here, look at this figure; a prism disperse is the incident radiation depending on it is refractive index and it is variation with wavelength. A prism can be used to disperses ultraviolet, visible and infrared radiation; all the three. That means, even in ICP, we will be using prisms as well as gratings. The material of construction again depends upon the wavelength region.

So, here I am showing you a prism, glass prism; white light is coming it is getting resolved in to different color and it comes out like this. Now if I put a small slit somewhere orange, I will get only orange remaining things will be blocked. Similarly, if I want green color I have to move the slit to bring rage and I will get only green light. So, similarly, there are there are different ways of doing this that is I can use a 60 degree prism or I can use a 30 degree prism.

So, what is 30 degree prism? 30 degree prism is what you see here that is, in this slide the one portion I have cut this into half the glass prism, exactly half and I have put a mirror on the diagonal. So, this has got a 30 degree angle whereas this has got a 60 degree angle. This is known as a Litro and this is known as Cornio mounting. So, the advantage is, the radiation comes through this, goes inside, hits the mirror, comes back and comes out. So, the distance travelled inside the prism, if I mirror return half of the side is almost same as a 60 degree prism. So, the material is saved if I use a Cornio mountain and the instrument can become smaller because I will be collecting the radiation on the same side.

So, this is important concept with respect to prisms.

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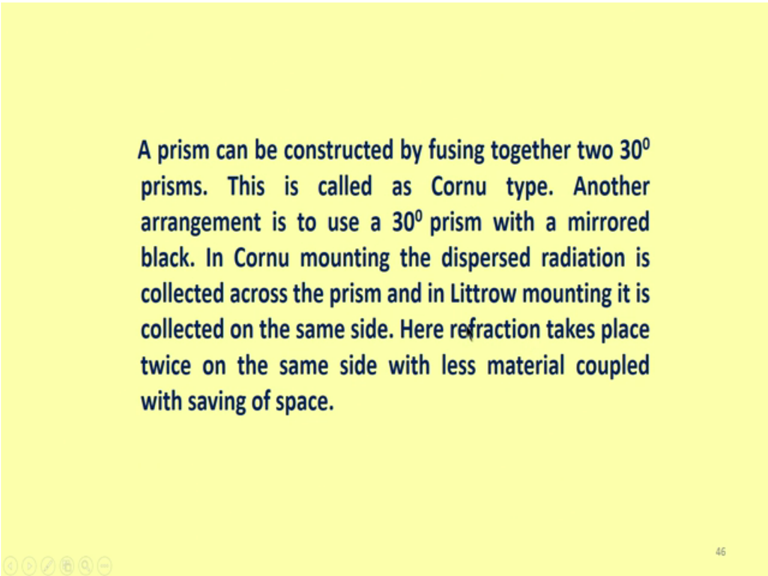

So, a prism can be constructed by fusing together two 30 degree prisms. This is called as Cornio that is 60 degrees. Another arrangements you use to use is a 30 degree prism with a mirrored black in Cornio mounting the dispersed radiation is collected across the prism and in electro mounting it is collected on the same side. Here the reflection takes place twice on the same side with less material coupled with saving of space.

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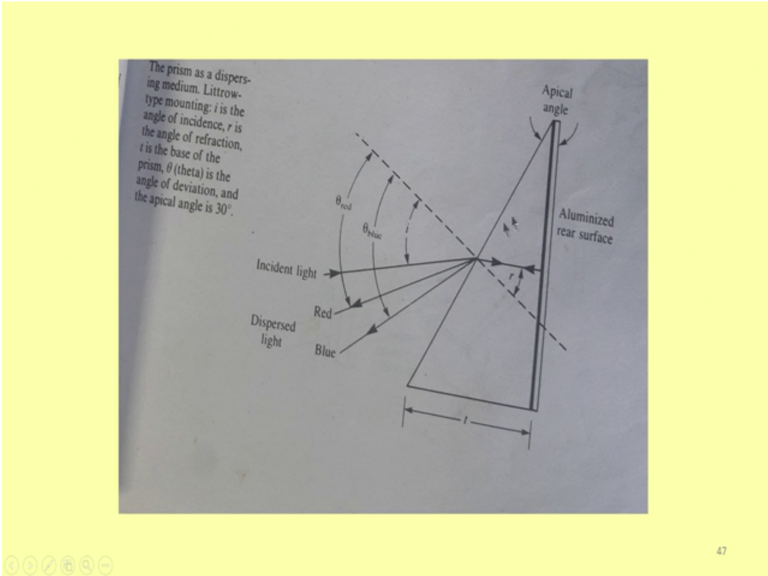

So, this is litrow mounting. You can take this is taken from Milarmeritendy, which I have given it has reference.

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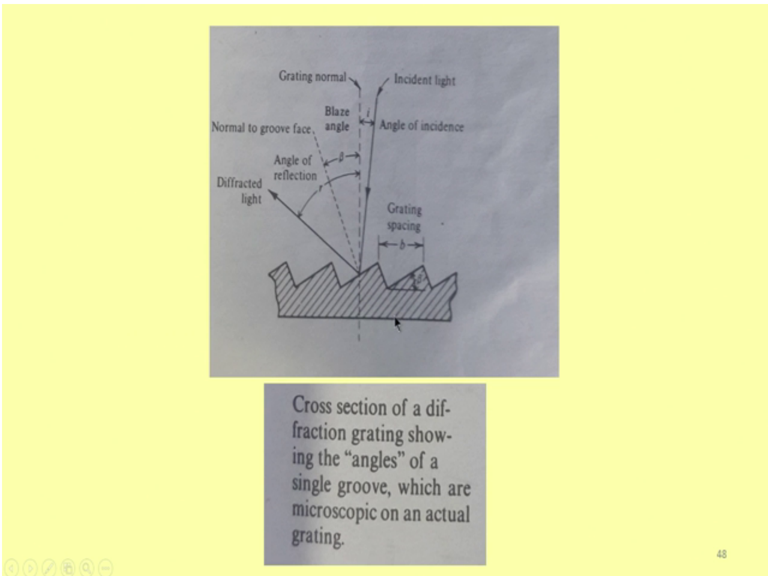

So, this is a grating. A grating contains a number of rulings and these rulings each ruling acts as a prism. So, there will be constructive interference as well as destructive interference.

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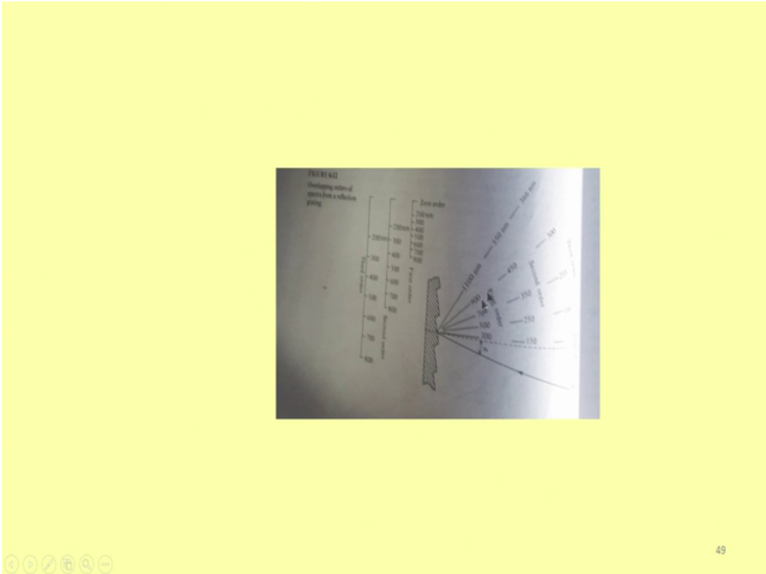

Different wavelengths are collected for each this thing that is known as order. The each one acts as a prism and constructive and destructive interference takes place. So, we will study more about diffraction later.

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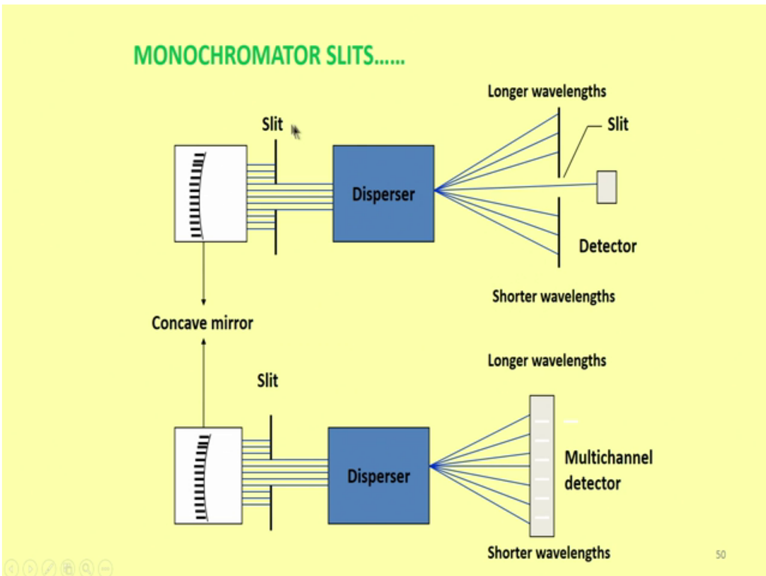

So, what is a Monochromatic Slit that is another important concept in the handling of electromagnetic radiation?

So basically, what we do is we have a light source and then I put a concave mirror. So, that gives parallel radiation and then I put a mechanical plate with a small hole in it and that gives me a parallel beam of light and then I can put a prism or any disperser and I can collect the if I put this slit here, I can collect the radiation from this, if I put a slit here, I can collect the radiation from here. So, mechanical slits are most important concept in most of these spectroscopic techniques. So, here I get shorter wavelengths and here I get longer wavelengths.

Because if I put a disperser, I get longer wavelengths but anywhere from one end to the other, there will be shorter wavelength to longer wavelength; full range we will be getting.

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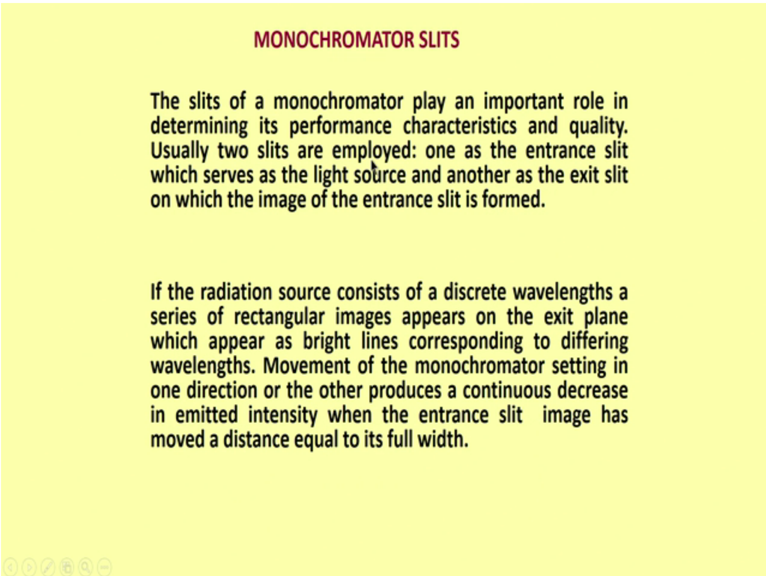

So, the slit of a monocromator play an important role in determine it is performance. And there are 2 slits, one is for entrance another is for exit. So, both of them are important. If the entrance slit is good, I get a parallel beam. If the exit slit is good, I get the good quantitation. So, if the radiation source consists of a discreet wavelengths and a series of rectangular images occur on the exit plane which appear as bright lines corresponding to different wavelengths.

So, moment of the monochromator setting in one direction or the other produces the a continues decreases in the emitted intensity when the entrance slit image has moved a distance equal to it is full width.

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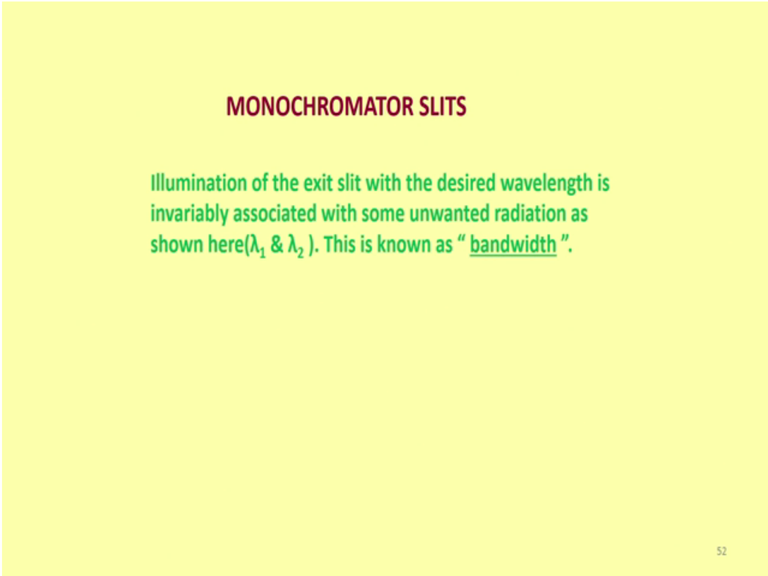

So, in what happens actually in the slit management. So, whenever where is elimination of the exit slit with the desired wavelength, it is invariably associated with some unwanted radiation as shown here. This is known as bandwidth.

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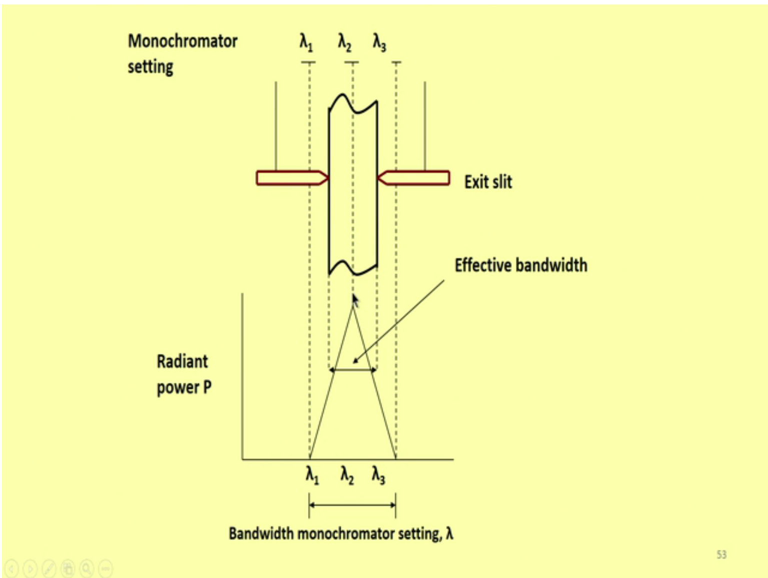

So, this is the picture you should remember. So, what is happening. Here I have the monochromator radiation and then I have a slit here. So, according to this slit I am getting a waved electromagnetic radiation of a wavelengths corresponding to lambda 1, lambda 2, lambda 3, like that. But the maximum intensity of the radiation is lambda 2.

Small portion of the lambda 1 is collected, small portion of lambda 3 is also collected and it is end ever of the every instrument manufacturer to reduce this lambda 1 and lambda 3 because we want to choose only lambda 2. So, this is known as bandwidth of the monochromator setting and this is half, 50 percent of the intensity is known as effective bandwidth ok.

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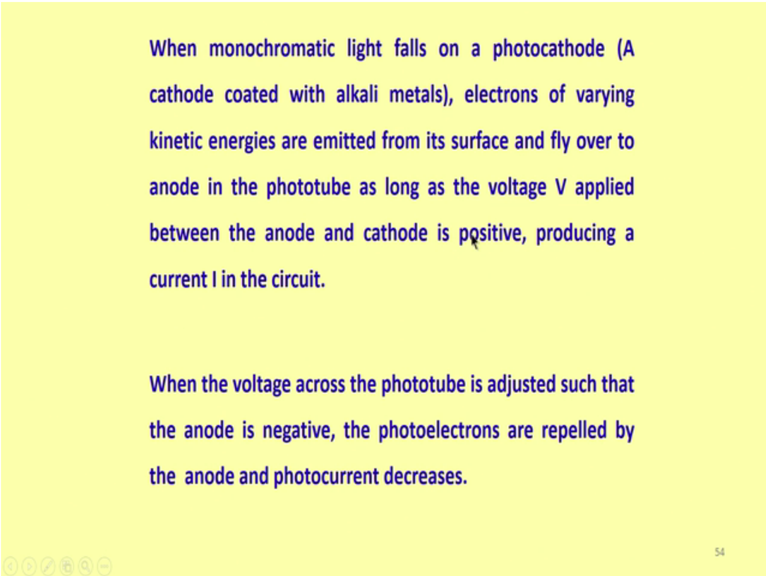

So, this is the radiant power. So, when monochromatic light falls on a photocathode, that is a cathode coated with alkali metals, photocathode nothing great about it. Alkali metal means Cesium, Lethem, etcetera. So, the electrons of may be in kinetic energy they are emitted from the surface and fly over to anode in the photo tube. As long as the voltage v is applied between the anode and cathode is positive, it produces a current and the concept of current generated from the photon is the basis of all spectrophotometry all spectroscopic techniques.

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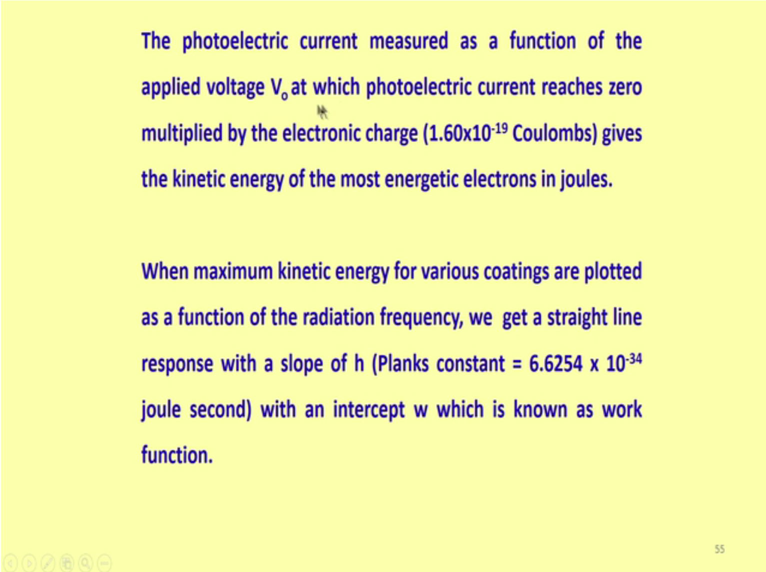

So, when the voltage across the photo tube is adjusted such that the anode is negative, the photo elate at which a photo electric current reaches 0, multiplied by the electron charge induced. So, we get, whenever we get maximum kinetic energy for various coatings, we plot it as a function of the radiation frequency. We get a straight slit response with a slope of h that is Planks constant with an intercept w which is known as work function.

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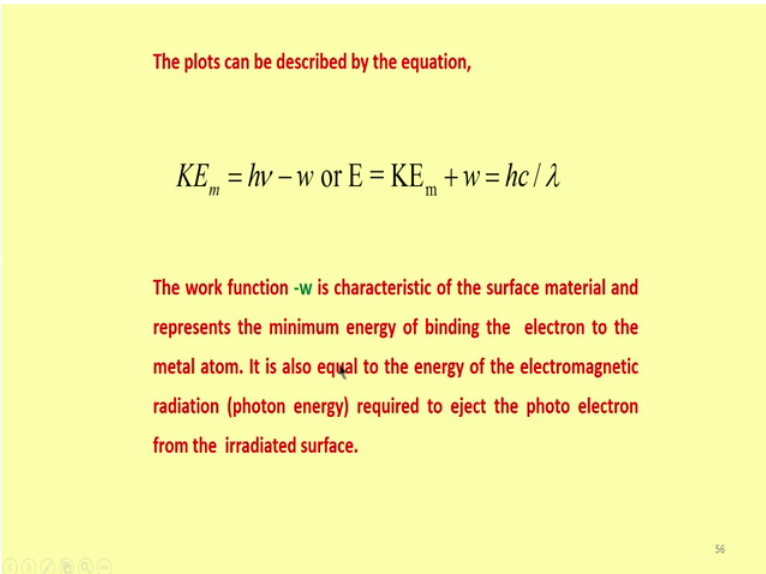

So, work function is the, work function is the measure of how good is your detector system. Because after all, electromagnetic radiation has to interact with the alkali coated detectors to generate current that is a basis of all spectroscopic techniques.

So, the plots can be described by the equation that is k e m is equal to h mu by minus w or e is equal to k into e m. So, the work function is a characteristic of the surface material and represents the maximum, represents the minimum energy of binding the electron to the metal atom. It is also equal to the energy of the electromagnetic radiation, I required to eject the photoelectron from the radiated surface.

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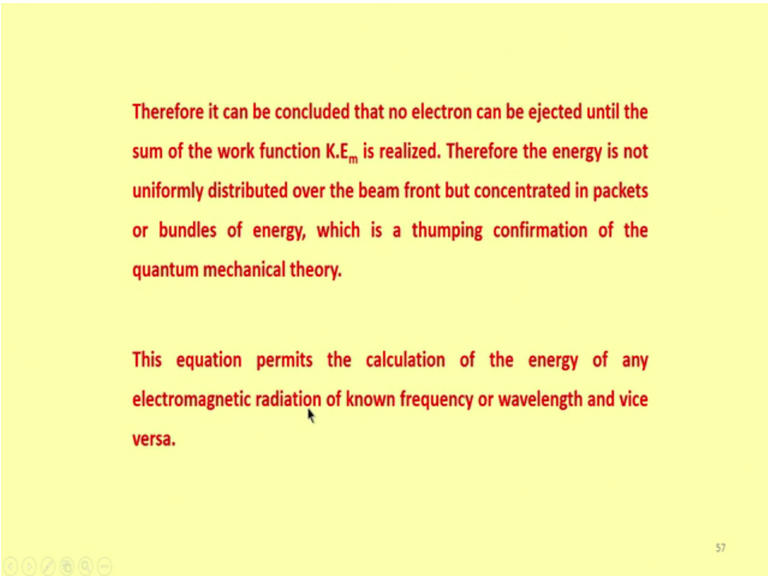

So, we can conclude that, no electron can be ejected until the some of the work function is realized. Therefore the energy is not uniformly distributed over the beam, but concentrated in packets of, bundles of energy which is the pink information of the quantum mechanical theory.

So, this equation permits the calculation of the energy of any electromagnetic radiation of known frequency or wavelength and vice versa.

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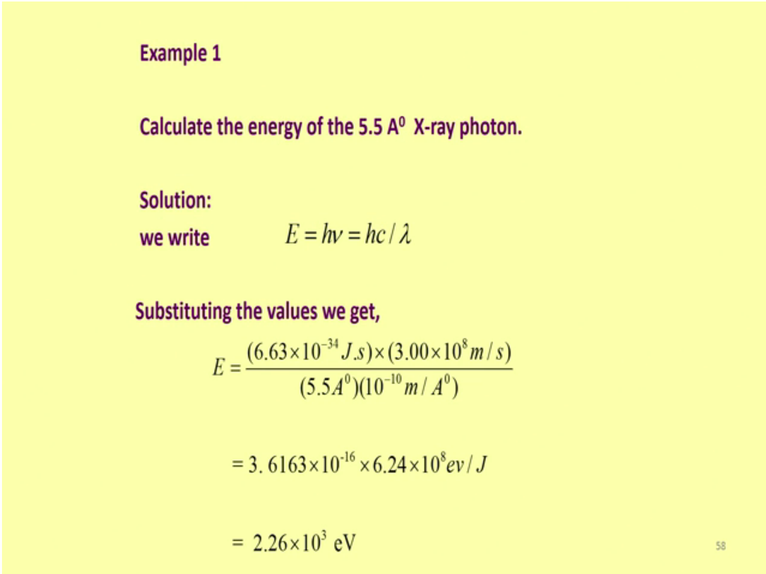

So, here I have small example for you. That is you have to calculate the energy of 5.5 Angstroms x ray photon. What we do is, we just write e is equal to h mu, h is lambda substitute the values in Joules and then speed up the light, Angstroms and then what you get is 2.26 into 10 raise to 3 electron volts.

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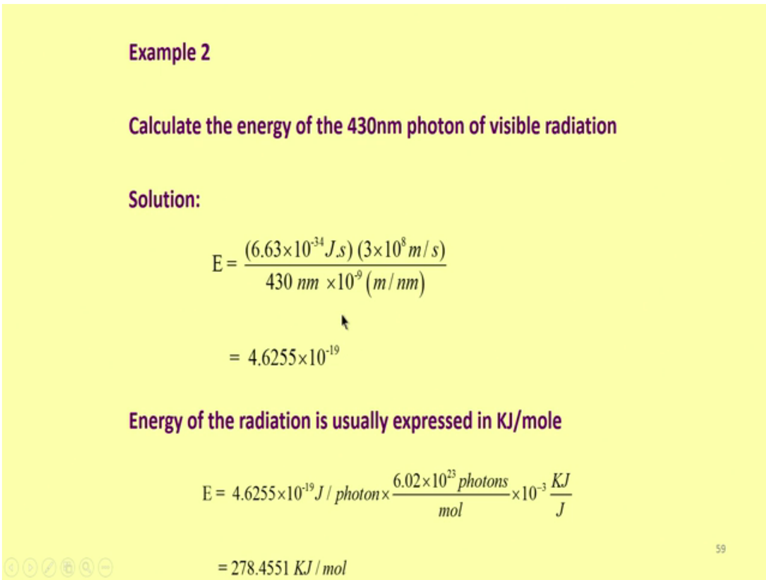

So another example, 430 nanometer, that is visible range. Again you can apply the same principle and you will end up with about 278.4551 kilo joules per mole.

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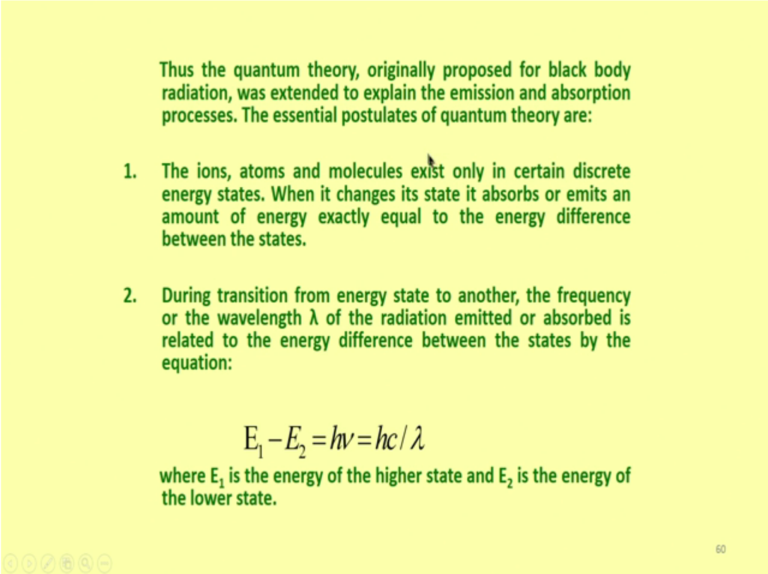

So, the quantum theory, originally proposed for black body radiation, was extended to explain the emission and absorption processes. The essential postulates are quantum theories are ions, atoms and molecules exist only in certain discreet energy states. When it is changes it is state, it absorbs or emits an amount of energy that is equal to the energy difference between the states. So, during the transition from energy state, from one energy state to another the frequency or the wavelength of the radiation is related to the energy difference between the states by the equation E 1 minus E 2 is equal to h mu that is understood. So, where E 1 is the energy of the higher state and E 2 is the energy of the lower state.

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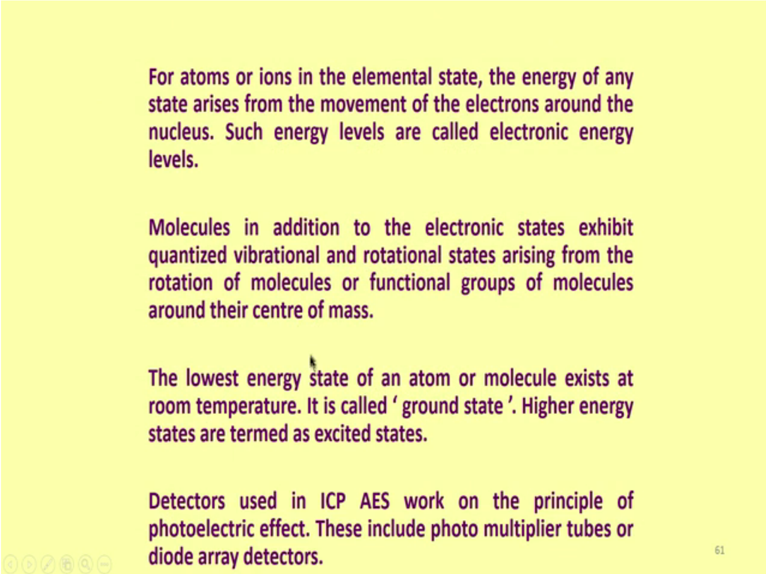

So, for atoms or ions in elemental state, the energy of any state arise from the moment of the electrons around the nucleus, such energy levels are called electronic energy levels. And lowest energy state of the atom or molecule is room temperature, this is called ground state. Detectors used in ICP, AES work on the principle of photo electric effect. These include photo multiplier tubes or diode array tubes.

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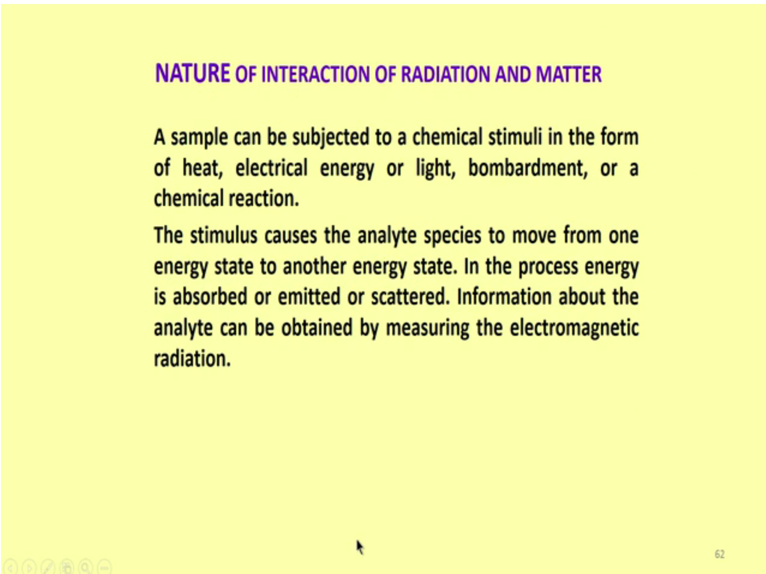

We will continue our discussion regarding the interaction of radiation and matter in the next class.

Thank you very much.