Infrared Spectroscopy for Pollution Monitoring
Prof. J. R. Mudakavi
Department of Chemical Engineering
Indian Institute of Science–Bangalore

Lecture- 12
Interaction of electromagnetic radiation with matter

It is how containing a discussion on the diffraction gratings.

(Refer Slide Time: 00:18)

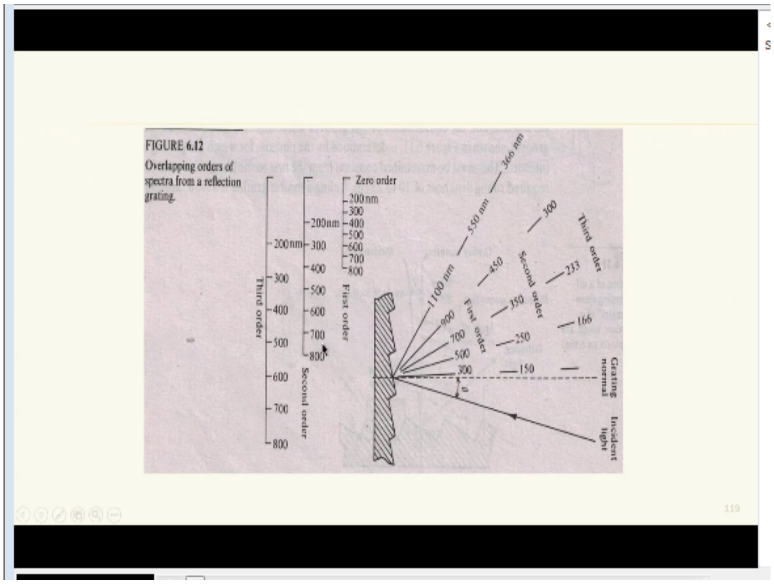


FIGURE 6.12

Overlapping orders of spectra from a reflection grating.

Here I am showing you slightly improved figure you can see the different ridges here okay. So, there this is known as grating normal that is it cuts the grating vertically okay this line is grating normal. And incident radiation comes like this and it will go ahead there and comes out at different wavelengths okay. So, this is the degree incident angle and the all radiations will be coming out like this.

I have shown here the different wavelengths, this is 300, 500, 700 900, 1100 that means if I change the rotate this grating from vertical position slowly like this first I can get 300 nanometers and then 500 nanometers. If I rotate it more and then slightly more rotation if I change this angle I will get 700 then 900 1100 that means right from 300 to 1100 nanometers I can get by rotating the grating okay.

So the different when I get 300 nanometers okay I have also get certain amount of radiation corresponding to 150 nanometers, that is wavelength half of the wavelength. Then I can get still lower around 60 or something like that, so this is known as first order, this is known as second order, this is third order like that different wavelengths I get the first 1 what I get is zero order.

Here it is here zero order I have plotted here that is it covers from 250 to 200 to 1100 okay, 200 to 800 here zero order. So, I get zero order, first order, second order etc. etc. and then this is second order, this is third order, zero order like that I will get different. But the intensity of the second order would be much less than the first order, it may be less than 50% or something like that intensity of the third order also would be much less.

So, if I want or not at any angle I get both orders both or 2 or 3 orders with different intensities may not be significant. But for very accurate work I cannot take at the first order straight away. Because there will be certain amount of radiation associated with the second order that is half of the wavelength. So if I want to use a only a very accurate work some people use 2 gratings first with the first grating they get the first order and then second order also.

And that radiation that comes out of that, they will make it fall on the another grating and again they get the first order, so at that time the intensity of the second order would be almost**.** There are ways of getting rid of the second order third order. But quite often it is not very important for routine analytical purposes. So 1 grating should be more than enough for typical applications okay.

(Refer Slide Time: 04:34)

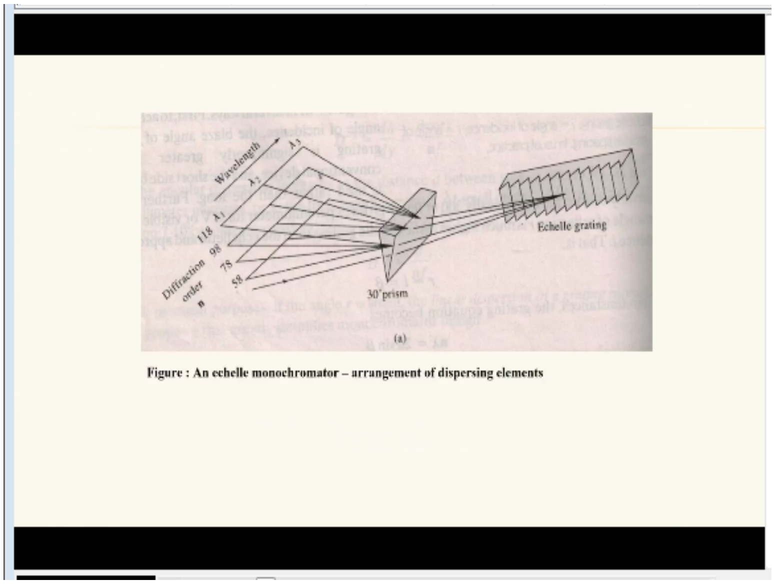


Figure : An echelle monochromator – arrangement of dispersing elements

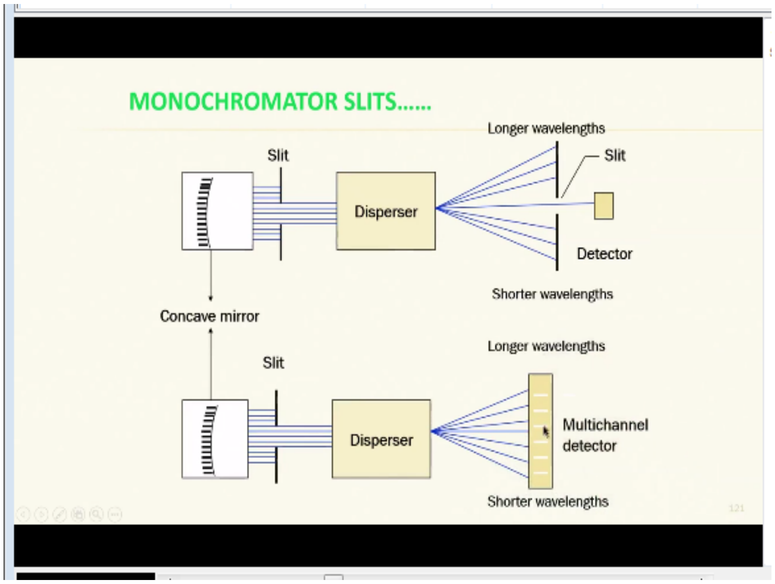
So, this is how sometimes people use an grating known as Echelle grating here I had to tell you that the number of rulings is what makes quality of a grating, typical rulings vary from 1200 to 30,000 rulings for centimeter. It is a great achievement, it is an engineering material is great achievement to draw 30,000 lines depressions per centimeter. And the maximum typical numbers used in spectrophotometer contain from 1200 to 1800 or something like that either 1200 lines or 1800 lines that means in a single grating you will get about 1200 prisms.

So the accuracy of the wavelength that comes out would be much more of very high quality compared to a prism. Because in prism there is only 1 prism here I have 1200 prisms for the same radiation. So a typical edge looks like this in this figure I have shown here know 30 degree prism is like this. So, if I have to use a diffractive meter I should use 1 with very high numbers. But there is special case I want you to understand that I can use smaller number of gratings containing about 70 to 80 per centimeter.

And then I can use the prism to separate the remaining all these things, so here what happens is the second order, third order gratings are automatically removed with minimum effort. So, instead of you be using 2 gratings I can use only 1 grating and a prism. This type of arrangement where the number of rulings are hardly 75 to 100, 130 etc., that is known as Echelle grating. So, I have shown you in this figure.

The Echelle grating is here okay and then I make the radiation fall here take it through this. And then I get the distraction orders here, so the wavelengths lambda1, lambda2 lambda3 I am getting in this area and this is beautiful way of making a simple now-a-days 90% of the instruments in infrared spectrometer they do contain Echelle gratings.

(Refer Slide Time: 07:41)



MONOCHROMATOR SLITS......

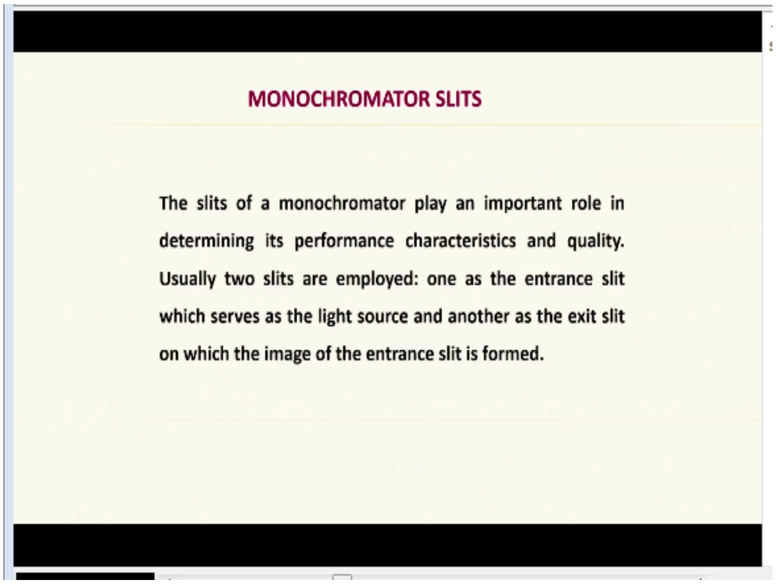
Now I want you to look at the top figure here I have a concave mirror and then all the radiation that comes out is all parallel that is the quality of the concave mirror that is why lot of concave mirrors are used in most of the instruments. And then I put a mechanical plate with a small hole that allows me to take out only a small portion of the incident radiation that is coming out and into the disperser.

This disperser could be either a prism or a grating or Echelle grating with a prism and all that oaky. So, from here I get all different wavelengths and then I put 1 more slit here okay to choose the radiation that is coming out like this either or like here I can put a slate or either change the disperser get different wavelengths or more the slit itself up and down that is also possible. So if I move down I get shorter wavelengths if I move up I get the longer wavelengths.

Now you can remove the photo, so there are different waves of doing this instead of concave mirror I can use a plane mirror. And then mechanical slit and then disperser and I can have number of slits here instead of a single hole like this on the top. I can have number of holes which will permit me to take out different wavelengths simultaneously both shorter wavelength and longer wavelengths.

So, if I put a detector on at each point I will have what is known as multi channel detector instrument very simple arrangement. But such instruments are also available including the infrared spectrometers okay.

(Refer Slide Time: 09:50)

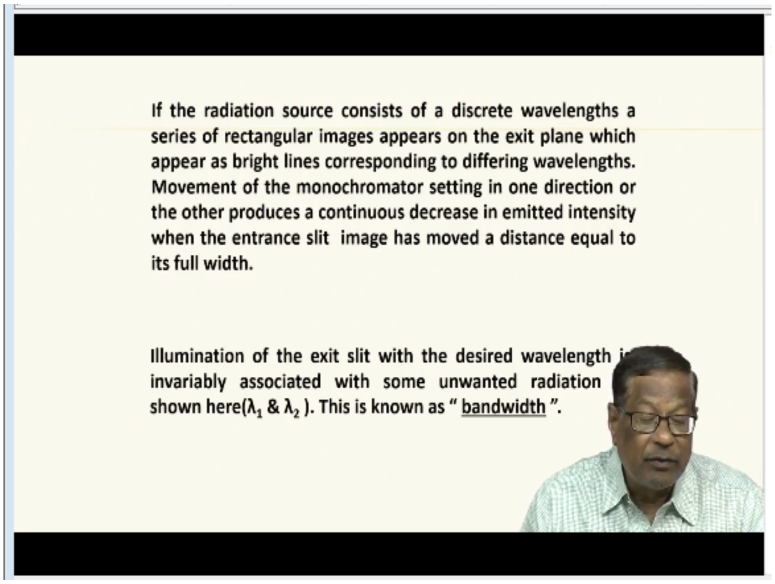


MONOCHROMATOR SLITS

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.

So, the monochromator slits play an important role in determining its performance characteristics and quality usually 2 slits are employed. 1 is entrance slit with I shown you earlier after the concave mirror and another 1 serve as the light source and another 1 as the exit slit on which the image of the entrance slit is formed. These are all very standard stuff described in most of the reference books which I have described prescribed for this course also okay.

(Refer Slide Time: 10:28)



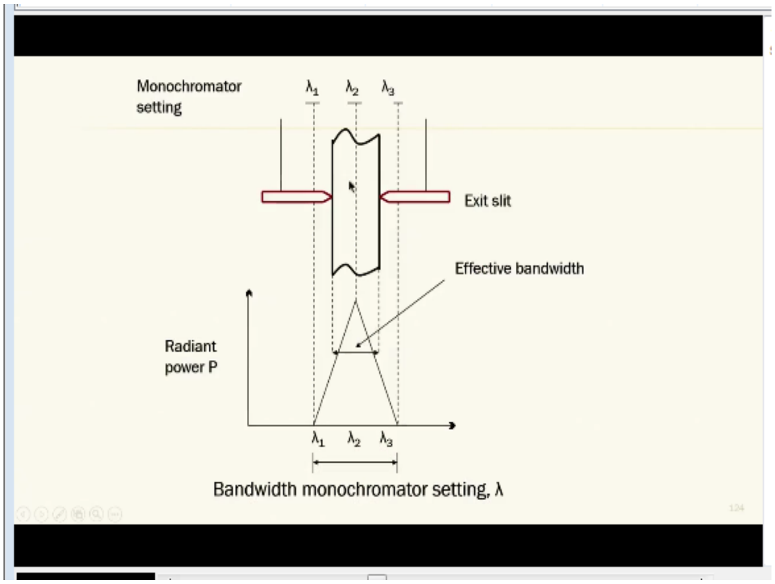
If the radiation source consists of a discrete wavelengths a series of rectangular images appears on the exit plane which appear as bright lines corresponding to differing wavelengths. Movement of the monochromator setting in one direction or the other produces a continuous decrease in emitted intensity when the entrance slit image has moved a distance equal to its full width.

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

So, if the radiation source consist of discrete wavelengths a series of rectangular images appears on the exit plane which appear as bright lines corresponding to different wavelengths that is all I understood. So, movement of the monochromator setting in 1 direction or the other produce as the continuous decrease in the emitted intensity and the entrance slit image has formed at a is moved at a distance equal to that of its full width.

So, illumination of the exit slit with the desired wavelength is invariably associated with some unwanted radiation. And this unwanted radiation normally is a radiation having slightly differing wavelength then what to have chosen. So whenever we use particular wavelength from a monochromator slit I do not get a single monochromatic radiation. But a band of radiation containing mainly the 1 what you have chosen+a little bit of this side and that side. So, that is known as band width okay, so this is the pictorial representation of a band width.

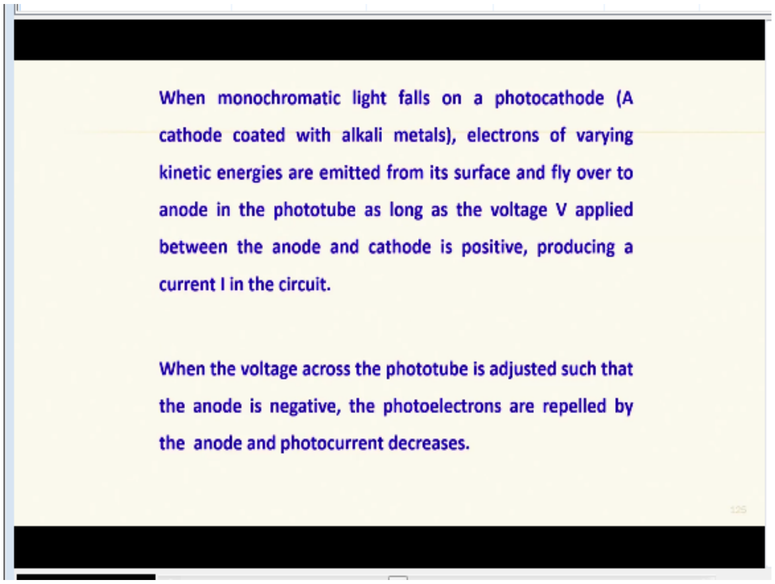
(Refer Slide Time: 11:52)



So, here what I want to show you is at the lambda2 is my desired wavelength okay. So, the maximum intensity this is the radiant power and this would be the intensity on the y-axis. And maximum radiation is here but I also get a radiation corresponding to lambda1 and lambda3. These are also nearby but maximum intensity lambda1 is almost nil here at this point this is another slit okay from here.

So, at this point at the edge lambda1 is nil, lambda3 is nil only lambda2 but somuhere around this. I get both lambda1, lambda2 and lambda3 and the lambda2 intensity would be very high. So, since I get all the 3 wavelengths corresponding to this radiation that is known as effective bandwidth okay. So, this may exit slit, so much of radiation keeps on coming but it will correspond to a little bit of lambda1 and lambda2 and the effective bandwidth. This described by the size of the exit slit also okay.

(Refer Slide Time: 13:18)



When monochromatic light falls on a photocathode (A cathode coated with alkali metals), electrons of varying kinetic energies are emitted from its surface and fly over to anode in the phototube as long as the voltage V applied between the anode and cathode is positive, producing a current I in the circuit.

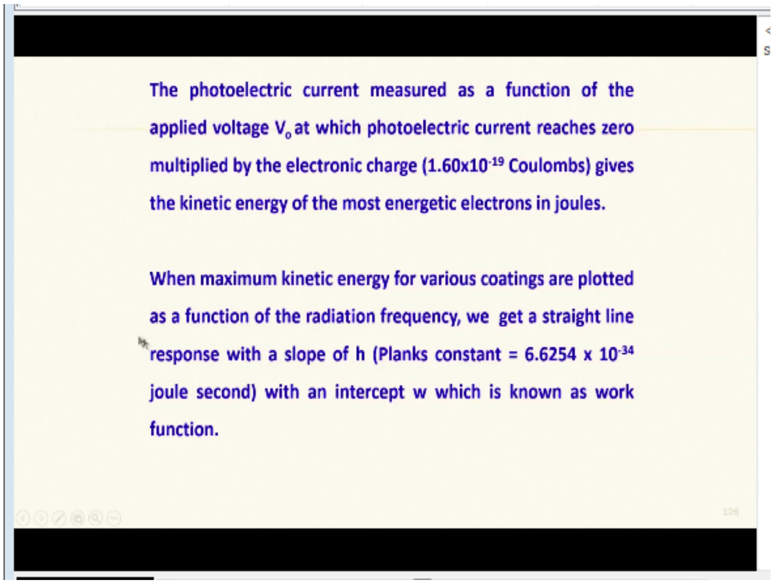
When the voltage across the phototube is adjusted such that the anode is negative, the photoelectrons are repelled by the anode and photocurrent decreases.

So, that is what exactly I have written here when the monochromatic light falls on the photocathode that is a cathode with coated with alkali metals electrons of varying kinetic energies are emitted from its surface and fly over to the anode in a phototube as long as the voltage V applied between the voltage and cathode is positive. It produces a small current, now we are talking about the interaction of electromagnetic radiation with detector okay.

Detector is nothing but a piece of metal on which alkali metals are coated. So, then what happens electro when the radiation impinges on this electrons of varying kinetic energy are emitted and a small current flows in the circuit. So, when the voltage across the phototube is adjusted such that anode is negative the photoelectrons are repel by the anode.

And the photocurrent decreases that means depending upon the voltage I get different kinds of current corresponding to the number of electrons that are released whenever the radiation falls on the detector. When I do not have the sample maximum current when I have the sample part of it is absorbed. So, the remaining part of the radiation that falls on the detector that will produce less current. So, this current difference can be correlated to the concentration of the pollutant whatever we are trying to determine.

(Refer Slide Time: 15:01)



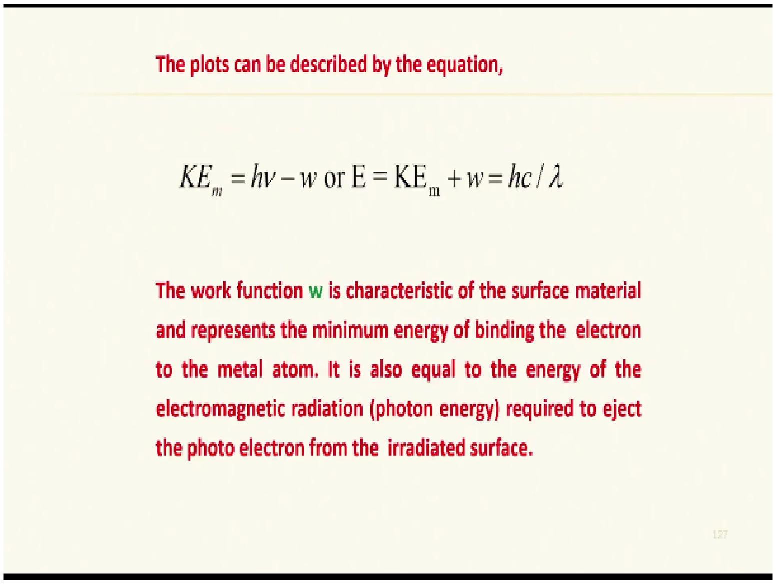
The photoelectric current measured as a function of the applied voltage V_o at which photoelectric current reaches zero multiplied by the electronic charge (1.60×10^{-19} Coulombs) gives the kinetic energy of the most energetic electrons in joules.

When maximum kinetic energy for various coatings are plotted as a function of the radiation frequency, we get a straight line response with a slope of h (Planks constant = 6.6254×10^{-34} joule second) with an intercept w which is known as work function.

So, coming back to this the photoelectric current is measured as a function of the applied voltage V0 at which photoelectric current reaches 0 that is multiplied by we can multiply the electron charged by the coulombs 1.60*10 raise to -19 that gives the kinetic energy of the energetic electrons in joules. So maximum kinetic energy for various coatings are plotted as a function of radiation frequency and we get straight line responsive should get.

A straight line response with the slope of h with an intersect w which is known as work function, this is all the theory of the detectors okay.

(Refer Slide Time: 15:43)



The plots can be described by the equation,

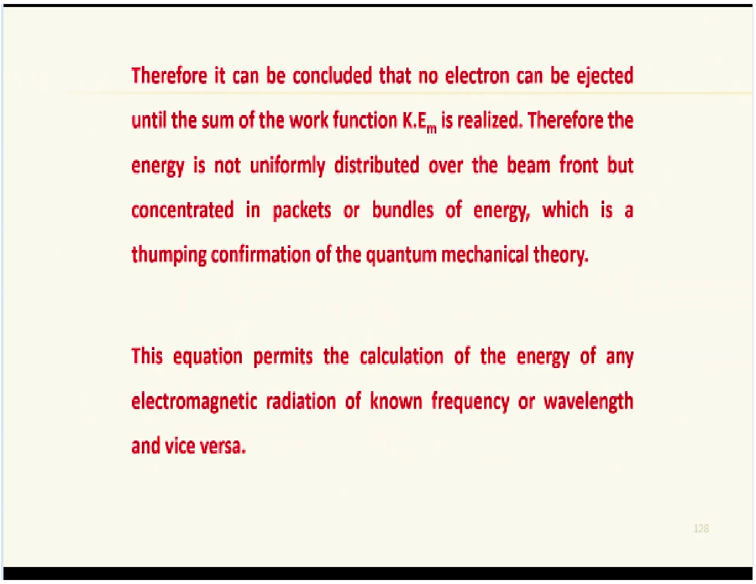
$$KE_m = h\nu - w \text{ or } \mathrm{E} = \mathrm{KE}_\mathrm{m} + w = hc/\lambda$$

The work function w is characteristic of the surface material and represents the minimum energy of binding the electron to the metal atom. It is also equal to the energy of the electromagnetic radiation (photon energy) required to eject the photo electron from the irradiated surface.

So, the plots can be described by the equation KEm=h mu-work function w, w is the work function. So, the E is nothing but KEm+w energy that is corresponds to hc/lambda, so w is the characteristic of the surface material and represents the minimum energy of binding the electron to the metal atom. So, the moment binding energy is excess equal and excess of the binding energy electron will be released and currently flow.

So, it is also equal to the energy of the electromagnetic radiation that is energy of the photon electromagnetic radiation requires to eject the photoelectron from the irradiated surface okay.

(Refer Slide Time: 16:38)

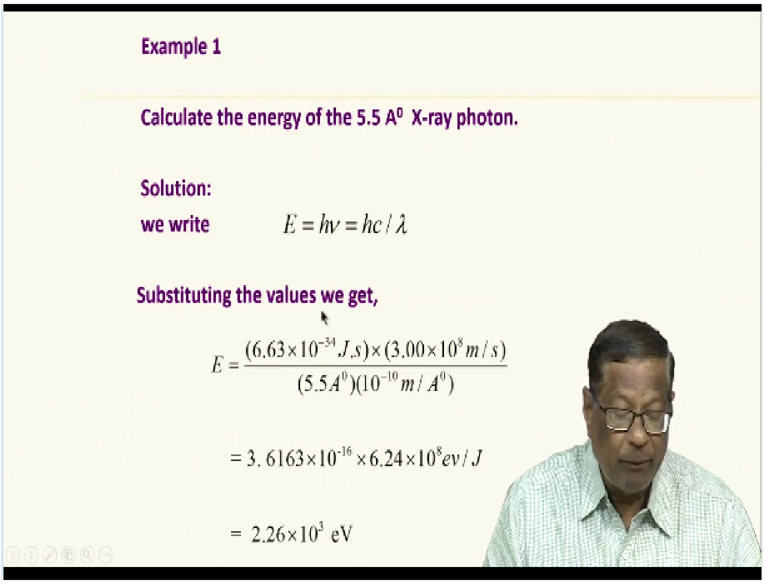


Therefore it can be concluded that no electron can be ejected until the sum of the work function $K.E_m$ is realized. Therefore the energy is not uniformly distributed over the beam front but concentrated in packets or bundles of energy, which is a thumping confirmation of the quantum mechanical theory.

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

So, it can be concluded that no electron can be ejected until the work function is exceed it okay that is K*Em. So, the energy is not uniformly distributed over the beam front but concentrated in packets or bundles of energy which is a thumping confirmation of the quantum mechanical theory. That is all about the detectors, so the equation permits the calculation of the energy of any electromagnetic radiation of known frequency or wavelength that includes infrared spectroscopy also okay.

(Refer Slide Time: 17:16)



Example 1

Calculate the energy of the 5.5 A^0 X-ray photon.

Solution:

we write $E = h\nu = hc/\lambda$

Substituting the values we get,

$$E = \frac{(6.63\times10^{-34} J.s)\times(3.00\times10^{8} m/s)}{(5.5A^{0})(10^{-10} m/A^{0})}$$

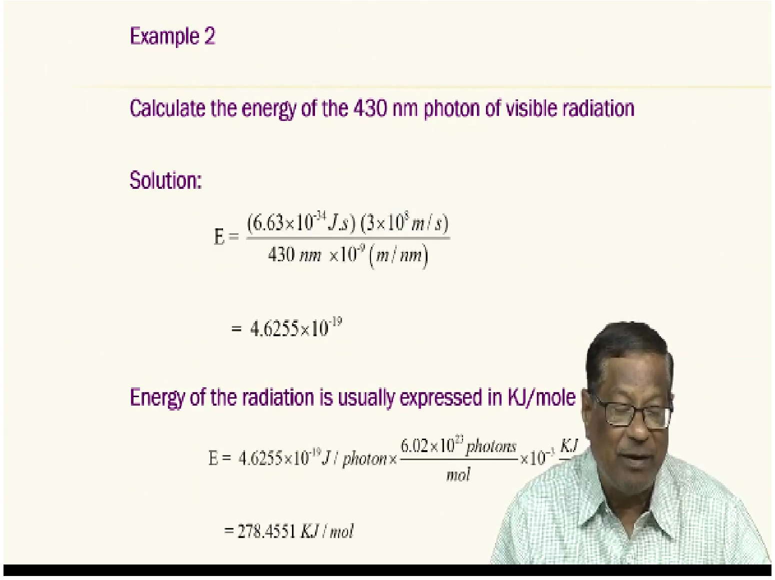
$$= 3.6163\times10^{-16}\times6.24\times10^{8} ev/J$$

$$= 2.26\times10^{3}\ \text{eV}$$

Now I can I will just arrange to give you a small demo regarding the energy of the electromagnetic radiation and how we can use it in our day today life. I have given I am going to present you 1 small example. Here you can calculate the energy of the 5.5 Armstrong unit radiation that is an X-ray photon. So, here you can fill up the numbers E=h mu or hc/lambda here you can put the h value.

Then see this 3*10 raise to 8 and then wave length, so if you solve this you can calculate the energy of the incident radiation corresponding to this wavelength. Now I can give any wavelength and ask you to calculate what is the corresponding energy of the electromagnetic beam. So that is the purpose of showing you this example okay, so across the electromagnetic radiation we can if I know the wavelength I can calculate the energy of the electromagnetic beam of that wavelength okay.

(Refer Slide Time: 18:36)



Example 2

Calculate the energy of the 430 nm photon of visible radiation

Solution:

$$E = \frac{(6.63\times10^{-34}\,J.s)\,(3\times10^{8}\,m/s)}{430\,nm\,\times10^{-9}\,(m/nm)}$$

$$= 4.6255\times10^{-19}$$

Energy of the radiation is usually expressed in KJ/mole

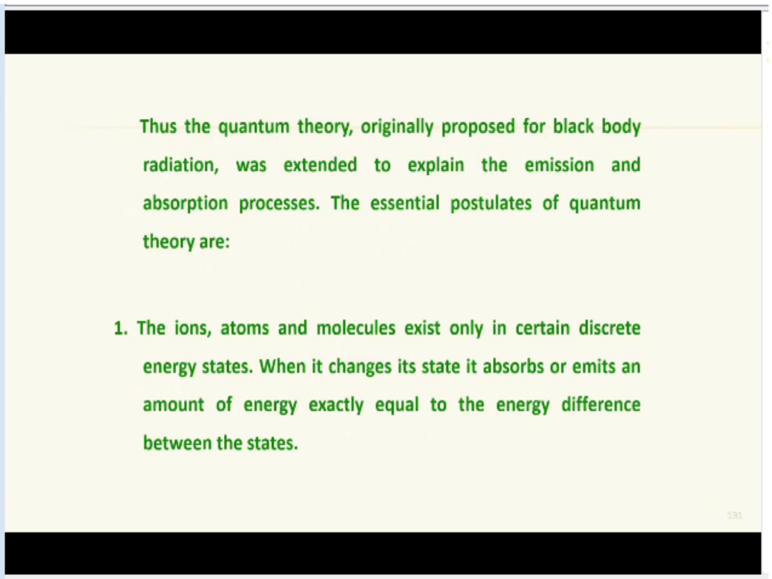
$$E = 4.6255\times10^{-19}\,J/photon\times\frac{6.02\times10^{23}\,photons}{mol}\times10^{-3}\,KJ$$

$$= 278.4551\,KJ/mol$$

Now here is 1 more example 430 nanometers earlier when was in X-ray, now I have in the visible region 430 nanometer. Again I use the same equation E=hc/lambda, so the numerator will remain the same that is 6.63*10 raise to -34 joules seconds*velocity of the electron and divided it by the wavelength. We will get 10 raise to -19 that is 4.65, so the energy is usually we express in kilo joules per mole.

So, I can write 4.6255 I had to multiplied by number of the photons per mole okay into 10 raise to -3 convert it into kilo joules in a normally joules means, so you get lot of numbers. So, if I convert that I get the energy of the 430 nanometer photon corresponding to 4278.4551 kilo joules per mole this is only a demo example. But maybe I will ask you in the exam also.

(Refer Slide Time: 19:56)



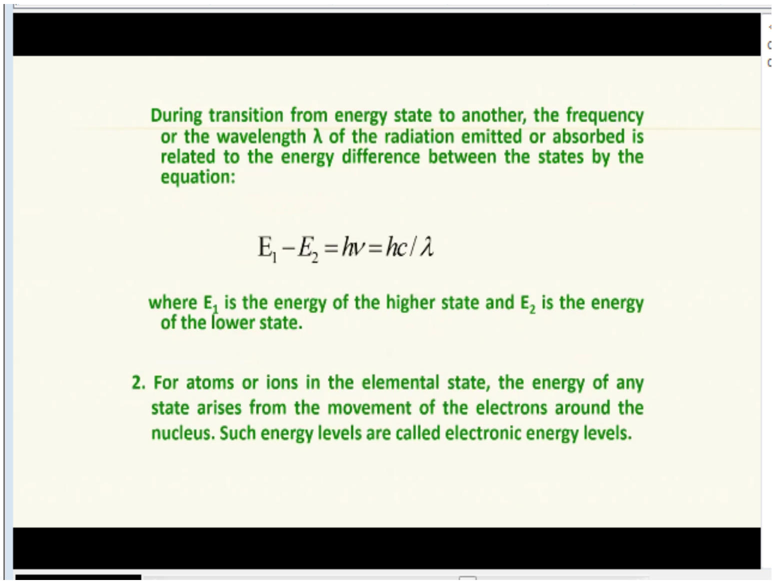
Thus the quantum theory, originally proposed for black body radiation, was extended to explain the emission and absorption processes. The essential postulates of quantum theory are:

1. The ions, atoms and molecules exist only in certain discrete energy states. When it changes its state it absorbs or emits an amount of energy exactly equal to the energy difference between the states.

So, the quantum theory originally was proposed for black body radiation a little now I want to explain to you quickly other aspects of instrumentation electromagnetic radiation. So, that we can precede on to the infrared spectroscopy part of it that is the main body of our course that will proceed quickly. Now I want to tell you that the quantum theory was originally proposed for black body radiation that was extended to explain the emission and absorption processes.

The essential postulates are like this the ions, atoms and molecules only exist only in certain discrete energy states. So, when it changes its state it absorbs or emits an amount of energy exactly equal to the energy difference between the 2 states this is 1 postulate.

(Refer Slide Time: 20:58)



During transition from energy state to another, the frequency or the wavelength λ of the radiation emitted or absorbed is related to the energy difference between the states by the equation:

$$E_1 - E_2 = h\nu = hc/\lambda$$

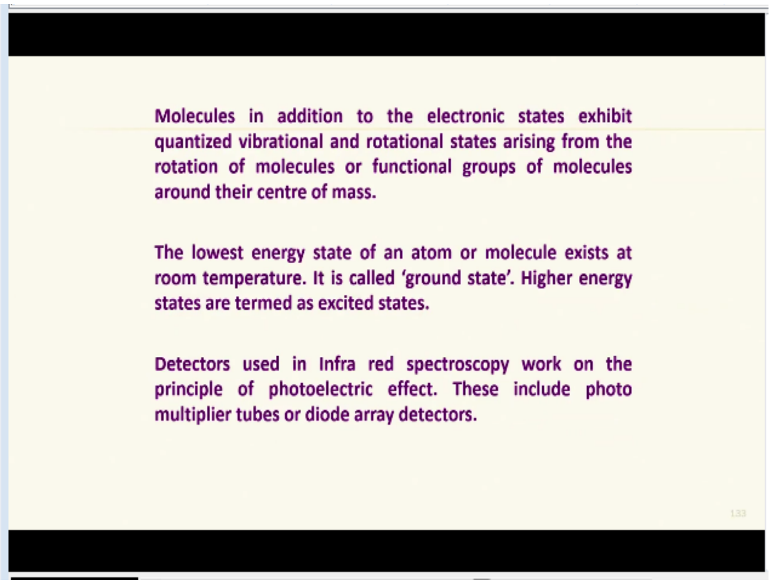
where E_1 is the energy of the higher state and E_2 is the energy of the lower state.

2. For atoms or ions in the elemental state, the energy of any state arises from the movement of the electrons around the nucleus. Such energy levels are called electronic energy levels.

Another 1 is during transition energy from 1 energy level to another energy level the frequency or wavelength of the radiation emitted or absorbed is equal to the energy difference between the states. So, I can write E1-E2 is equal to h mu or hc/lambda and by E1 is the energy of the higher state and it was the energy of the lower state. Now I can also say for atoms and ions in the elemental state the energy of the state raises from the movement of the electrons around the nucleus.

This we have already discussed a little bit in the introduction part itself during atomic structure. So, such energy levels are called electronic energy levels.

(Refer Slide Time: 21:44)



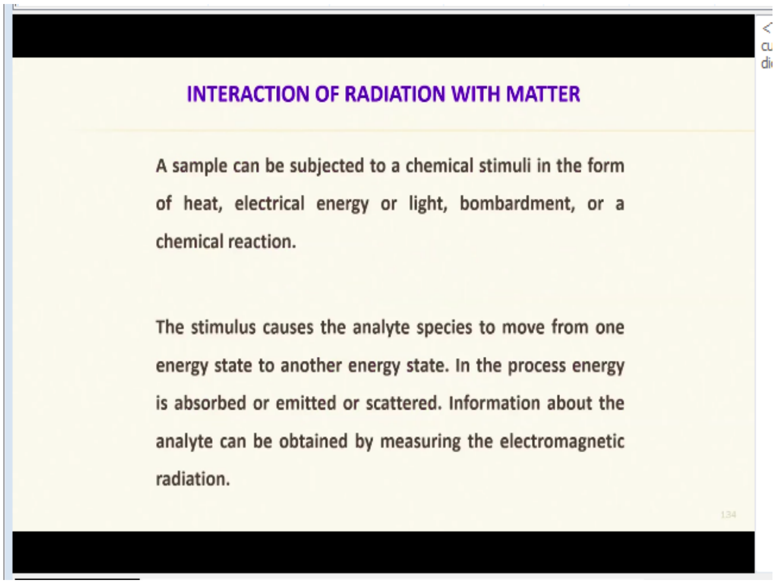
Molecules in addition to the electronic states exhibit quantized vibrational and rotational states arising from the rotation of molecules or functional groups of molecules around their centre of mass.

The lowest energy state of an atom or molecule exists at room temperature. It is called 'ground state'. Higher energy states are termed as excited states.

Detectors used in Infra red spectroscopy work on the principle of photoelectric effect. These include photo multiplier tubes or diode array detectors.

Then I have vibrational energy levels and rotational energy levels, so the lowest energy state of atom or a molecule that exist at room temperature that. So, the energy populated at room temperature is called as ground state, higher energy states are termed as excited states. So, detectors used in infrared spectroscopy work on the principle of photoelectric effect which I enumerated just now. So, these include photomultiplier tubes and diode array detector these are the technical terms for the detectors used in infra red spectroscopy.

(Refer Slide Time: 22:28)



INTERACTION OF RADIATION WITH MATTER

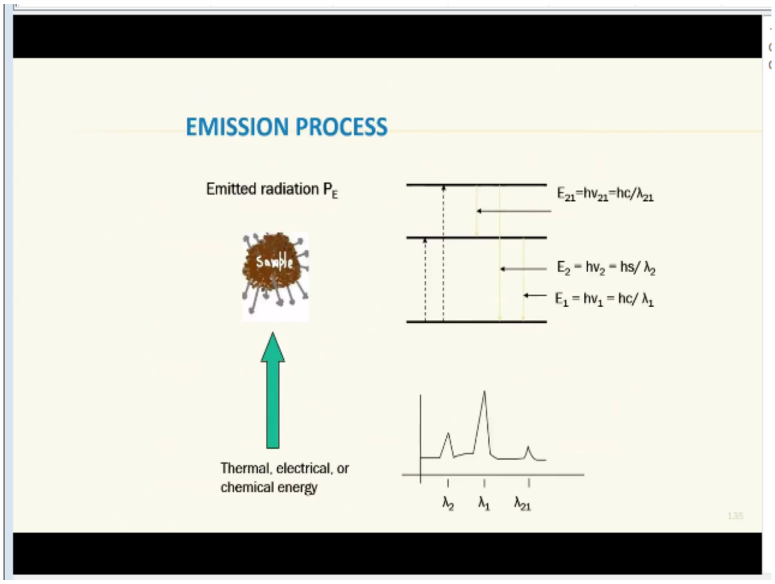
A sample can be subjected to a chemical stimuli in the form of heat, electrical energy or light, bombardment, or a chemical reaction.

The stimulus causes the analyte species to move from one energy state to another energy state. In the process energy is absorbed or emitted or scattered. Information about the analyte can be obtained by measuring the electromagnetic radiation.

So, you can continue our discussion on the interaction of radiation with matter. So, a sample can be subjected to a chemical stimuli in the form of heat, electrical energy or light, bombardment or chemical reaction. So the stimulus causes the analyte species to move from 1 energy to higher energy state. So in the process energies absorbed or stated. So, information about the analyte can be obtained by measuring the electromagnetic radiation see in most of the atomic spectroscopy including infrared, molecular spectra and other things.

The measurement basically is of electromagnetic radiation not of the sample. But sample will have an effect on the energy of the electromagnetic radiation that it is going to interact with, so most of the analytical instruments measure the energy of the electromagnetic radiation. So, we can get the information about the analyte but obtaining electromagnetic radiation itself okay.

(Refer Slide Time: 23:52)



EMISSION PROCESS

Emitted radiation P_E

$E_{21}=hv_{21}=hc/\lambda_{21}$

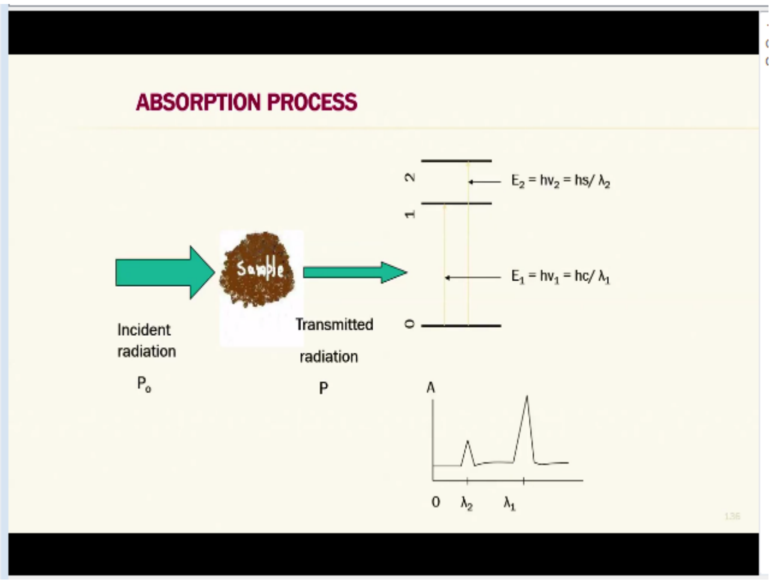
$E_2 = hv_2 = hs/ \lambda_2$

$E_1 = hv_1 = hc/ \lambda_1$

Thermal, electrical, or chemical energy

So, this is how normally we depict the emission process here I have a sample I supply energy it goes from this state to higher energy state. And then this is E1, E2 E21 etc. different levels and the energy difference between this and this is when there is no interaction when there is a interaction, when there is no interaction like that at different wavelengths.

(Refer Slide Time: 24:27)



ABSORPTION PROCESS

Incident radiation P_o

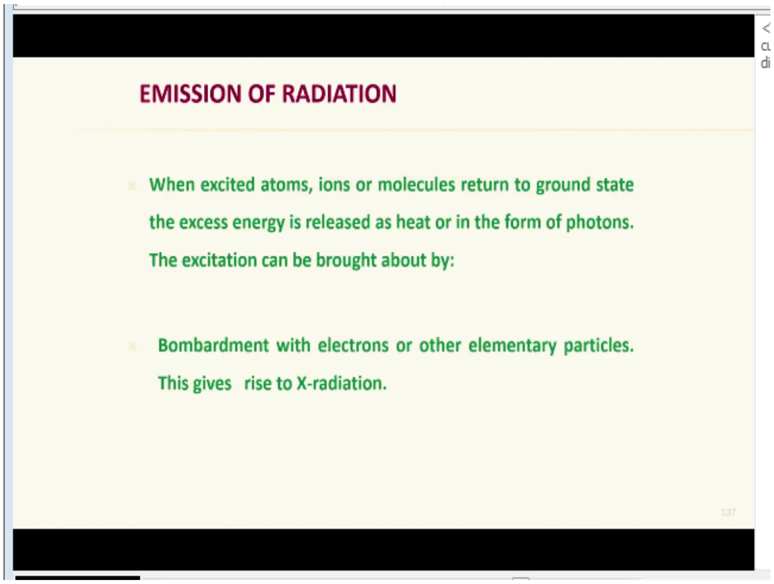
Transmitted radiation P

$E_2 = hv_2 = hs/ \lambda_2$

$E_1 = hv_1 = hc/ \lambda_1$

So, that is emission now absorption here part of the energy is absorbed and what comes out would be the transmitted radiation and its intensity would be lower than the incident radiation p0. So, again I have similar energy levels 0, 1 and 2 I have E1=hmu1 that is equal to hc/lambda, E2 is this difference between these 2 are represented as 2 peaks corresponding to those transitions.

(Refer Slide Time: 25:04)



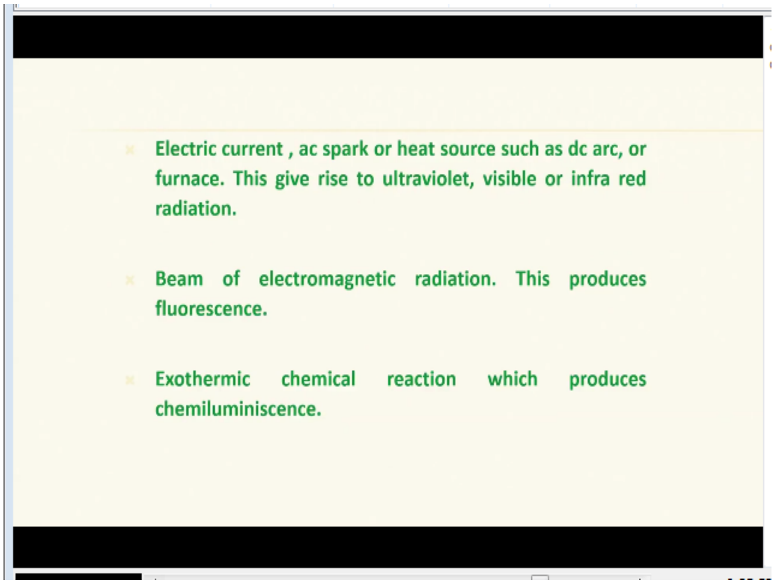
EMISSION OF RADIATION

- When excited atoms, ions or molecules return to ground state the excess energy is released as heat or in the form of photons. The excitation can be brought about by:
- Bombardment with electrons or other elementary particles. This gives rise to X-radiation.

So, the emission of radiation is another 1 but we are not going to consider much about the emission. Because the way I am going to talk about infra red, absorption spectrum. So, but just for the sake of gravity let us spend little time about the emission also. So when excited atoms, ions or molecules return to the ground state sometimes the excess energy is released as heat or in the form of radiation that is photons.

So, the excitation can be brought about by bombardment with electrons or other elementary particles that give raise to X-radiation okay.

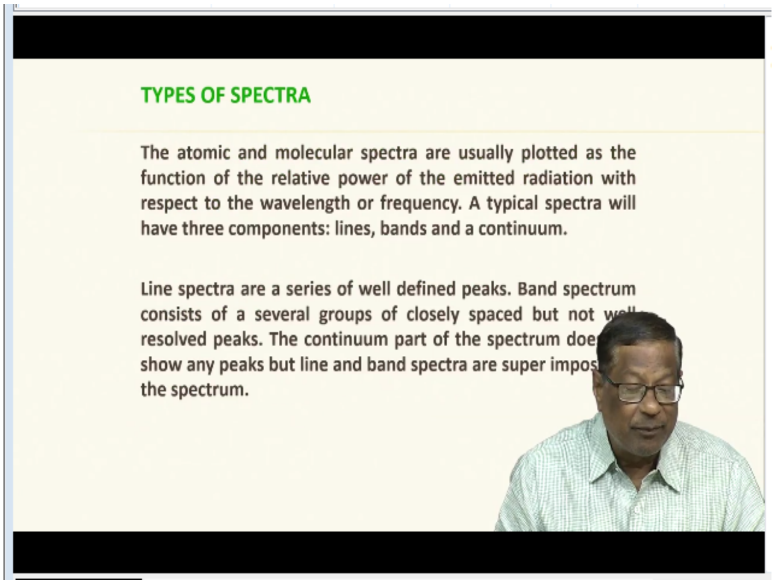
(Refer Slide Time: 25:51)



- Electric current , ac spark or heat source such as dc arc, or furnace. This give rise to ultraviolet, visible or infra red radiation.
- Beam of electromagnetic radiation. This produces fluorescence.
- Exothermic chemical reaction which produces chemiluminiscence.

Now electric current as spark or heat source such as dc arc, furnace etc. can be used as a energy sources this gives raise to ultra violet, visible light, infrared radiation etc. And beam of electromagnetic radiation this produces fluorescence sometimes, exothermic chemical reaction produces chemiluminiscence. But we are not going to consider any of these but these are the different things you should be knowing about.

(Refer Slide Time: 26:24)



TYPES OF SPECTRA

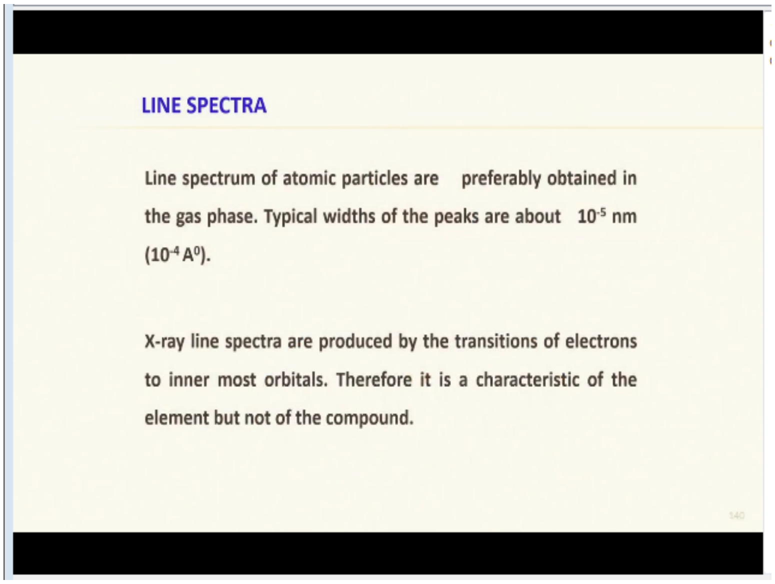
The atomic and molecular spectra are usually plotted as the function of the relative power of the emitted radiation with respect to the wavelength or frequency. A typical spectra will have three components: lines, bands and a continuum.

Line spectra are a series of well defined peaks. Band spectrum consists of a several groups of closely spaced but not w resolved peaks. The continuum part of the spectrum doe show any peaks but line and band spectra are super impos the spectrum.

So, there are different types of spectra the typical spectra have 3 comp1nts 1 is lines, bands and a continuum. So, lines spectra are a series of well defined peaks, that is band spectrum consists of a several groups of closely spaced but not well resolved peaks. And continuum part you know as visual it has no boundaries it just as sort of illuminated area that is contain your spectra. So, by sometimes the lines spectra and band spectra are super imposed on 1 another also.

So, that is also seen especially in solar spectrum. But that is not important as far as our course on infra red is concerned.

(Refer Slide Time: 27:26)



LINE SPECTRA

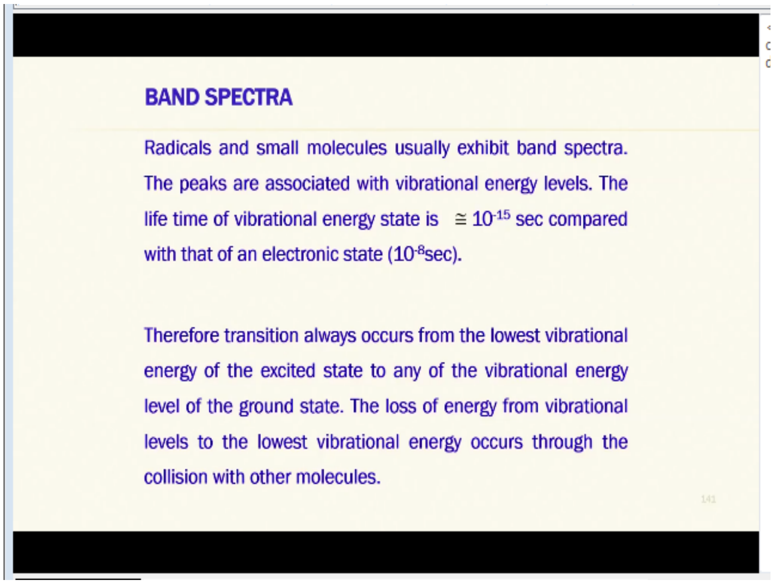
Line spectrum of atomic particles are preferably obtained in the gas phase. Typical widths of the peaks are about 10^{-5} nm (10^{-4} A^0).

X-ray line spectra are produced by the transitions of electrons to inner most orbitals. Therefore it is a characteristic of the element but not of the compound.

So line spectrum of atomic particles are preferably obtained in the gas phase especially in the gas phase we get line spectra. Because the matrix effects are very less in the gas phase, so typical widths of the peaks are of the order about 10 raise to -5 nanometer or 10 raise to -4 Armstrong units. And x-ray line spectra are produced by transitions of the electrons when they fall from higher energy level to the lower energy level okay.

So, from higher shell to lower shell they emit certain radiation of lower energy that is x-rays oaky. And band spectra produced by radicals, small molecules and bigger molecules also but the peaks are associated with the vibrational energy levels.

(Refer Slide Time: 28:31)



BAND SPECTRA

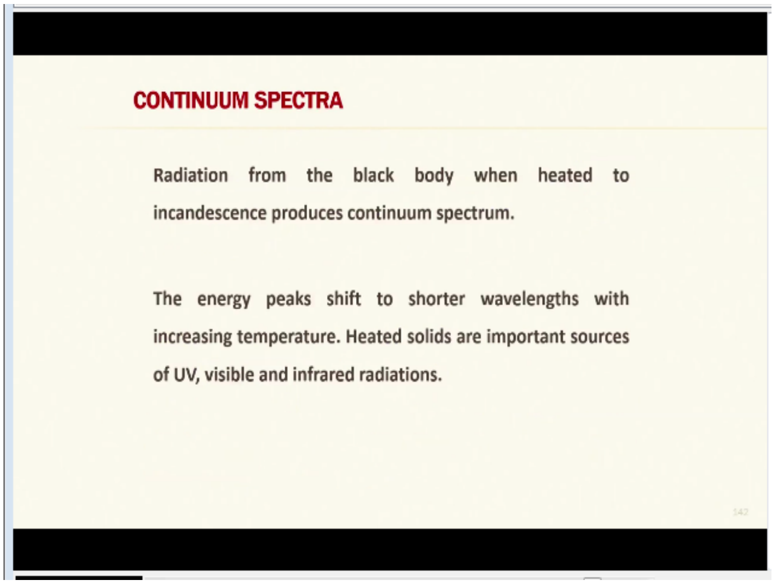
Radicals and small molecules usually exhibit band spectra. The peaks are associated with vibrational energy levels. The life time of vibrational energy state is $\cong 10^{-15}$ sec compared with that of an electronic state (10^{-8}sec).

Therefore transition always occurs from the lowest vibrational energy of the excited state to any of the vibrational energy level of the ground state. The loss of energy from vibrational levels to the lowest vibrational energy occurs through the collision with other molecules.

So, the life time of vibrational energy state is approximately 10 raise to -15 seconds compared with that of the electronic state excitation that is about 10 raise to -8 second the almost double the electronic state is almost half of vibrational energy state changes. So the transition always occurs from the lowest vibrational energy level of the excited state to the any of the vibrational energy level of the ground state.

The loss of energy from vibrational levels to that of the ground floor and ground state lowest energy level occurs through the collision with other molecules.

(Refer Slide Time: 29:24)



CONTINUUM SPECTRA

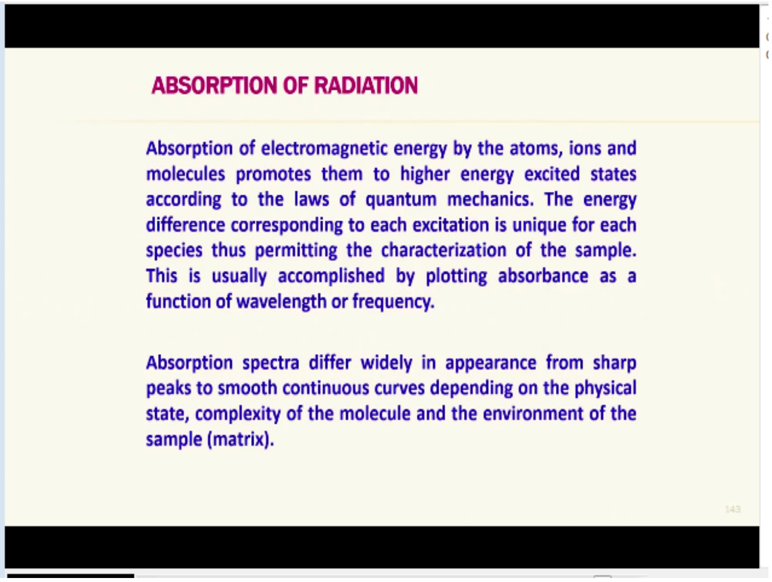
Radiation from the black body when heated to incandescence produces continuum spectrum.

The energy peaks shift to shorter wavelengths with increasing temperature. Heated solids are important sources of UV, visible and infrared radiations.

I hope you are able to understand what I am trying to tell you okay. Now the first I take certain amount of material excited to higher energy state from there it falls slowly couple of steps until it reaches the ground level of the vibrational level of the excited state. It comes to 0 of the excited state and then it falls to the 0 of the ground state. So, that is what we are talking about, so continuum spectra there is radiation from the black body when heated to incandescence, it produces continuum spectrum.

I think they every bodies family are with these, so early mornings sunlight containing red, blue, yellow etc. these are all sort of continuum spectrum, so the energy peaks shift to shorter wavelengths with increasing temperature and heated solids are important sources of UV, visible as well as infrared radiation, that means the lamps which we use should be of heated solids only okay.

(Refer Slide Time: 30:44)



ABSORPTION OF RADIATION

Absorption of electromagnetic energy by the atoms, ions and molecules promotes them to higher energy excited states according to the laws of quantum mechanics. The energy difference corresponding to each excitation is unique for each species thus permitting the characterization of the sample. This is usually accomplished by plotting absorbance as a function of wavelength or frequency.

Absorption spectra differ widely in appearance from sharp peaks to smooth continuous curves depending on the physical state, complexity of the molecule and the environment of the sample (matrix).

So, what I want it to tell you is the sources of the radiation for electromagnetic radiation or usually bulbs which you are very familiar Thomas Alva Edison's bulbs tungsten lamps etc., now-a-days there are LED lamps this that etc. fluoresce, hydrogen lamps so many types. But all of them contain a heated surface, so the most of the radiation sources are basically heated surface even though they are called as bulbs technically. So we will continue our discussion in the next class, thank you very much.