Atomic and Molecular Absorption Spectrometry for Pollution Monitoring

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Lecture - 07
Interaction of interaction of EM radiation with matter III

So, greetings, once again we meet to continue our discussion on the interaction of electromagnetic radiation with the matter. In the previous classes we have seen the how the electromagnetic radiation behave when it interacts with a matter, interacts with the matter.

So, we have seen reflection, refraction, diffraction and other phenomenon and then I have also have discussed about the slits monochromators slits, because whenever we want a particular radiation corresponding to a specific wavelength, we need to choose from the given bundle of the electronic radiation of different frequencies what we want to choose. So, that is how the; that is the job of monochromators slits and this figure I had shown you in the last presentation what it means is basically.

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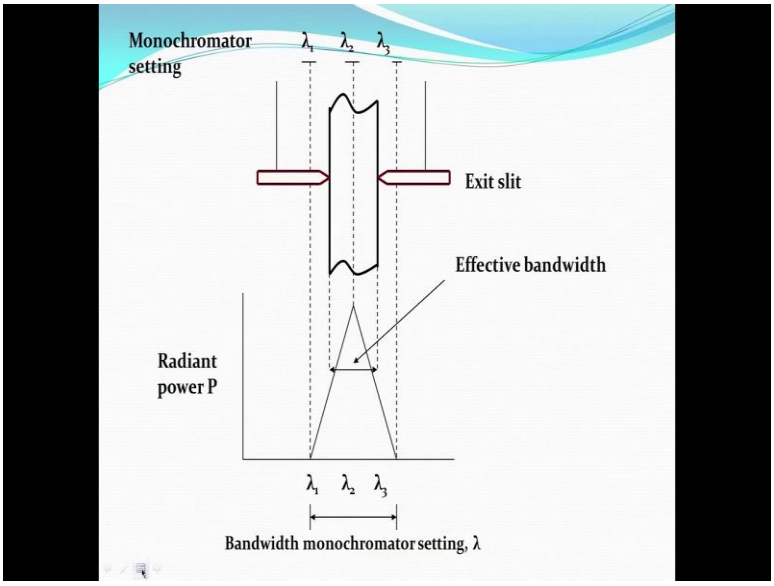

So, in normally what do we have is a source of electromagnetic radiation and then I have lens or something.

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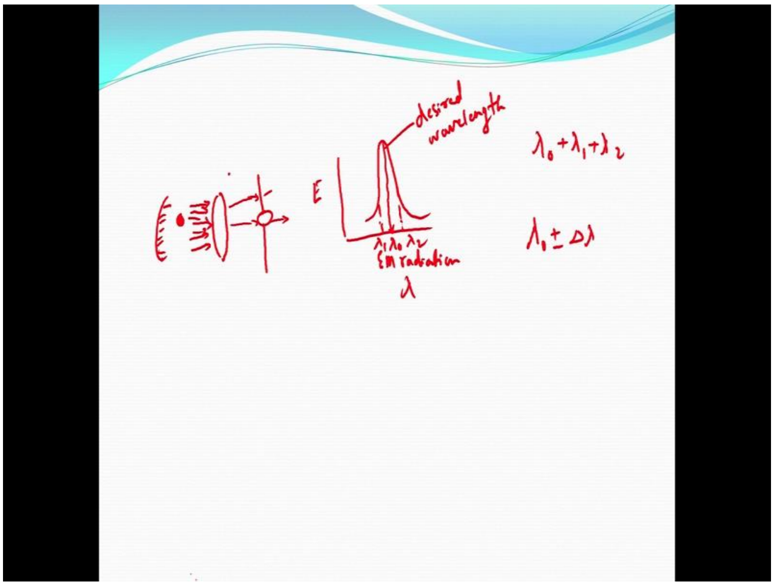

So, if the radiation is coming, this is the concave mirror which will give you all the radiation in the parallel form. So, here lens or prism or something like that will give you different wavelength. Suppose we put a prism there, all you need is a slit and this slit is nothing, but a mechanical plate with a small hole in that and this slit can be moved. So, if it moves here the radiation will come from here, but if the slit moves up the radiation will be coming through this. So, depending upon the movement of the slit we will be getting different wavelength, and when we get different wavelength if you plot the energy of the electromagnetic radiation wavelength this is lambda.

So, the peak what you will get is something like this, this is the wavelength what you want to use desired wavelength, but you will also get what is some unwanted, but nearby where radiations. So, this will be lambda 0, this will be lambda 1, this will be lambda 2. So, the any the slit will give you a mixture of lambda 0 plus lambda 1 plus lambda 2. So, lambda therefore, that wavelength what you get would be lambda 0 plus or minus delta lambda. So, delta lambda means lambda 1 may be on the right side that is higher wavelength, and lambda 2 may be on the left side that is lower wavelength.

So, this is what I was trying to show you in my last slide. So, in this figure what I have is I have shown the same thing as lambda 1, lambda 2, and lambda 3 and you will always end up with a bundle of wavelength which is having maximum peak is what your desire let us say 430, but then you have add delta lambda to that. So, delta lambda may be 5.

So, you will always end up with 425, 430 and 435; so plus or minus 5 nanometers in depending upon the lenses or the slit. So, the requirement of particular wavelength is always a function of the slit diameter. So, design of the slit is always very important in all spectrophotometers as well as all other spectroscopic techniques also. So, this is what I was trying to tell you.

Our next point of discussion would be the photoelectric effect, this is again part of our continual discussion regarding the interaction of electromagnetic radiation with matter.

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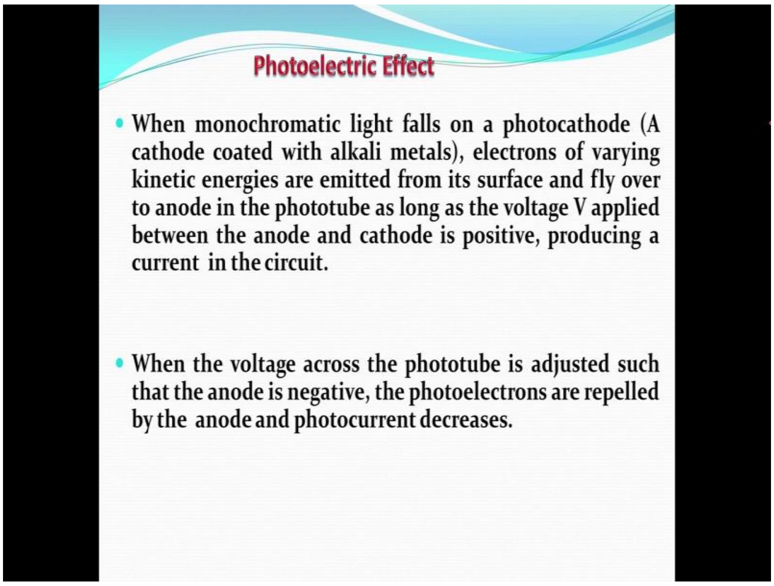

Now, when we say assume that in the just like in the previous slide we have got lambda 2 is the wavelength what I got, and this lambda 2 wavelength if I it is made to interact with a particular metal or a photocathode, what is a photocathode a cathode is coated with alkali metals. So, electrons of varying kinetics energies are emitted from its surface and fly over to the anode because in the electrons are attracted to the anode. So, as long as the voltage v is supplied between the anode and the cathode is positive produce it produces a current. So, if I make the mono take the monochromatic light; however, pure it may be.

So, if I make it fall on a metal plate then the metal plate, electromagnetic radiation falls on the metal plate the electrons are ejected; where the ejected electrons will go they will go to the cathode. So, if I put cathode in front I have a material here radiation is coming and falling here and it will eject electrons, electrons will be attracted to the cathode and to be I will also need an anode. So, if I maintain a positive difference between the potential between anode and cathode electrons are always going towards the cathode and then a small amount of current will be generated, this is the effect of electromagnetic radiation falling on a material that is interacting with a metal whose work function is low which allows electrons to be released from the metal and that is alkali metal and a current is produced.

So, if I want to know what is the quality of the electromagnetic radiation, I must let it fall on a photo cathode and measure the current. So, the measurement of the current give me a tool to assess the electromagnetic radiation. So, when the voltage across the phototube is adjusted such that the anode is negative, photoelectrons are repelled from the anode, we see electrons carry negative charge anode is also having negative charge. So, they get repelled and photocurrent decreases. So, if the potential difference between the anode and the cathode if it is increasing, if it is high the current will be more.

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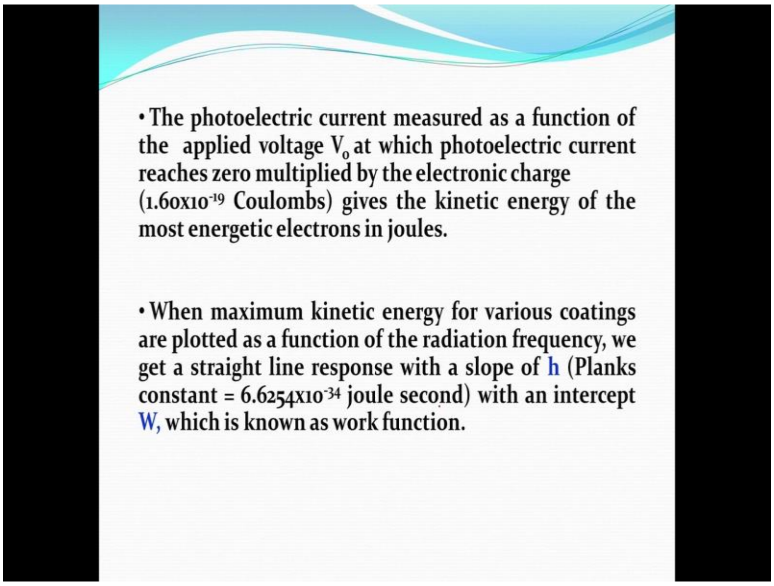

So, it is measured as a function of the applied voltage at which the photoelectric current reaches 0 multiplied by the electronic charge that is coulombs. So, that give the kinetic energy of the most energetic electrons in joules it is a very simple process all you got to do is measure the current and multiplied by 1.60 into 10 raise to minus 19 that will give you joules.

So, when maximum kinetic energy for various coatings are plotted as the function of the radiation frequency we will get straight line and the slope is Planck's constant the that is 6.6254 into 10 raise to minus 34 joules per second, with an intercept W and this W is known as work function. So, this work function is the characteristic of every alkali metal or every metal for that matter. So, until the work function is reached the electrons will not be ejected from the cathode.

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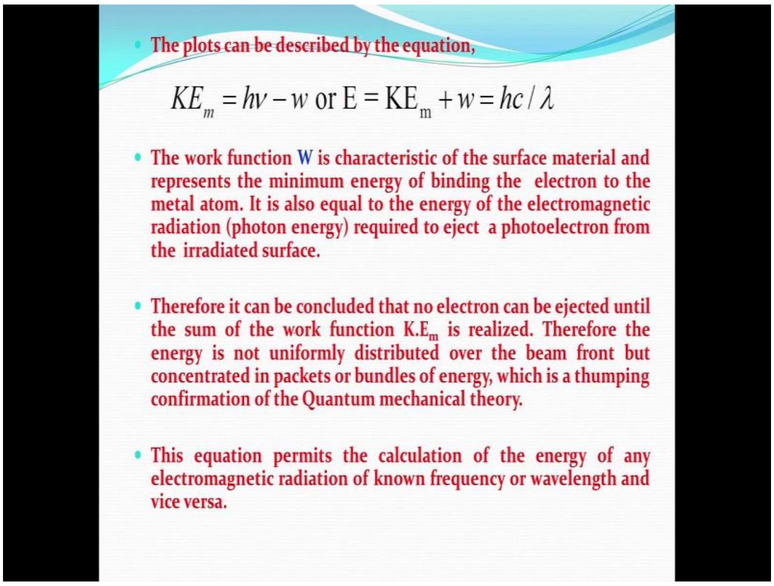

So, the plot what we have been talking is given by the equation KE m is equal to h nu by minus w where w is the work function nu is the frequency h is plank constant, KE is kinetic energy of the metal. We can also write it as the E is equal to KE into m plus w or several in several ways which I have always shown here that is also equal to hc by lambda. What is h? His Planck's constant c is velocity of light and lambda is wavelength.

So, the work function W as I was telling you is characteristic of this surface material and the work function represents the minimum energy of the bind of the bind of binding the electron to the metal atom; if you provide excess energy the electron will be going out it will be flying away and from the when it is released from the metal it will fly towards the cathode, and during that process the current will be generated.

Therefore it can be concluded that no electron can be ejected until these some of the work function is realized and that can be quantified as kinetic energy of a metal, K dot E m therefore, the energy is not uniformly distributed over the beam front, but it is concentrated in packets or bundles. So, this is a thumping confirmation of quantum mechanical theory; what it says the energy difference between the 2 levels is always a constant and it is not continuous, that mean if I keep on supplying the energy continuously you will not see any electric current, but the moment it reaches a particular value and exceeds you will start seeing the current. So, this work function is a very important concept of the electromagnetic radiation.

So, the equation permits the calculation of the energy of the electromagnetic radiation of known frequency or wavelength or vice versa either way.

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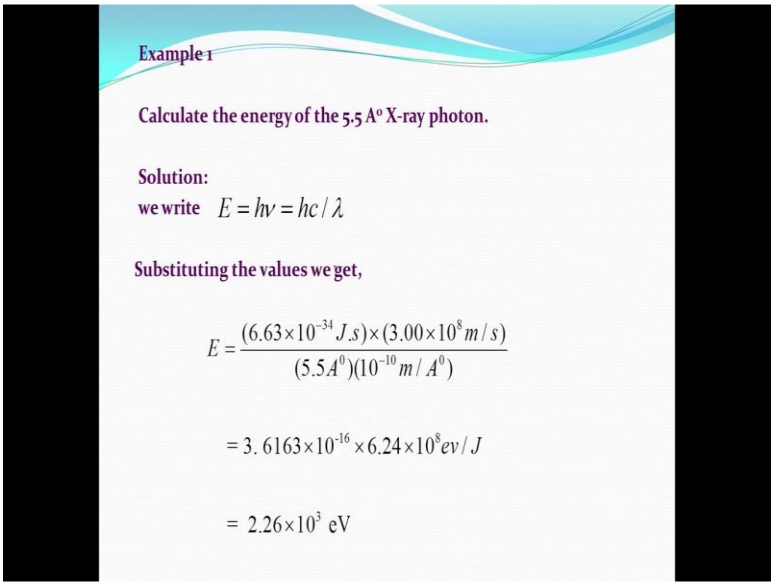

So, this is the important thing now I want to show you demonstrate to you how we can calculate the energy of radiation. Now in the example in front of you I have this 5.5 angstrom x ray photon. So, I want to know what is the energy of this wavelength that is coming out whenever I have taken electrons and bombarded a turn metal and x ray is generated, the x ray generated is having wavelength of 5.5 angstrom unit, what is its energy. So, the solution is very simple we use the equation E is equal to h nu that is equal to hc by lambda, and what I have here is all I got to do is substitute the values of h that is 6.63 into a 10 raised to minus 34 joule seconds multiplied by speed of light hc c is 3.00 into 10 raised to 8 meters per second and then I have to divide it by the wavelength that is 5.5 angstrom normally we convert it into meters.

So, I multiplied by 10 raised to minus 10 meters per second one angstrom is 10 raised to minus 10 meters per second, and if I put this values what I get is 2.26 into 10 raised to 3 electron volts that is the unit. Therefore, given any wavelength I can calculate the value of the electron energy of electromagnetic radiation vice versa, if I know the energy of radiation I can always calculate what is the wavelength of the electromagnetic radiation take a look at next example.

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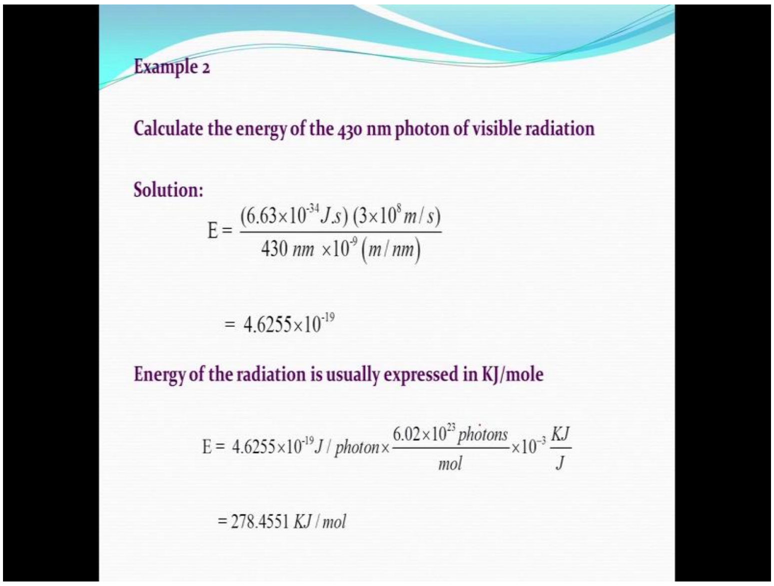

So, next example is again it is a wavelength I am giving that is 430 nanometer, I am calling instead of calling electromagnetic radiation I am calling it as a photon. So, calculate the energy of the 430 nanometer photon of visible radiation this falls in visible range. So, how do I do? I just have to repeat what I have done in last example. So, write E is equal to hc, hc by lambda h is 6.63 into 10 raised to minus 34 multiplied by 3 into 10 raised to 8 divided by wavelength that is 430 nanometers that is provided to you, and then that is multiplied by 10 raise to minus 9 that is meters per nanometers.

So, if you solve it you will end up with 4.6255 and into 10 raised to minus 19 that is the energy of the radiation, that is usually expressed in kilojoules and if I do that I will end up with 278.455, 1 kilo joules per mole this is a very simple this thing.

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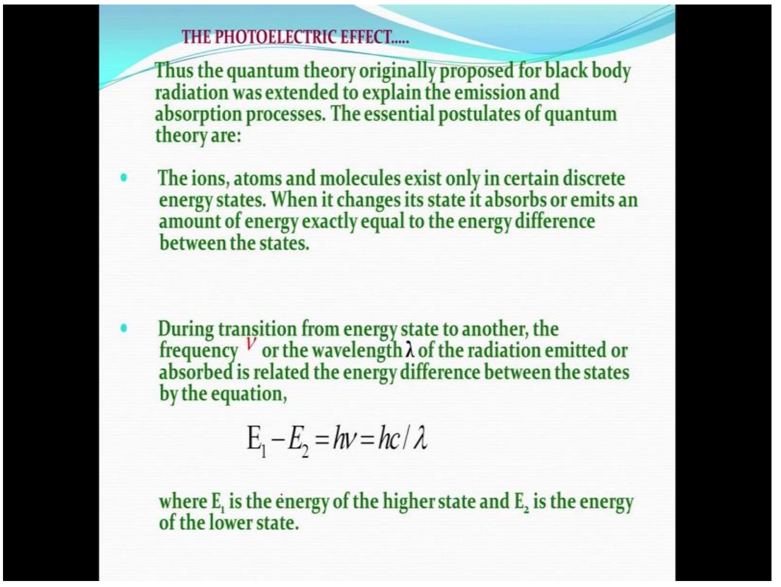

And basically what we have been discussing is part of black body radiation. Now what is this black body radiation? If you take any black material metal for example, you keep on heating it take iron for example, at room temperature it is dark and black you keep on heating it will be become red, and then it will start giving you radiation it will start giving you red, yellow as the temperature increases as the temperature of metal increases it will give you all kinds of radiation.

So, the essential the black body radiation has been extended to explain the emission and absorption processes. It is very simple, at room temperature it absorbs all at higher temperature it will start emitting the radiation because it gets hot you will see red color yellow color of the same metal. So, our eye is sensitive to lights.

So, the ions atoms and molecules in general exist only in certain discrete energies states, this is a basic quantum mechanical theory. So, when it changes it is state it absorbs or emits the radiation amount of energy exactly equal to the energy difference between the 2 levels between the states. If I take certain amount of material, I give energy. So, I give energy material gets heated up. So, the electrons and other things will get excited they will start vibrating and after sometime the electrons will go to the next higher energy level you supply more energy electrons will go to still higher level some more. So, at some stage they will escape from the electromagnetic field of the atoms and the molecules. So, this is what happens normally.

So, whenever there is a change in the excitation in energy state the energy the change is exactly equal to the energy difference between the states it is not continuous, it is quantumized. So, it is quantized therefore, during transition from one energy state to another the frequency or wavelength of the radiation emitted or absorbed is related to the energy difference between the states; the equation is very simple we have been discussing it all the time E 1 minus E 2 equal to h nu equal to hc by lambda, where E 1 is the energy of higher state and E 2 is the (Refer time: 19:05) energy of lower state. This E 1 and E 2 are arbitrary it can be E 2 or one also it does not make any difference what we are simply saying is it is one higher state one is lower state the energy difference is given by hc by lambda.

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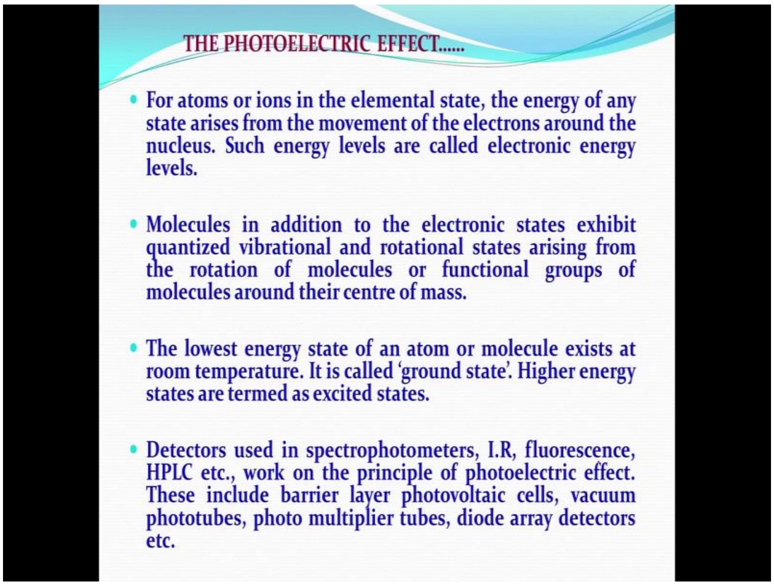

So, the photo in photoelectric effect we continue our discussion what happens; for atoms or ions in the elemental state that is hydrogen in the gaseous state, iron in the metallic state and chlorine in gaseous state something like that, the energy of the state arises from movements of the electrons around the nucleus. So, such energy levels are called as electronic energy levels. So, the electronic energy levels are always associated with the electron moving around the nucleus.

So, what happens to molecule then? In molecules the in addition to electronic state there is a possibility that the electrons are affected by other atoms in the same molecule, because molecule is a group of atoms. So, an electron belonging to particular atom may be associated in some way with the other elements of the same group for example, if I take COOH the electron and hydrogen may be affected by C O O atoms and the electrons nucleus etcetera. So, an electron in a molecule the electron is always associated with the other atoms also atomic cloud basically we are talking about atomic cloud, and the behavior of the atomic cloud in atoms and molecules are slightly different.

So, this we should understand. So, that is what we are saying. So, there could be some amount of vibrational and rotational states arising from the rotation of molecules or functional groups of the molecules themselves. So, if you imagine hydrogen atom it is spherical atom simple, but if you imagine like COOH group, there will be carbon oxygen, oxygen and then hydrogen. So, the molecule could be a linear molecule or a bent molecule like this. So, the electrons apart from going to next higher energy level they could also be vibrated in the vertical and the horizontal direction. So, the electrons can even they can occupy an electronic energy level the next higher electronic energy level, but each electronic energy level is associated with the number of vibrational energy levels. And to extend the logic further each vibrational electronic vibrational energy level is associated with a number of rotational energy levels.

So, the point is you can imagine a tall building with a number of floors stories: first floor second floor like that there are number of steps if you are standing in the ground floor, and kick a football you may hit the first floor or second floor third floor like that depending upon your energy, and the imagine that first floor, second floor are all representing electronic energy level. So, to reach the first floor there will be steps, but when the electron is a foot ball is hit on the first floor there is no guarantee that it will it will land on the first floor itself, it may land 1 or 2 step above the stair case or 1 or 2 case below the stair case like that. I can, now I can imagine that the steps associated with the first floor there are vibration energy level of the excited atoms. Same thing happens with if I take it to slightly lower dimension each vibrational energy levels again I can imagine as number of floors, and from one vibrational energy level if the electron goes to the next vibration energy level it could be a associated with number of smaller rotational energy levels.

So, that is what all this steps are associated with the functional groups of the molecules around the center of the mass. Because if it is only hydrogen I know that it can be a simple spherical molecule, but any other thing could be linear non-linear and 3 dimensional 2 dimensional, several kind of several possibilities of the electronic structure exist. So, the lowest energy state of atom or a molecule exist at room temperature, this is a fundamental simple assumption; why because at room temperature normally the energy is minimum we are not supplying any energy. So, whatever is the room temperature that amount of energy is available to all molecules. So, that is called as ground state. So, 99 percent of the atoms and molecules and groups functional group etcetera at room temperature we assume that they are in the ground state.

So, the higher energy state if I heat them I am supplying energy. So, the electrons and the molecules etcetera they have to go to next higher energy level. So, these are termed as excited states. So, we have 2 kind of energy levels one is ground sate another is excited states. So, the excited state when the reach the when the electrons reach the detectors are used in spectrophotometers infrared fluorescence HPLC etcetera, they all work on the photo photoelectric effect and the equipment used to determine the current photoelectric current means the effect means current is generated. So, you have to measure the current and to measure the current what we need is small electric equipment measuring the instrument that is known as barrier layer cell photovoltaic cell vacuum photo tube photomultiplier tube, diode array detectors etcetera all these things are required the determination of the electromagnetic radiation and their energy. So, we always said the electromagnetic radiation will always be can always be measured using the photo electric effect.

So, that give us a tool to determine the effect of electromagnetic radiation on matter in which it interacts. So, what I am we are essentially saying is take matter allow electromagnetic radiation to interact, measure the electromagnetic radiation take out the matter see what is the original condition. What is the difference? The difference is the amount of current that is generated whenever we are making measurement, and that is done by the photomultiplier tube diode array tube vacuum tubes photo tubes barrier layer photovoltaic cell etcetera.

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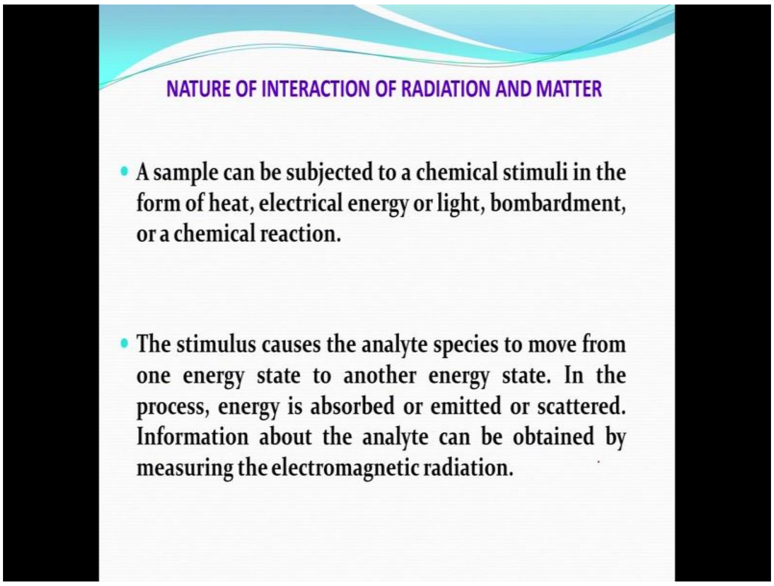

So, continuing our discussion nature of interaction of radiation in matter what do we call the heat or supply of energy to molecule it is called as chemicals stimuli; it may be in the form of a heat, it may in the form of electrical energy or it may be just bombardment or it may be a simple chemical reaction also.

So, the stimulus core what happens what happens when the stimulus is given? The analyzed species move from the one energy level to another energy level state, if you increase the temperature they go to the higher energy state if you decrease the temperature they go to the lower energy state, in the process energy is either absorbed or emitted, scattered also. So, information about the analyte can be obtained by measuring the electromagnetic radiation.

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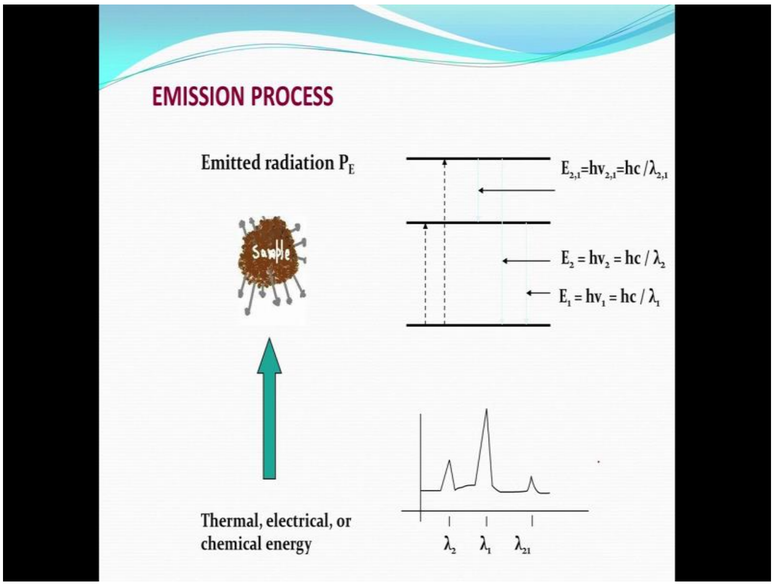

So, this is what we are planning to do in spectrometry, and at this point I want to show you what is emission process and what is absorption process. Imagine here I have the radiation thermal electrical or chemical energy, I have the sample here the process is emission. So, when the electron goes form ground state on look at the right side the electron I am transition I am showing with a dotted line, so the when it comes back to the ground state it emits the radiation that I has absorbed.

So, whenever I am supplying a stimuli, it goes to the next higher energy state, but when it comes back to the ground state the amount of the energy absorbed is lost that is released that is what we said it can absorb emit or scatter. So, the in emission it gives you certain amount of electromagnetic radiation equivalent to the energy difference between the 2 a states. So, this is emission.

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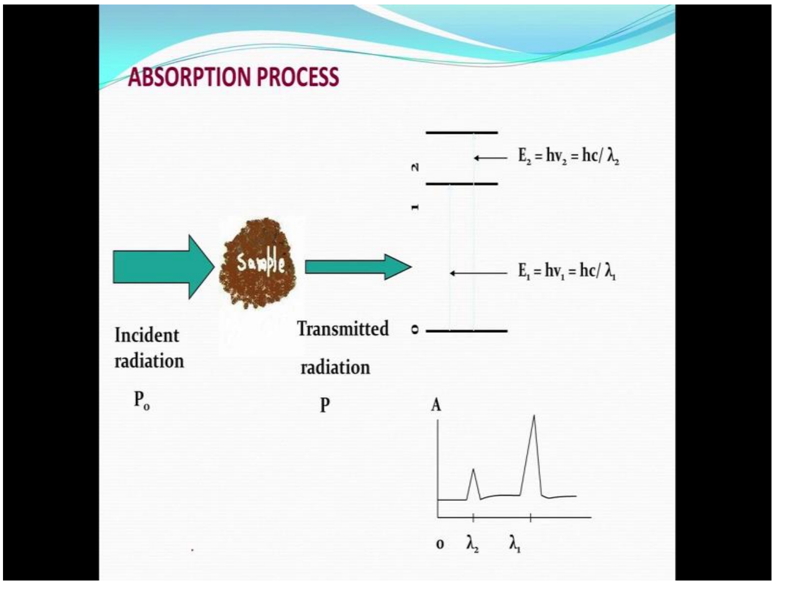

So, what happens in the absorption? Here the samples sample is here incident radiation is at the back transmitted radiation is on the right. So, the energy difference is gain a given out as heat it is not the radiation. So, the heat is the effect of absorption. So, the amount of energy corresponding to the electromagnetic radiation before is higher most sample interaction will be lower.

So, this energy difference is known as absorption, the whatever amount of energy we supplies is absorbed. So, when it absorbs the molecule may go to next higher energy level.

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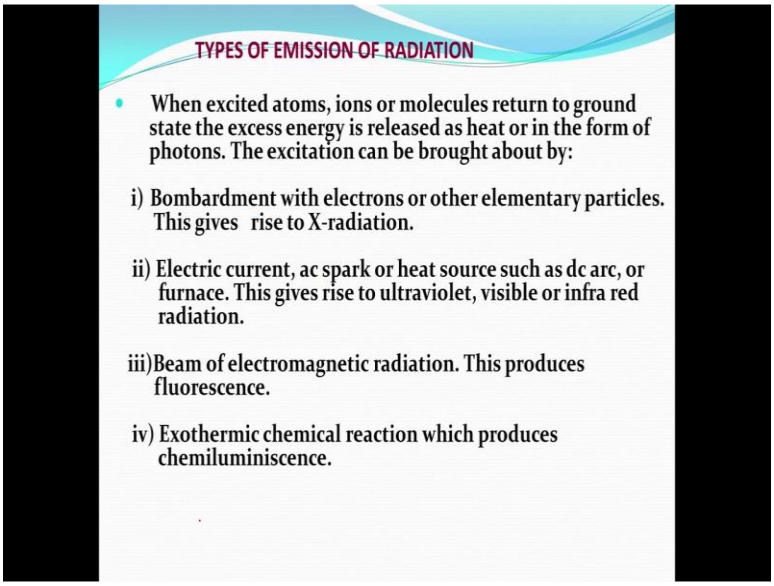

So, there are different types of emission radiations, when excited atoms or ions or molecules return to the ground excess energy is released is released as heat this I already changed told you just now and that is in the form of photons, the excitation we can bring it by bombardment of the elementary particles that give raise to x-ray, electric current AC spark etcetera beam of electromagnetic radiation also we can use for excitation, this produces fluorescence all this things we will be studying in our course and exothermic chemical reaction also produces some amount of light that is known as chemoflorascent.

So, we are going to study absorption, emission and chemoflorascent and fluorescent all these are part of this spectroscopy molecular spectroscopy. So, we will stop here for 2 minutes, 5 minutes and then we will come back we will have another small session with respect to other properties of this spectra.

Thank you.