Modern Instrumental Methods of Analysis

Prof. J. R. Mudakavi
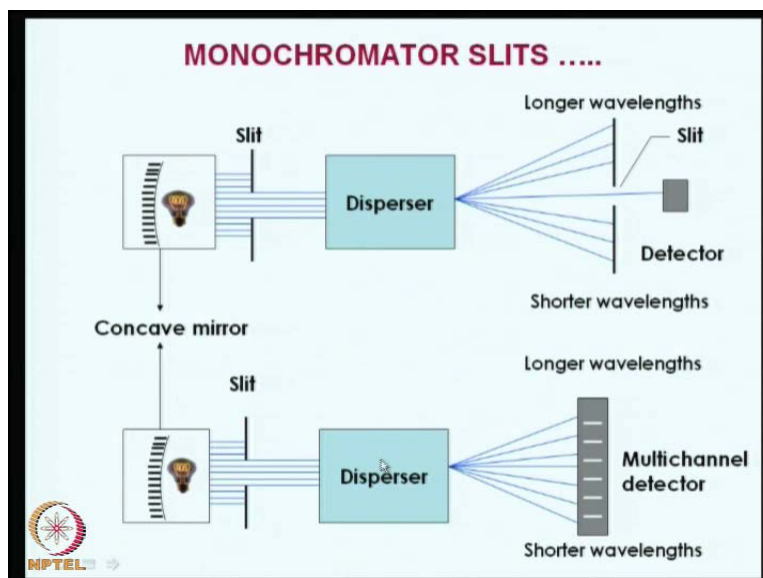
Department of Chemical Engineering

Indian Institute of Science, Bangalore

Lecture No. # 04

Interaction of Matter with Radiation

Let us now take a look at another component of an instrument and its interaction with the electromagnetic radiation.
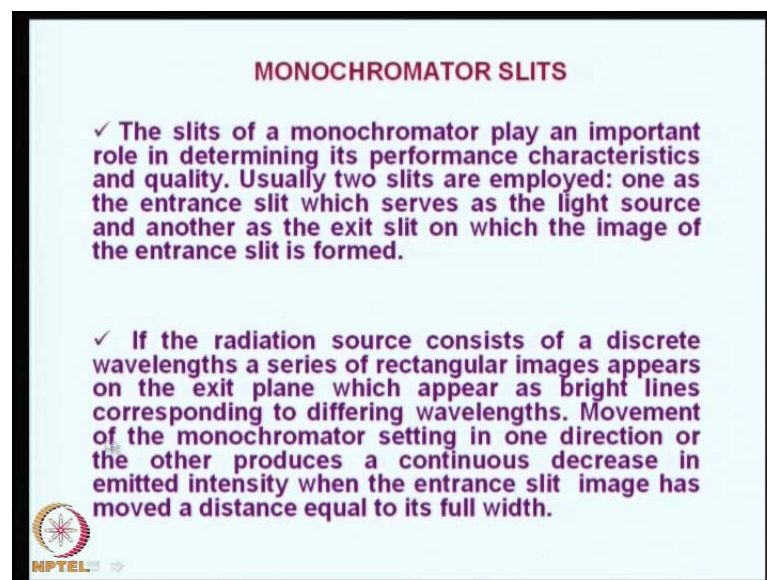
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To tell you very frankly, we are talking about slits. And, there is no mechanical interaction except that these slits allow the radiation from one end up to the other end; that is, it will allow the radiation to pass through with a fixed aperture. Usually, in all spectrophotometers, etcetera, you need two slits: one is the entrance slit and another is the exit slit.

Now, if you take a look at this (Refer Slide Time: 01:02) figure, there is a light source and there is a concave mirror here at the back side; and then, I have a slit in front of it and then it goes to a disperser like either a prism or a grating. And then, after the dispersion, the radiations come out and they are collected onto another screen in which a

slit is made. So, basically, this slit gives a mirror image. The image of the entrance slit is supposed to fall on the image of the exit slit. So, you can see that the function of the slit is to convert the radiations into a parallel beam of light.

Now, you can see here (Refer Slide Time: 01:59) also, we can place a detector here at the end of the exit slit and we can collect the radiation coming through the second slit. So, here in the bottom one, we can have a multichannel detector, which can collect all the wavelengths that are coming out from the disperser. For example, if you have a prism, you will remember that seven colors had come out of the white light and same thing is true with diffraction units. So, if I can place a multichannel detector here, at the end of the slit, I can collect all the information that is related to the incident radiation.
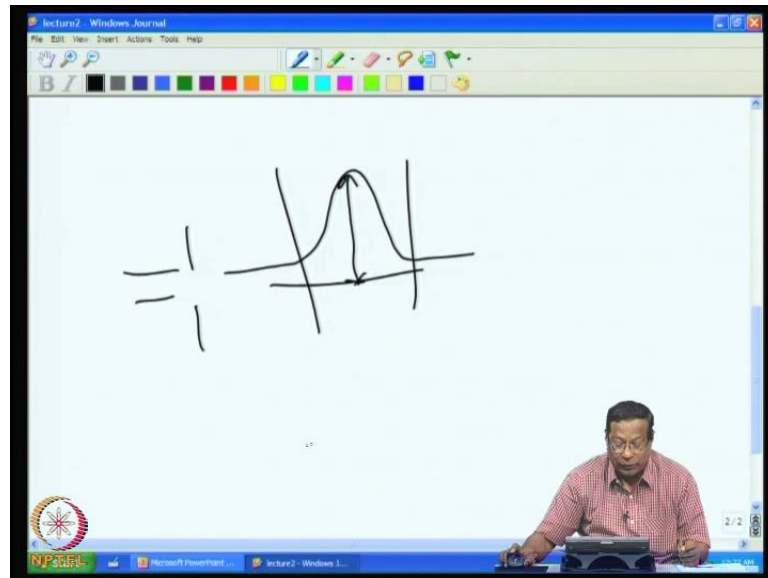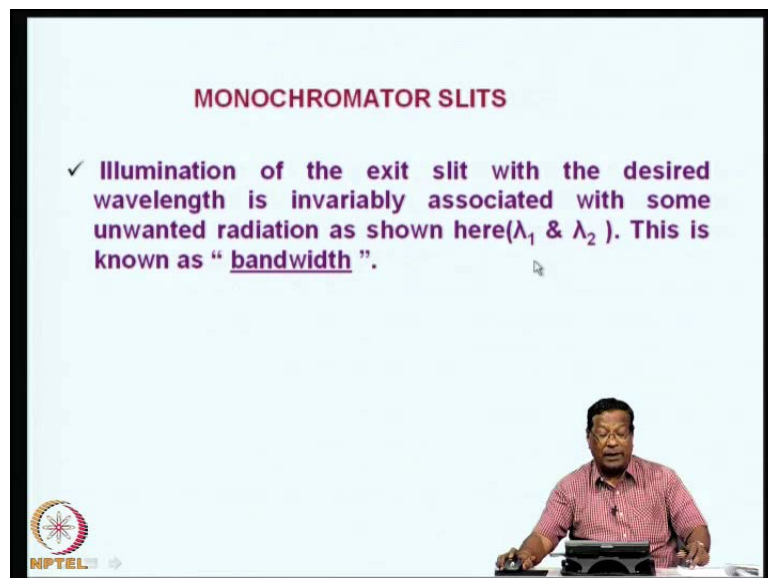
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The slits of a monochromator basically play a very important role in determining its performance characteristics and quality. Usually, two slits are employed: one is the entrance slit, which serves as the light source and another as the exit slit on which the image is formed. If the radiation source consists of a discrete wavelength, a series of rectangular images appears on the exit plane, which appear as bright lines corresponding to different wavelengths. Movement of the Monochromator setting in one direction or the other produces a continuous increase or decrease in the emitted intensity when the entrance slit image has moved a distance equal to it is full width.

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What we mean by that is having a slit here and then the radiation coming out will be like this. And, here you would see that there is a wavelength corresponding to a maximum peak. And, this is what we will be referring subsequently.

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Illumination of the exit slit with the desired wavelength is invariably associated with some unwanted radiation as shown here lambda 1 and lambda 2, which I did not show it there. This is known as bandwidth.

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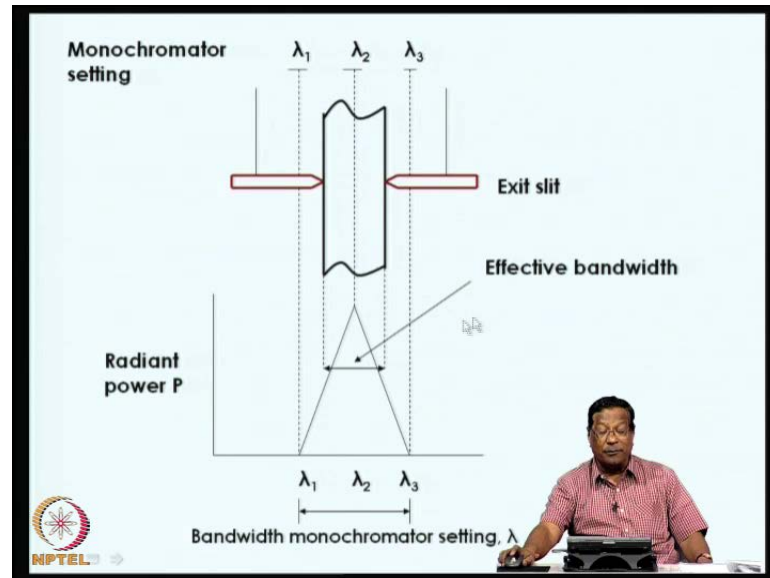
For example, here you can see lambda 1, lambda 2, lambda 3. Here this is the entrance slit and this is the exit slit; that means one wavelength corresponding to lambda 2 is maximum here. But, you cannot really avoid the contribution coming from lambda 1 and lambda 3, which is also collected from any given slit. This is a very natural phenomenon of all slits. And, it is important that the slit should be as small as possible to collect the desired wavelength. Now, you can see here that what is required is lambda 2, but some amount of lambda 1 is coming, lambda 3 is coming and this half width. This is known as effective bandwidth. And, this area – the wavelengths corresponding to all these three are known as bandwidth. And, this is half bandwidth, effective bandwidth.

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The effective bandwidth is also called as spectral band pass or a spectral slit width. It is half of the bandwidth when the two slit widths are identical. It is very important. Two slit widths should be identical; otherwise, you will not have a good spectrum. When the effective bandwidth is decreased to one half the wavelengths of the three beams, complete resolution can be obtained; otherwise, there will be always bunching of the radiations that come; and, it would not give you the spectral purity. So, that is another aspect.

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Now, let us look at what is known as a photoelectric effect. We are continuing our discussion based on the intervention of the electromagnetic radiation with matter. Now, you would see that the photoelectric effect was discovered as far back as 1887 by Heinrich Hertz, who reported that a spark jumped more readily between two charged spheres when their surfaces were charged illuminated with light.

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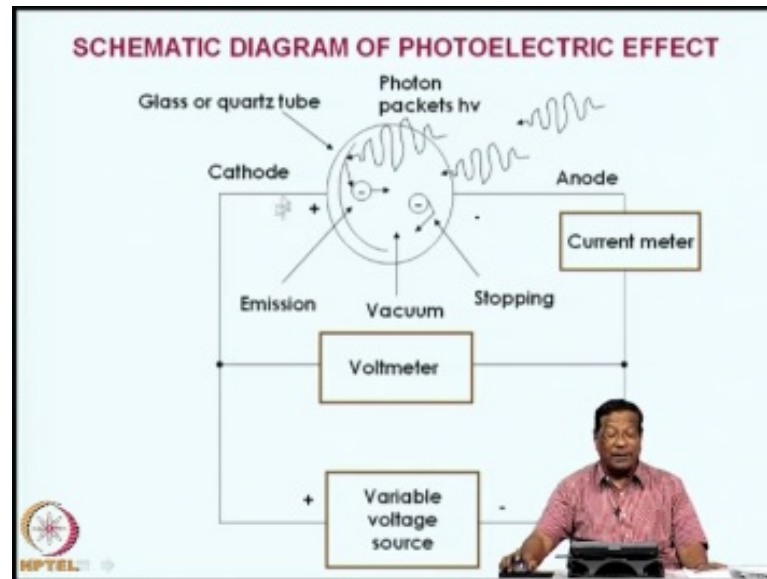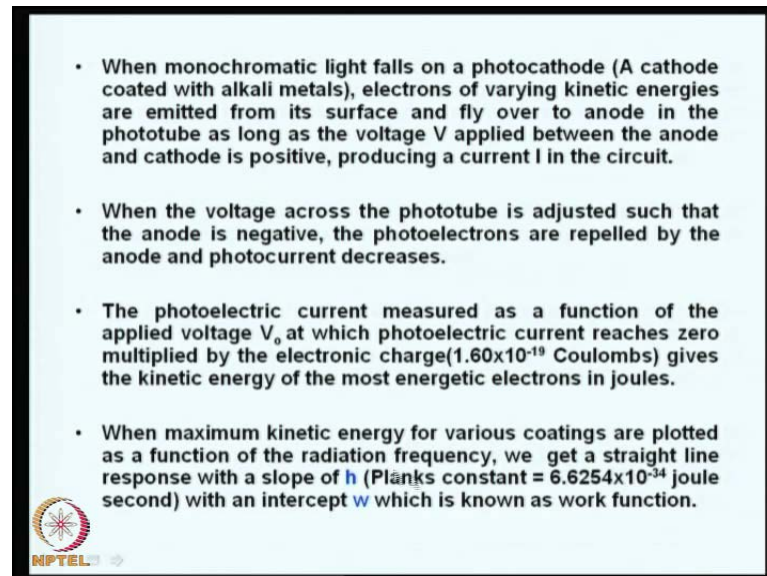
You can see here this is a way of vacuum photo tube. And, here there are photons, that is, light beams falling on a cathode and there is anode. And, this is connected to a voltmeter and a variable voltage source. And, this is a vacuum basically. And then, emission now occurs here. This is basically… Outer one is a basic glass or quartz tube. Now, in that we have fixed a cathode and there is an anode and the electrons are supposed to flow from cathode to anode. And then, we have a current meter to measure how much of the current is being generated.

Now, this is basically a very simple thing. And, if the cathode is coated with a specific substance like alkali metals or something like that, the electron and you shine some light on this (Refer Slide Time: 08:09) cathode, the current will increase. That is the basic phenomenon; that means electrons are jumping faster to the anode. This phenomenon is known as photoelectric effect.

Photoelectric effect (Refer Slide Time: 08:28) is very well known since 1887. But, only in 1905, Einstein offered a simple and elegant explanation for the photoelectric effect. But, experimental confirmation again came only in 1916 with Millikan's systematic studies. We will not go into details of these studies, but we will see that the photoelectric effect is a very important phenomenon and several detectors work on this principle.

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- 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.

- 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.
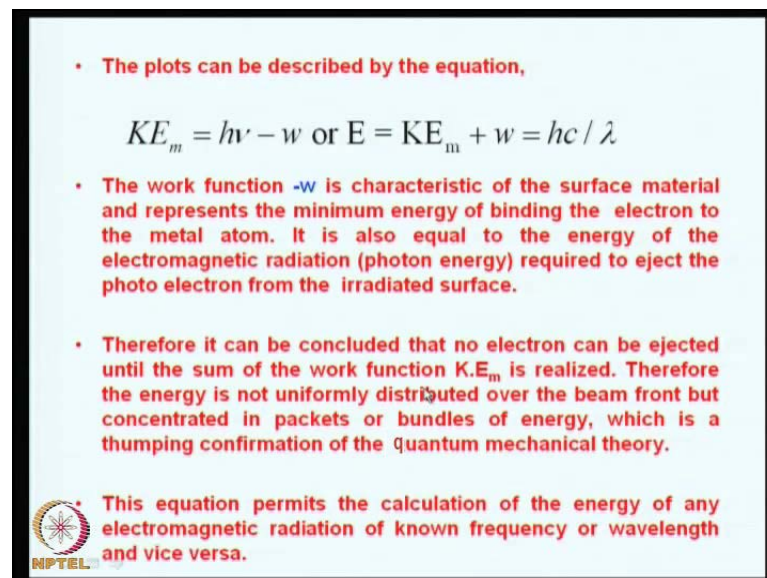
What is photoelectric effect basically? When monochromatic light falls on a photocathode, electrons of varying kinetic energies are emitted from its surface and fly over to the anode in the phototube as long as the voltage V is applied between the anode and cathode is positive. It produces a current I in the circuit. Now, when the voltage across the phototube is adjusted in such a way that the anode is negative and cathode becomes positive, then what happens is the electrons are repelled by the anode and photocurrent decreases. At some stage if you keep on changing the voltage, the electrons will stop moving from anode to cathode.

The photoelectric effect current therefore is measured as a function of the applied voltage, V 0 at which photoelectric current reaches zero multiplied by an... If you multiply this voltage with the electronic charge, that is, 1.60 into 10 raised to minus 19 coulombs, etcetera, this gives the kinetic energy of the most energetic electrons in joules. So, with this principle when you measure the stopped voltage multiplied by (Refer Slide

Time: 10:43) this, you can calculate what is the kinetic energy of the electrons generated in the phototube.

When maximum kinetic energy for various coatings are plotted as a function of the radiation frequency... Basically, you are introducing the electromagnetic radiation making them fall on the cathode. So, when you do this and plot as a function of radiation frequency, that means you are taking radiation from different frequency allowing them to fall on the cathode and then note down its kinetic energy or voltage, then you plot those things, we get a straight line response with a slope h and an intercept.

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- The plots can be described by the equation,

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

- 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.

- 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.

The plots can be described by the equation, K into E m is equal to h nu minus w; where, w is called as work function. And, you can also write the same equation as E is equal to K into E m plus w and that should be equal to h c by lambda; that is, Planck's constant, characteristic wavelength of the velocity of the light and wavelength of the incoming radiation. The work function, minus w is a characteristic of the surface material on which the cathode is coated. This represents the minimum energy of binding the electron to the metal atom. It is also equal to the energy of the electromagnetic radiation, that is, photon energy required to eject a photo electron from the irradiated surface.

So, what we can conclude out of this? It can be concluded that no electron can be ejected until the sum of the work function, that is, K into 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, basically, what we are saying is energies quantized. So, until you reach that energy, you cannot eject an electron. So, you have to keep on giving the energy until that voltage is reached. Only at that stage, electrons will start coming from the cathode and flow to the anode. So, this is essentially quantum mechanical theory. Therefore, the thumping confirmation of the quantum mechanical theory comes from this photoelectronic effect.

And, this equation basically permits this equation (Refer Slide Time: 13:56) K into E m plus w is equal to hc by lambda. This equation permits the calculation of the energy of any electromagneti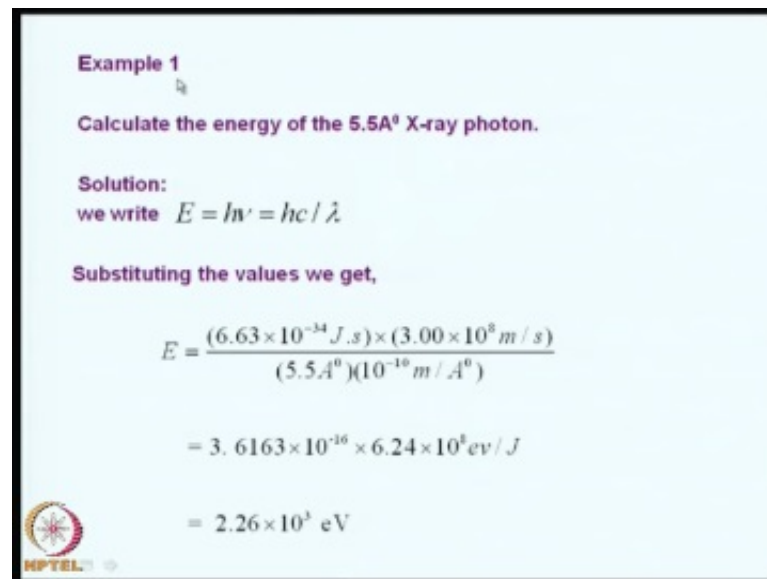c radiation of known frequency or wavelength and vice versa. Either you should know the energy, wavelength or frequency; then, you can calculate the energy of the electromagnetic radiation.

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Example 1

Calculate the energy of the 5.5A⁰ X-ray photon.

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

Substituting the values we get,
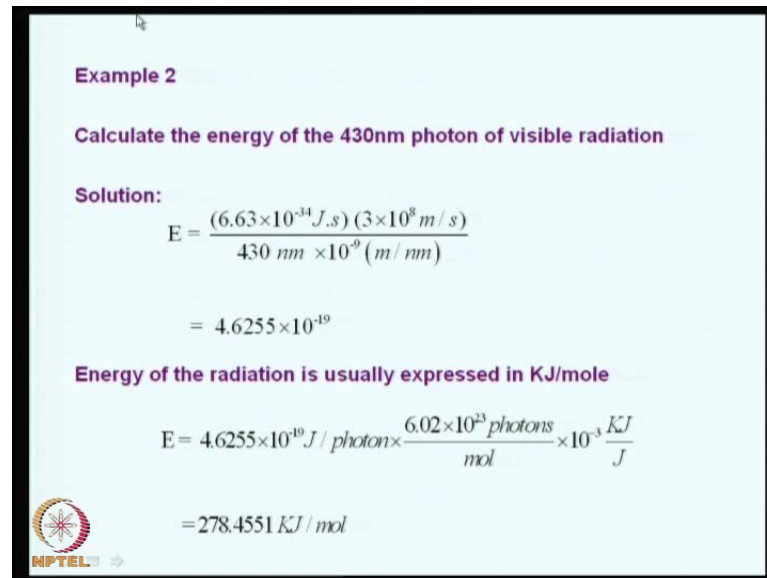
$$E = \frac{(6.63 \times 10^{-34} J.s) \times (3.00 \times 10^{8} m/s)}{(5.5 A^{0})(10^{-10} m/A^{0})}$$

$$= 3.6163 \times 10^{-16} \times 6.24 \times 10^{8} ev/J$$

$$= 2.26 \times 10^{3} \ eV$$

For example, take a look at this. We want to calculate the energy of 5.5 angstrom units of an X-ray photon. Now, what do we do? We basically write an equation like E is equal to h nu, which is equal to h c by lambda. Now, we know h, we know c and lambda we know; we just have to calculate energy. Now, substituting these values, we will get E is equal to 6.63 into 10 raised to minus 34 joules second, that is, the unit multiplied by 3 into 10 raised to 10 meters per second, that is, velocity of light – divided by this

wavelength. You will see we have converted that into meters. So, what we get is 2.2 6 into 10 raised to 3 electron volts.

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Example 2

Calculate the energy of the 430nm photon of visible radiation

Solution:

$$E = \frac{(6.63 \times 10^{-34} J.s)\,(3 \times 10^8\, m/s)}{430\, nm\, \times 10^{-9}\,(m/nm)}$$

$$= 4.6255 \times 10^{-19}$$

Energy of the radiation is usually expressed in KJ/mole

$$E = 4.6255 \times 10^{-19} J/photon \times \frac{6.02 \times 10^{23}\, photons}{mol} \times 10^{-3} \frac{KJ}{J}$$

$$= 278.4551\, KJ/mol$$

The second example I have taken to explain is to calculate the energy of 430 nanometer photon of visible radiation. First one was X-ray; second one is visible radiation. Now, we use the same equation; put the values of E h and c and 430 nanometers; convert it into meters; and then, what you get is this number multiplied by photons and you will get so many kilo joules per mole. So, for visible region, we express it as… The energy of the electromagnetic radiation – we express it as kilo joules per mole; whereas, for (Refer Slide Time: 16:04) X-ray radiation, we express it in electron volts. So, this aspect you should remember.

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THE PHOTOELECTRIC EFFECT.....

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.

2. During transition from energy state to another, the frequency ν or the wavelength λ of the radiation emitted or absorbed is related the energy difference between the states by the equation
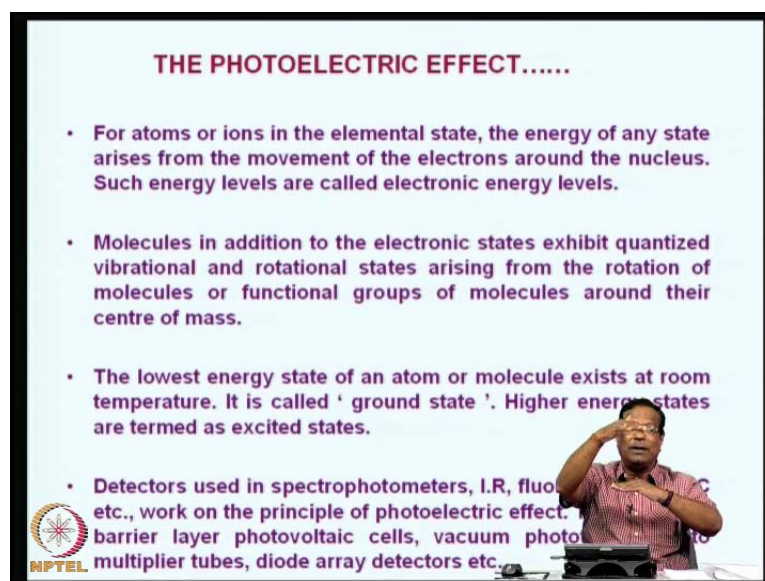
$$E_1 - E_2 = h\nu = hc/\lambda$$

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

What is this photoelectric effect? The quantum theory originally proposed for the black body radiation was extended to explain the emission and absorption of processes. The essential postulates of quantum theory – we can say that one is ions, atoms and molecules exist only in certain energy levels; that is, when it changes its state, it absorbs or emits an amount of energy exactly equal to the energy difference between the two states. During transition what happens? From one energy state to another, the frequency or the wavelength of the radiation emitted or absorbed, which is related to the energy difference between the states by the equation E 1 minus E 2 is equal to h nu; that is, h c by lambda; where, E 1 is the energy of the higher state and E 2 is energy of the lower state.

Now, this is very simple to understand. There are two energy states: one is E 1; another is E 2. The transition has to take place, but it will take place only when you supply an exactly known quantity of energy; then only, the transition takes place. Suppose you supply less, it would not happen; that is, for us to remember, the work function of every material is known and tabulated. Therefore, we can make detectors of different materials.

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Continuing our discussion on this, 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 as electronic energy levels; that means all atoms and ions in the elemental state either it may be in the gaseous state or metal, etcetera, the energy of the state arises from the movement of the electrons around the nucleus. Electrons keep on going round and round. The energy is always associated with the movement of the electrons and they are all placed in different orbits around the nucleus. Such energy levels are called as electronic energy levels.
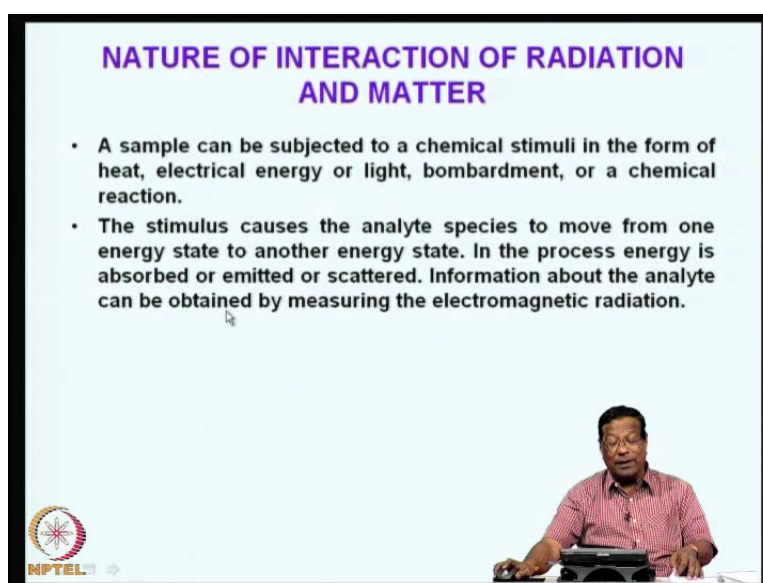
Now, molecules in addition to the electronic states exhibit quantized vibrational and rotational states arising from the rotation of the molecules or functional groups of molecules around their centre of mass. Now, you can imagine that molecules are a group of atoms forming different substances and each substance will have certain amount of spectra and spectral characteristics. And, apart from the electronic states, we have vibrational and rotational states associated with each electronic level. For example, if you take only atoms, ions, what happens is there is one electronic energy level, another electronic energy level (Refer Slide Time: 19:50) here, another one will be at higher and higher energy levels; whereas, with each electronic level, we have vibrational energy levels like this. This is the electronic level – middle my finger you can imagine; the bottom one would be vibrational energy level; the top one will be another vibrational

level; like that there will be a number of vibrational energy levels associated with each electronic vibrational energy.

Same analogy can be extended further if you have a vibrational energy state. Again there would be number of rotational energy levels. So, the spectrum of a molecule always contains electronic energy levels. With each electronic level, there are associated vibrational energy levels. And, with each vibrational energy level, there would be number of still closely spaced rotational energy levels; they are also quantized. So, the lowest energy state of an atom or a molecule exists at room temperature obviously; otherwise, it will not be stable. This is called as ground state. Higher energy states are termed as excited states. So, when an electron jumps from ground state to next higher energy level, those states are known as excited energy levels. And, when it falls, emits radiation, it falls to the lower energy level, still lower energy level, still lower energy level, until it reaches a ground state, which is the lowest energy state.

Detectors used in (Refer Slide Time: 21:42) spectrophotometers, infrared spectrometry, fluorescence, HPLC – they all work on the principle of photoelectric effect. These include barrier layer photovoltaic cells; and then, some of them are vacuum phototubes, photo multiplier tubes, diode array detectors, etcetera. These things we will be studying when we are studying the instrumentation of different analytical technique.

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NATURE OF INTERACTION OF RADIATION AND 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.

Now, let us look at the nature of interaction of radiation and matter, that is, a sample let us say. A sample can be subjected to chemical stimuli in the form of heat or electrical energy or light or it can be bombarded or a it can be subjected to a chemical reaction. The stimulus should cause the analytic species to move from one energy state to another energy state. In this process, energy is either absorbed or emitted or scattered. The absorption and emission of the energy takes place in quantas, but scattered radiation does not takes place like that. Information about the analyte can be obtained by measuring the electromagnetic radiation, that is, either falling on the sample… Suppose I have a sample. Electronic radiation is coming like this; part of it is absorbed emitted or scattered; and then, part of the radiation would be going through the sample and collected on the other side. So, this information about the intensity or energy of the analyte can be obtained by measuring the electromagnetic radiation.

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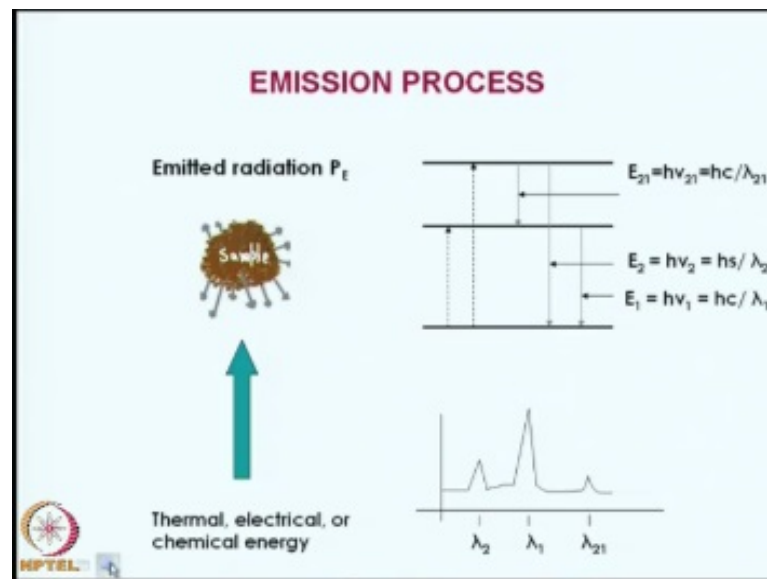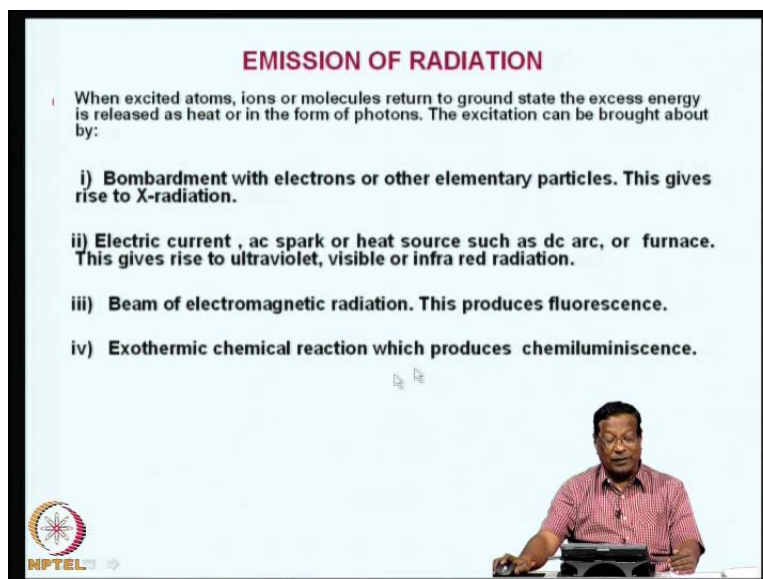
For example, you can see here. This is basically an emission process. Here I have the sample; I am giving stimuli here. It may be thermal electrical or chemical energy. And, here the energy levels are there: E 1 is equal to h nu 1 or h c by lambda 1; E 2 should be h nu 2 or h c by lambda 2; E 2 1 should be h nu 2 1 or h c by lambda 2 1. So, these are the different wavelengths that are coming out of the system. So, this is one type of stimuli.

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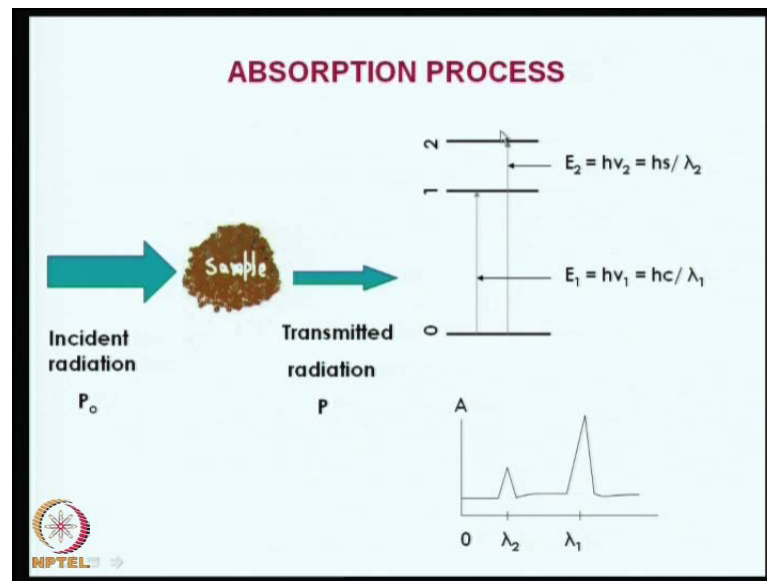
Now, you can have absorption. Then, what happens? Incident radiation is there falling on the sample; and then, part of it is transmitted, part of it is absorbed; and, you would see the spectrum here. And, this is the basic ground state; this is the excited state 1; this is the excited state 2. The electron can get excited from here to first excited state; and, that is, h c by lambda 1; and, this is… From here, it can go to… From the ground state, it can even go up to second excited state or third excited state or fourth excited state, like that which are placed above this. Mind you, all these notations are only theoretical; that means pictorial representation of what is happening. So, this is absorption.

Now, emission of radiation – when emission occurs, excited ions or ions or molecules, excited atoms – when they return to the ground state, excess energy will also emitted as heat or in the form of photons. It may be either heat; the material may get heated or some light may come out of the system. The excitation can be brought about by these techniques. You can probably bombard with the electrons or other elementary particles like helium particles, neutrons, etcetera. This gives rise X-rays, X-radiation. Now, you can pass electric current or ac spark or heat source, such as dc arc or furnace, put it in the furnace. This gives rise to ultraviolet, visible or infrared radiation. You can also excite a material by passing a beam of electromagnetic radiation. This produces fluorescence. It is very simple.

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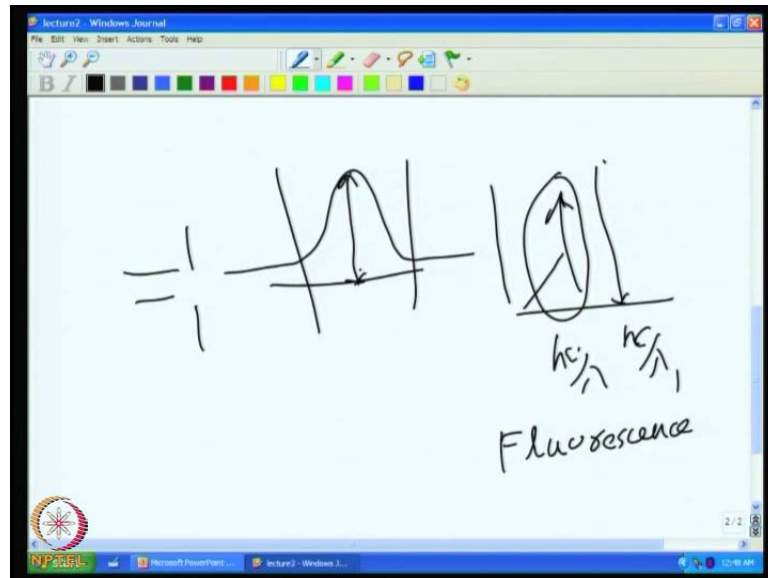
Now, the fluorescence something like this – you have a radiation falling on this and this goes to the next excited state; and then, part of… When it comes back to the ground state, it does not emit the radiation corresponding to h c by lambda, but it corresponds to h c by lambda 1; that means the incident radiation is not emitted, but a radiation of some other wavelength that is being emitted. So, this is known as fluorescence. So, what is the difference between absorption and fluorescence? Absorption is part of the energy is absorbed; and, when it comes back, the energy is lost either as heat or simply the intensity of the radiation is lost.

Now, in fluorescence, when you are exciting the molecule, you take a particular radiation falling on the sample; and then, the electrons will go to the next higher energy state. Loose part of their energy comes back to the ground state. And, during that process, the excess energy is not lost as heat, but as a radiation of another wavelength, that is, lambda 1, what you saw here (Refer Slide Time: 28:50). So, this is known as fluorescence. Another phenomenon – this produces fluorescence.
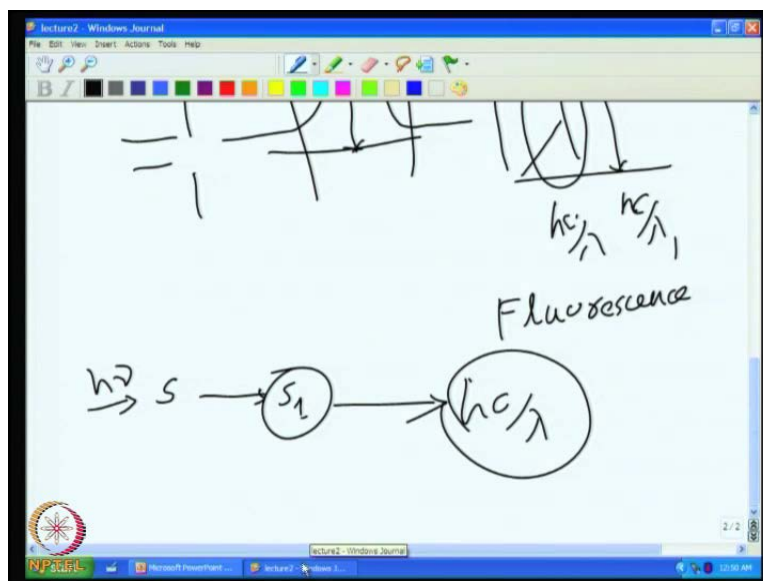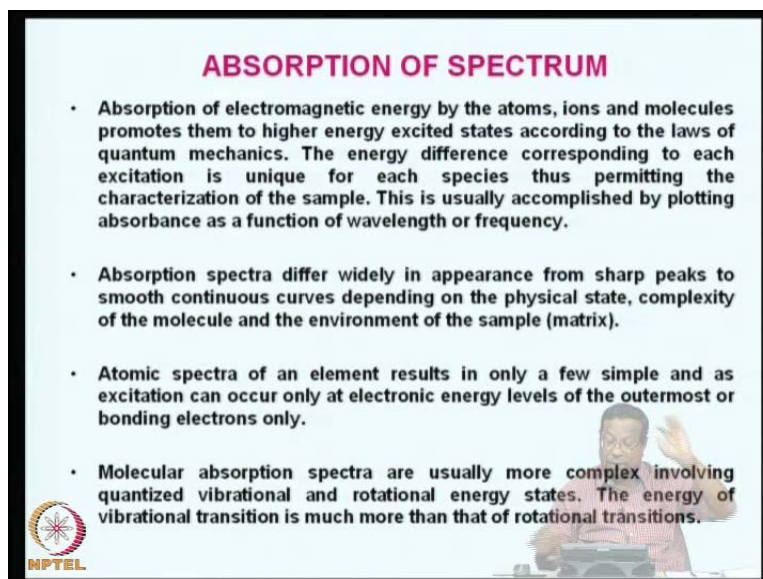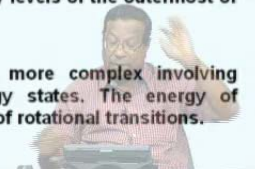
Sometimes what we do is we take exothermic reaction. And, in exothermic reaction, we make a substance to undergo a reaction by supplying energy. And, the substance goes to another state S 1. From here it undergoes a reaction and then gives out the radiation corresponding to a specific energy. And, because of the reaction, the radiation emission occurs. And, this is important in some of the analytical techniques also. And, basically, this is known as chemiluminiscence. So, what happens, when excited items – ions or molecules are returning to the ground state, if the energy is very high, this gives rise to X-radiation, X-rays. And, if it is less, the ultraviolet, visible, infrared radiation may come out. And then, if the beam of radiation comes out of different wavelength, then it is known as fluorescence. And, when you subject a substance to a chemical reaction, it may produce electromagnetic radiation corresponding to different wavelengths. And, that is chemiluminiscence. This is also a very important factor especially in determination of gases like NOx, etcetera in the environment. We may be studying this in our course if the time permits.

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Now, you can see that absorption spectrum basically occurs for the case of atoms, ions, molecules, etcetera when the electromagnetic radiation promotes the outer electrons to higher energy excited states according to the laws of quantum mechanics. The energy difference corresponding to each excitation is unique for each species. This permits the characterization of the sample. For example, the energy difference may correspond to a functional group, such as carbon CO or OH groups or COOH or ester, something like that. So, if there is any specific change corresponding to a functional group existing in a molecule, the absorption can be used for the characterization of the sample straight away. This is usually accomplished by plotting absorbance as a function of wavelength or frequency.

The absorption spectra of different compounds differ widely in appearance from sharp peaks to smooth continuous curves depending upon its physical state, complexity of the molecule and the environment of the sample, that is, what we call matrix. Now, you can see that a substance may be in the form of gaseous substance or it may be a liquid or it may be a solid. Now, the environment in which the sample is there is also very important, because the environment may influence the spectrum and the spectral behaviour subsequently. So, what happens, the atomic spectra of an element results in only a few simple lines and excitations can occur only at electronic energy levels of the outermost or bonding electrons only. So, for atoms, for elements, only the electronic spectra are possible.

Now, what happens to a molecule? There are electrons in the molecules also. So, electronic spectra changes must take place whenever we let the electromagnetic radiation pass through the sample. But, they are usually more complex especially because of the presence functional groups. And, what happens to these functional groups? They have vibrational and rotational energy states, which are quantized. So, any electronic excitation would lead to changes in the vibrational as well as rotational energy levels. So, the energy of vibrational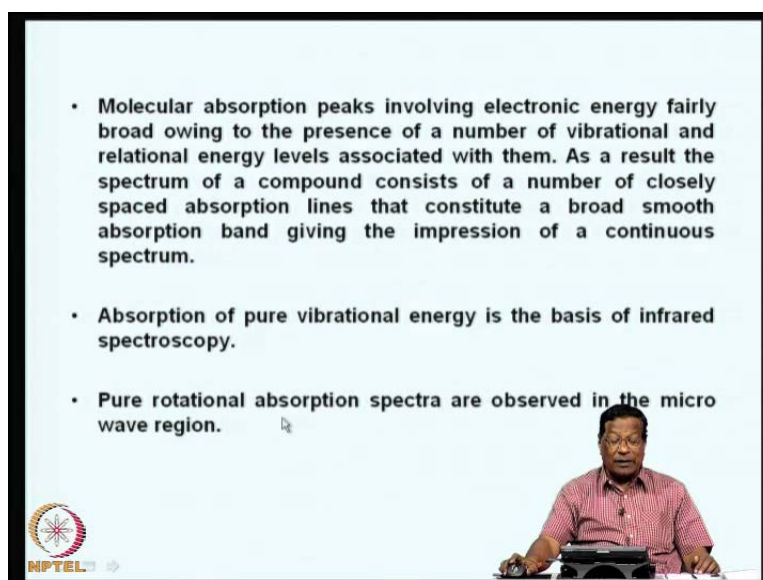 transition is much more than that of rotational transition. Now, you can see that the energy corresponding to electronic transition is higher than the vibrational; and, vibrational transitional energy is much higher than the rotational transitions.
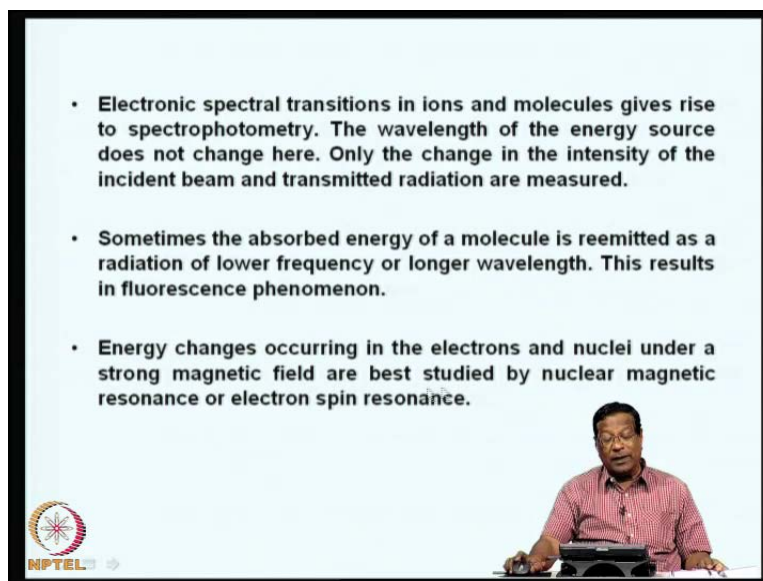
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Molecular absorption peaks involving electronic energy are fairly broad owing to the presence of these vibrational and rotational energy levels associated with them. As a result, the spectrum of a compound consists of a number of closely spaced absorption lines that constitute a broad and smooth curve giving the impression of a continuous spectrum. But, absorption of pure vibrational energy is the basis of infrared spectroscopy. And, pure rotational absorption spectra are observed in the microwave region.

Now, electronic spectral transitions in ions and molecules gives rise to spectrophotometry; that means in spectrophotometry, what we would be studying are the electronic transitions. So, the wavelength of the energy source does not change here; that means we pass electromagnetic radiation of a known wavelength and it passes through a substance and then it goes out of the substance. The substance absorbs part of the energy and the difference between the intensity of the incident light as well as the transmitted light is measured as a function of the concentration of the substance. This is known as spectrophotometry. Now, the spectrophotometry can be in UV range region as well as in visible region. So, there are spectrophotometers, which are dedicated visible spectrophotometers or combining both, that is, ultraviolet as well as the visible range.

Sometimes the absorbed energy of a molecule is reemitted as a radiation of lower frequency or longer wavelength. I have already explained to you this. And, this results in fluorescence phenomenon. Sometimes what happens is the energy changes occurring in the electrons and nuclei under a strong magnetic are best studied by nuclear resonance or electron spin resonance. Even the atomic excitation, that is, electronic excitations when they are conducted under a strong magnetic field, again they split in the magnetic field that is known as Zeeman effect; that we will be studying later subsequently when we are studying the atomic absorption spectrophotometry.

At this point, it is required for us to take a look at what we have learned so far. Now, I want to summarize part of the learning what you have undergone since last three lectures. Basically, we have started with the definition of analytical science. Now, there is a minute small beautiful difference between analytical science and analytical chemistry. Basically, analytical science is a dynamic changing field called upon to solve several kinds of problems mentioned above with the technology that constantly provides new measurement tools. The challenges extend from the identification and measurements of parts per billion levels and sometimes parts per million levels, sometimes in milligrams levels, etcetera in various matrices.

The example I have given you include the automobile exhaust and the APXS analysis on the moon. And then, another example what I have given you is about the determination of fluoride by the SPADNS method. All these examples represent various faucets of different kinds of analytical challenges faced in the modern times. Another example which I have given you very subsequently is about the dimethlyglyoxime analysis for the nickel and palladium. Till 1970, this method was employed for the determination of nickel when it was replaced by flame atomic absorption. And, the challenges what they have been handled since that time are mostly with the use of analytical instruments and that too modern instrumental methods of analysis, etcetera.

So, what we have achieved basically is to understand some of the basic steps in obtaining an analytical perspective, that is, approximately equivalent to analytical approach. What are those things? One is identification and defining the problem. This has to be done by the analyst. And, design the experimental procedure including sampling, pretreatment and chemical analysis. And, third aspect is carry out the experiments and gather the data. Then, this is followed by the analysis of the experimental data and presenting a solution to the problem. So, we have considered the different challenging situations. Some of them include resolving the contradictory evidence of a sportsman, taking steroids. And, another is evaluating the endosulfan exposure for humans, children and pregnant ladies; and then, developing rapid and relative detectors for chemical warfare or online analysis of the environment; and then, real time modeling and monitoring of the oil spill near a port and developing miniaturized sensors for real time analysis.

Now, what are the analysts strong points? They include accuracy, precision, sensitivity and detection limit. And, the requirement is all the amount of the sample that is available

and collection, storage, transport and pretreatment of the sample, has to be finalized by the analyst. Third is number of samples to be analyzed. This is another aspect that is to be decided by the analyst. Then, follows validation of the method, report presentation, cost considerations based on the above, etcetera. So, we have looked at some of the definitions subsequently, which you should feel comfortable, because we are going to choose and use the units quite often.

Some of the words specific to the analytical science includes sample as a validation followed by interference, methods or protocol, atomic mass, atomic weight, mole, weight percent, volume percent, ppm, ppb – parts per billion and then parts per trillion, molarity, normality. All these things you would have studied in your high school and in your college level. And, those things we have seen. Subsequently, we have seen the basic classification of an analytical science, that is, classical methods and instrumental methods. And, in the instrumental methods, we have seen number of methods that are used based upon the chemical principles as well as the equipments that we use quite often across the board.

In the second lecture, we have seen that most of the modern instrumental methods of analysis relate to the changes taking place in the atomic levels. Therefore, we have spent some time in studying the atomic structure. There we have seen Dalton's theory. And then, we know what are the fundamental particles; that are electrons, protons, neutrons, positrons, neutrinos, antineutrinos, mesons, deuterons, alpha particles, etcetera. And then, we have studied what is the modern atomic theory based on Dalton's hypothesis. And, we have studied the nuclear structure followed by the typical nuclear reactions, which are initiated by beta emission, neutron emission, positron emission, orbital electron capture and proton emission.

And then, we have studied the different kinds of nuclear reactions that can happen by either capture reactions, particle-particle interactions, fission reactions, spallation followed by fusion reactions. In all these things, whenever nuclear change takes place, there is conversion factor. We have used Newton's conversion factor, that is, E is equal to m c square; that is, the release of energy taking place in the form of heat or as radiations. The mass change corresponding to the conversion of hydrogen into helium is approximately… We have studied that it is 0.0302 AMU, which is equivalent to 28.12 MeV of the energy per helium atom or 6.45 into 10 raised to kilo calories per gram atom

of the helium; that means this is equivalent to the temperatures prevailing on the sun. So, the nuclear reactions are also very important for us. And, there are analytical determinations required in handling the nuclear reactions also.

Subsequently, we have moved over to the electronic structure of the atoms. And, there we have studied the Rutherford model; and, some of the experimental evidences obtained by Sir J. J. Thomson have been utilized in arriving at a typical electronic structure of an atom around the nucleus. So, basically, Bohr's theory – it says that the electrons go round and round the nucleus, which is at the centre; and, most of the orbits, the electrons keep on encircling the nucleus at a very high rate equivalent to mvr is equal to nh upon 2 pi, which we call quantized. And, he also postulated that as long as the electron remained at a given orbit, it neither radiates energy nor it absorbs the energy. So, when the electron moves from one orbit to another, it is considered to change the quantum number. And, we have seen, the basis of all these is the spectrum of hydrogen atom, which corresponds to Lyman series, Balmer series, Paschen series, Brackett series and Pfund series.

And, based on these things, we have arrived at the electronic distribution in the atoms; that is, first thing is rule of 8, that is, inert gas atoms with the exception of helium containing 8 electrons in their outermost orbit. And, these elements are helium, neon, argon, krypton, xenon, radon, etcetera. And then, we have arrived at the different populations of maximum number of electrons – 2, 8, 18 and 32. And then, these electronic configurations of inert gases atoms we have seen. Sub-division of the electronic groups we have seen. And, the electrons movement are best described in terms of 4 quantum numbers, that is, principal quantum number, orbital angular momentum, then magnetic quantum number, followed by the spin quantum number. Based on this, we have arrived at the conclusion that no two electrons in an atom can have the same quantum numbers and the spectroscopy of all the atoms is based on the changes in the energy levels of the electrons at different levels. So, the interaction of electromagnetic radiation with matter has assumed enormous importance for us. And, we have spent some time in understanding these interactions.

Basically, we have seen that electromagnetic radiation, acoustic waves, ion beams, electron beams, etcetera represent a form of energy. A majority of the modern instruments are based on the interaction of the electromagnetic radiation with the sample. Analytical science dealing with such interactions is known as spectroscopy. So, we have

looked at the several properties of the electromagnetic radiation, that is, ranges, electron reactions, frequencies, wavelengths and how an electromagnetic radiation moves either as a wave or as a particle. And, we have seen the equations for representing these reactions. And then, we have also looked at how the energy of an electromagnetic radiation can be calculated if we know the wavelength or frequency; that is, E is equal to h c by lambda; where, h is Planck's constant; c is the velocity of light; and, lambda is the wavelength.

And then, we have looked at the other types of interactions, where there is refraction and reflection and polarization of radiations, transmission of radiations through a prism or through a grating. And, we have also seen what are the different types of the reactions that can be happening when the matter interacts with different kinds of prisms and gratings and slits; how the spectrum is obtained; what is the band pass width; what is half width, etcetera. And, all these things we are going to consider subsequently in our reaction in our studies using the modern instrumental methods of analysis.

Another very important aspect, that is, we have spent some time is to look at the photoelectric effect. The photoelectric effect even though discovered as early as 1887, it simply is one of the most wonderful thing that has happened to the analytical science, because when monochromatic light falls on a photo cathode, it releases the electrons. And, the release of electron corresponds to the generation of the current. And, this is the basis of 90 percent of the detectors that we employ in most of our instruments.

Basically, photoelectric current is measured as a function of the applied voltage, V 0 at which photoelectric current reaches zero multiplied by its electronic charge, gives the kinetic energy of the most energetic electrons in joules. So, this maximum kinetic energy can be plotted. And then, the energy of this slope is given by the Planck's constant and the intercept gives the photon energy required to eject the photoelectron from the irradiated surface. So, we have done of couple of examples to calculate the energy of 5.5 angstrom X-ray radiation followed by one of visible radiation. So, the quantum theory proposed originally for black body radiation has been extended to explain the emission and absorption processes. So, the essential postulates we have studied. And, at the end of that, we have seen the different types of spectra: continuum spectra, band spectra and then line spectra, etcetera.

And, with these systems, we have studied the requirements for different kinds of transitions that happened: one is atomic transitions, molecular transitions, etcetera. And, these things give rise to various spectroscopic techniques; that is, pure rotational absorption is observed in the microwave region; and, vibrational absorption spectrum is observed in the infrared region, etcetera. And, all these changes that are taking place in an atom are usually studied by various kinds of modern instrumental methods of analysis. And, that we will be studying in the next class. We will start with the spectrophotometry in the next class.