**Indian Institute of Technology**
**Kanpur**

**NP-TEL**
**National Programme**
**on**
**Technology Enhance Learning**

**Course Title**
# Advanced Characterization Techniques

## Lecture-12

**by…**
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Welcome so we are going to start a new topic today that is on advanced spectroscopic techniques we know that now a day's spectroscope techniques have taken a huge lead in material characterization that is mainly because we need to know not only the companions of the different materials we process but also we need to know the electronics states recitation states and may other features which we will discuss during the process of this lectures.

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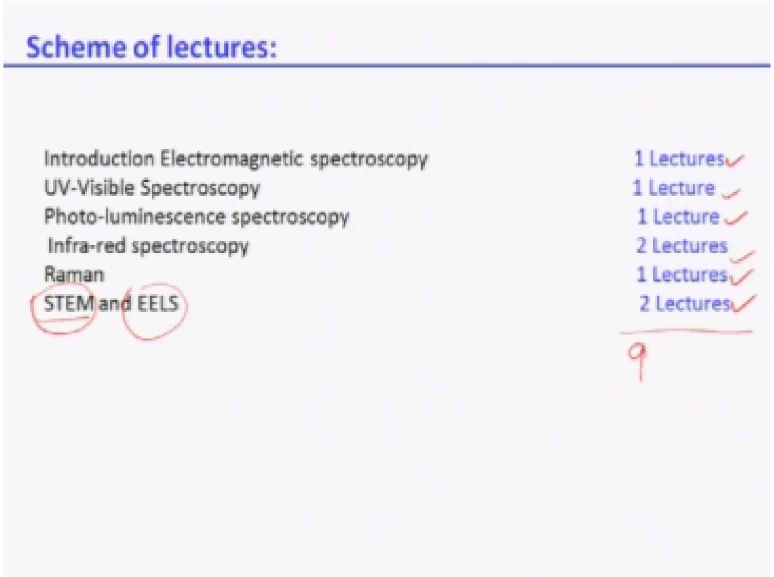

Scheme of lectures:

| | |
|---|---|
| Introduction Electromagnetic spectroscopy | 1 Lectures ✓ |
| UV-Visible Spectroscopy | 1 Lecture ✓ |
| Photo-luminescence spectroscopy | 1 Lecture ✓ |
| Infra-red spectroscopy | 2 Lectures ✓ |
| Raman | 1 Lectures ✓ |
| STEM and EELS | 2 Lectures ✓ |
| | 9 |

The way I have outlined the different lectures for these part of the course is as follows very first I shall introduce you the electromagnetics spectroscopy's theory in on lecture then I shall discuss different techniques which reused in the spectroscopic arsine first one is called EV visible spectroscopy this will take us one lecture this will be followed lamination spectroscopy for again one more lecture infrared spectroscopy which is used almost day to life for the material processing.

Will take about2 lectures then Raman spectroscopy which is discovered in 1930's by noble yet CV Raman we will be done in one lecture lastly steam the scanning transmission electro microscopic technique and EELS energy loss spectroscopy techniques will be discussed in 2 lectures I have already discussed about the basics of steam in the microscopic techniques I will concentrate the applications of the steam of an followed by obviously the EELS which is used to obtained different kinds of spectroscopy information's. So in a nut shell I will spend about 9 lectures in this part of a course.

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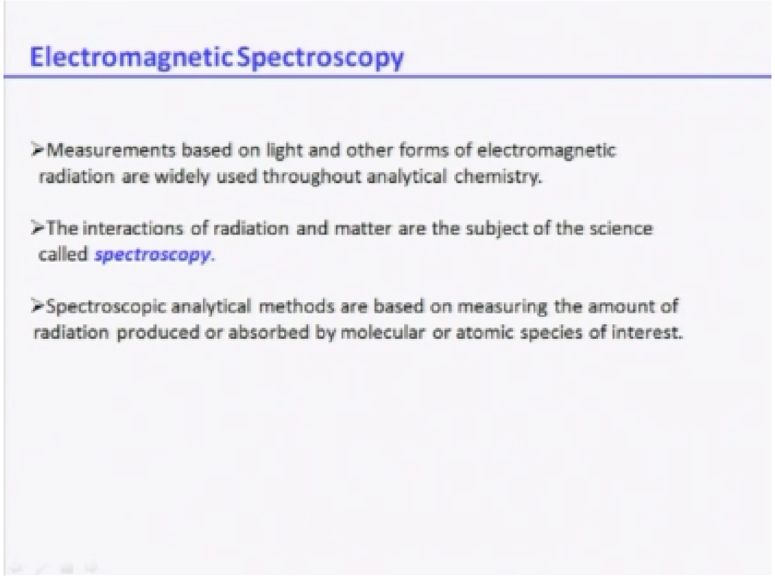

Electromagnetic Spectroscopy

- Measurements based on light and other forms of electromagnetic radiation are widely used throughout analytical chemistry.
- The interactions of radiation and matter are the subject of the science called *spectroscopy*.
- Spectroscopic analytical methods are based on measuring the amount of radiation produced or absorbed by molecular or atomic species of interest.

So let us begin first thing which I will do is some introduction to the electromagnetic spectroscopic theory we know that in our curriculum material science curriculum spectroscopic techniques are not though extensive play so you might have got some introduction in some of the courses but the knowledge of the of these area in the present curriculum is very small so and because this an advanced course.

So we need to first know the basics as we know that the spectroscopic techniques actually deals with measurements based on light or any other forms of electromagnetic radiation but say and these are widely used in generate chemistry for your information now a day's people use when in other end also so basically deals with interaction with this radiation and the matter and that is the subject of spectroscopy so it basally I can say all that spectroscopy is at a very rude mentally level.

In nothing but interaction of the radiations like light x-ray, gamma ray or any other part of the electromagnetic radiation with the material and we analysis whatever comes out after the interaction EDS whcuih is used in scanning electromicroscopic techniques is another spectroscopic technique where electron interactions with the material and we get signal out of that and then we analysis that and this techniques sexually can give us all kinds of virtual information regain the structure of the material. Like molecular atomic species they are structure electronic structure band structure many other things.

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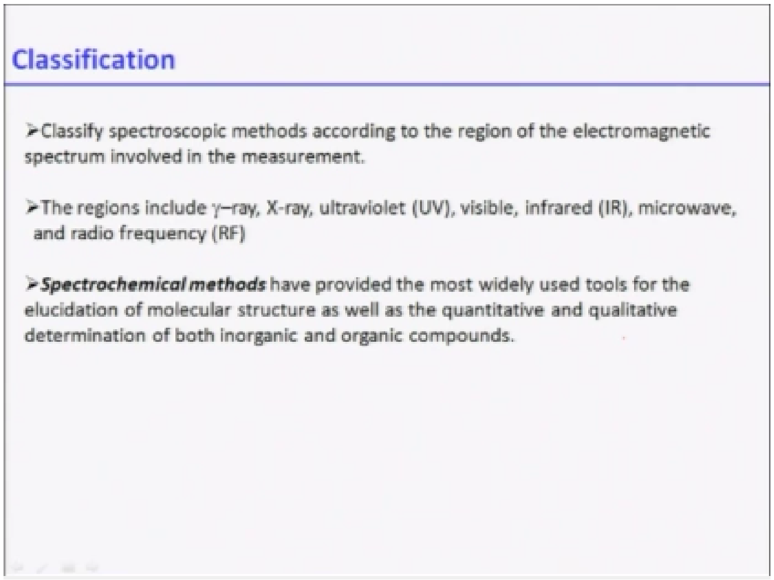

## Classification

- Classify spectroscopic methods according to the region of the electromagnetic spectrum involved in the measurement.
- The regions include γ–ray, X-ray, ultraviolet (UV), visible, infrared (IR), microwave, and radio frequency (RF)
- ***Spectrochemical methods*** have provided the most widely used tools for the elucidation of molecular structure as well as the quantitative and qualitative determination of both inorganic and organic compounds.

So therefore we can classify this techniques very easily depend any type of the region of the elector magnetic spectrum involved in the investigation and as we know the electromagnetic spectrum which is shown here.

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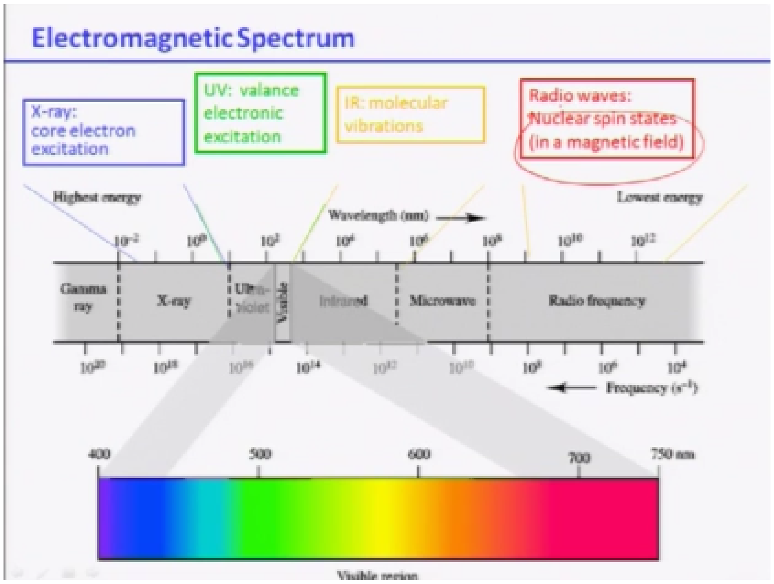

Electromagnetic Spectrum

X-ray:
core electron
excitation

UV: valance
electronic
excitation

IR: molecular
vibrations

Radio waves:
Nuclear spin states
(in a magnetic field)

It spans from radio frequency like very high wave lengths $10^{12}$ mille nanometers are very low frequency obviously $10^{4}$ $10^{8}$ to very high energy lattice come a ray the frequency obtained to the power 20/ s or EECH and so therefore with if this is what is the electromagnetic spectrum we can utilize different part of the spectrum for the spectrum scope analysis starting from radio waves which are used for nuclear Spean states measurements like NMR studies nuclear material then we have higher where which can be used for understand in the molecular vibrations.

Then we have UV visible spectroscopy's techniques which consists of both alter violent on the visible range which can be used to study the balance electronic excitation in the material and x – rays can be used for correlation excitation like excess total excess spectroscopy and many other techniques are there all the other spectroscopes so that means depending on the kind of investigation we would like to do the uses of the elector magnetic radiation will depend on that.

So basically it works downs to the frequency of the radiations which will be used for excitation of the material at the beginning,

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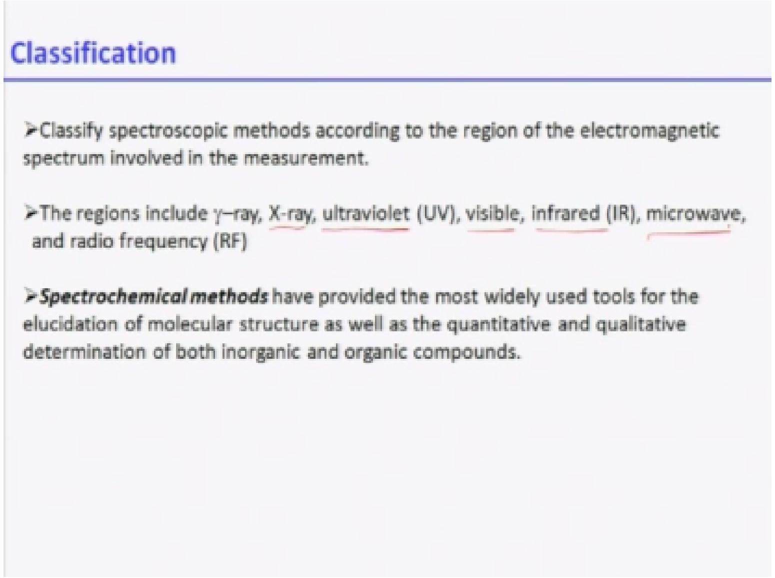

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And so therefore if I go back so regions from γ ray, x- ray ultraviolet, visible, infrared, microwave and radio frequency all of these can be used for spectroscopic analysis was most notable so answer x- ray, ultraviolet ray, visible, infrared and as well as microwave so we normally for a beginning arrow we differentiate the spectroscopic techniques are classify the spectroscopic technique acquired into the wavelength of radiations in this way.

Spectra chemical methods we know that it provides the information like a molecular structure both in quantitative and qualitative way for all kinds of material involved I think irrespective in organic, organic compounds.

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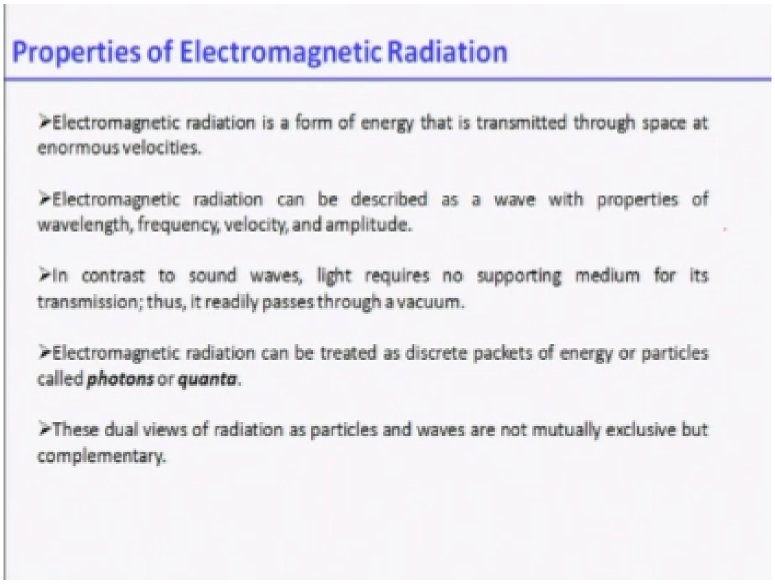

## Properties of Electromagnetic Radiation

- Electromagnetic radiation is a form of energy that is transmitted through space at enormous velocities.
- Electromagnetic radiation can be described as a wave with properties of wavelength, frequency, velocity, and amplitude.
- In contrast to sound waves, light requires no supporting medium for its transmission; thus, it readily passes through a vacuum.
- Electromagnetic radiation can be treated as discrete packets of energy or particles called ***photons*** or ***quanta***.
- These dual views of radiation as particles and waves are not mutually exclusive but complementary.

Well so therefore you know that electromagnetic ration used in the spectroscopic techniques so you must have some idea about the properties of electromagnetic radiation you have studied in your+2 or even in bather studies bather degrees but I have just like to retrain it this issues electromagnetic radiation basically nothing but a form of energy that is transited through space and a very high velocity light.

And they can be obviously described by wave or like it as a wave length it can be velocity can be relate wave length and frequencies and obviously like any other wave it as amplitude we know that in contest to sound waves the light requires no supporting medium w know that sun light from sun travels such a long distance without any media so thus that means it can pass through back room.

So the is problem and as far as blank theories of the concerned we can always considered electromagnetic radiation to be consisting of discrete packets of energy are particles called protons or point up we know that the energy is equal to h u of the photons where new is the frequency and h is the plane constant, so that is again from plans theory and also we know that means what that means electromagnetic radiation is can be either treated as a way or treated as a particle this way we have do the particle duality is all tell to with the many of the scales.

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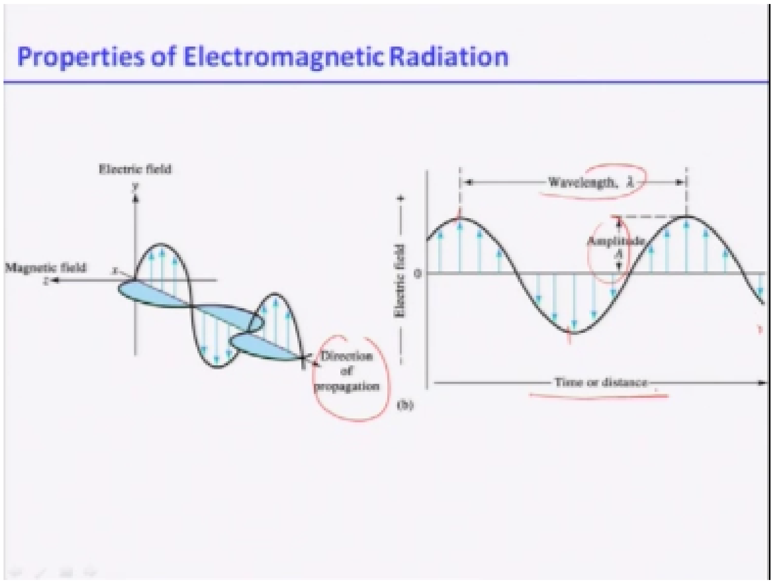

Properties of Electromagnetic Radiation

So by schematic diagram I can say that they re light comes or any electro radiation comes at an you know at 900 angle from the electric field and the magnetic field, so x and y sorry y and z of the two direction of the electrical magnetic fields, then the radiation comes in a different these actions z direction x direction which is the known as here direction of the propagation and we can always de presents this way the way so wave as a particular wave length double γ which is from the tough to tough.

Or maybe the pick to pick position distance and this approaches it and this is the time of the time of the distance which we can described these are all very simple discretion of the wave.

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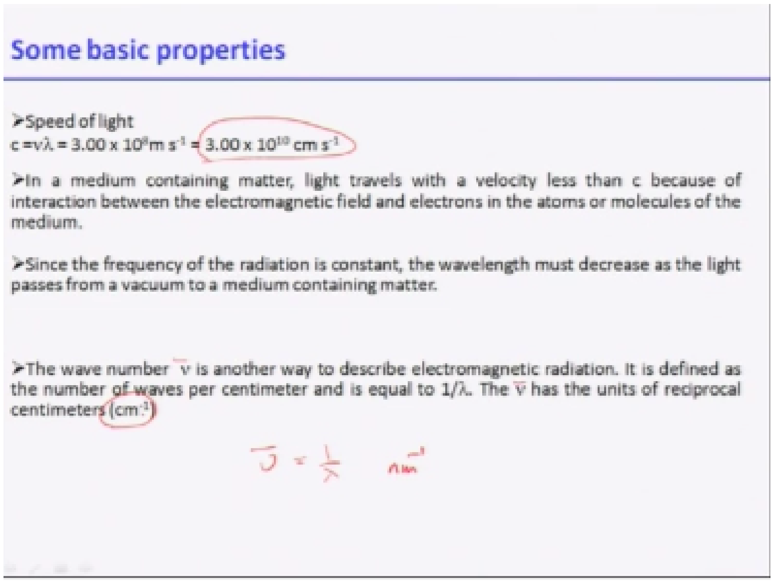

## Some basic properties

- Speed of light
  $c = \nu\lambda = 3.00 \times 10^8 \, m \, s^{-1} = 3.00 \times 10^{10} \, cm \, s^{-1}$
- In a medium containing matter, light travels with a velocity less than c because of interaction between the electromagnetic field and electrons in the atoms or molecules of the medium.
- Since the frequency of the radiation is constant, the wavelength must decrease as the light passes from a vacuum to a medium containing matter.
- The wave number $\bar{\nu}$ is another way to describe electromagnetic radiation. It is defined as the number of waves per centimeter and is equal to $1/\lambda$. The $\bar{\nu}$ has the units of reciprocal centimeters ($cm^{-1}$)

$\bar{\nu} = \frac{1}{\lambda}$ $nm^{-1}$

Now if we want to go into some more details we know the speed of light is fixed this is given by this value 300 per 10cm/s in a medium kind of material or matter light travels with the velocity less than c because it interacts with the material and basically that electromagnetic radiation interaction of the electrons in the atoms are molecules in the medium and that is of the velocity of the light get reduced, since sequence of the radiation is constant so therefore wave lengths will decrease as frequency increases and you know a light passes from background to the medium contain matter.

Wavelength will also decrease many times we represent weight number μ/ another way to describe the electromagnetic radiations and this is used in the spectroscopic techniques that is why I like to know it is nothing but 1/γ so therefore it is a unit of inverse of γ, γ is a unit of nano meter so this as a unit of nano meter inverse or it can may have unit of centimeter inverse also that means the unit of distance inverts.

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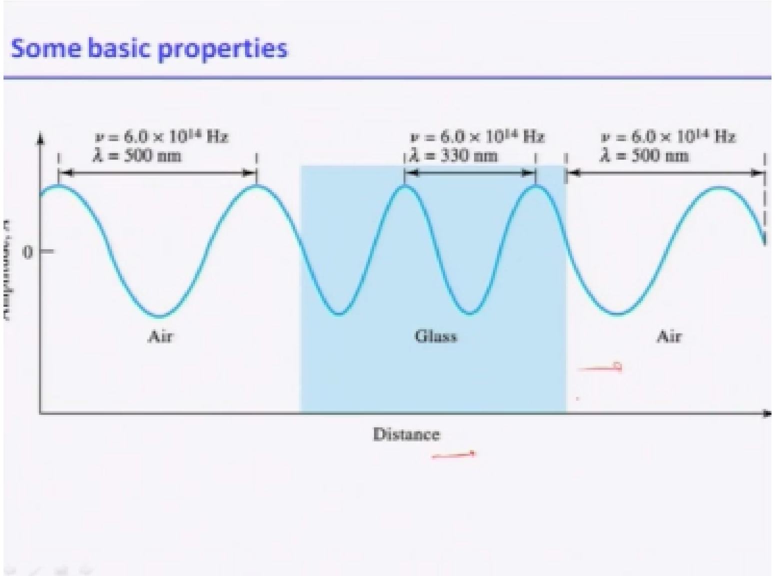

Some basic properties

This is what is shown here this is the amplitude this is the distance as you can see here the wavelength and amplitude in air is suppose given $\gamma^{15}$ 500 nano meters and when the same radiation enter the glass the wavelength decreases so from 500 it becomes 330 and subsequently frequency reconcile even same is so that means energy has changed basically energy sorry it is a some path some of the interaction of the material as change the wavelength around taking an comes out from the glass.

It returns the same of the wavelength so this the some of the basics features which we can see now-a-days in all kinds of material.

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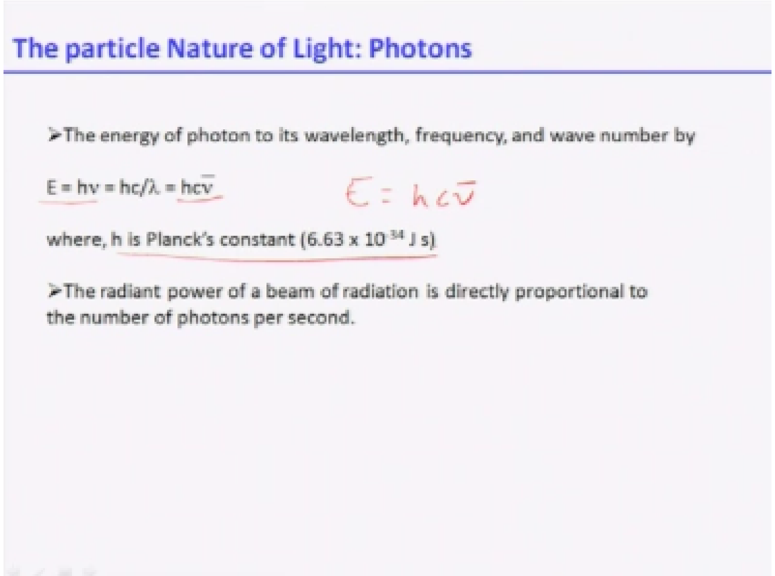

## The particle Nature of Light: Photons

- The energy of photon to its wavelength, frequency, and wave number by

$E = h\nu = hc/\lambda = hc\bar{\nu}$ $E = hc\bar{\nu}$

where, h is Planck's constant ($6.63 \times 10^{-34}$ J s)

- The radiant power of a beam of radiation is directly proportional to the number of photons per second.

And if you want to talk about particle nature as I discuss that they are photons so therefore energy of the any kind of radiation can be represent by Planck's law that is r = hu which is nothing but hcλ where c is the velocity of light or radiation and this can be again represent hcu bar so this is what now-a-days we normally use hcu bar is the energy so if you known u bar that is the wave number we can calculate this energy and we know that h is the flame constant which is the value $6.63 \times 10^{-34}$j/s.

So radiation part of any beam actually mean of radiation does not matter of the electromagnetic of the x-ray or γ ray or even whether the bean it directly proportion to the number of photons per second.

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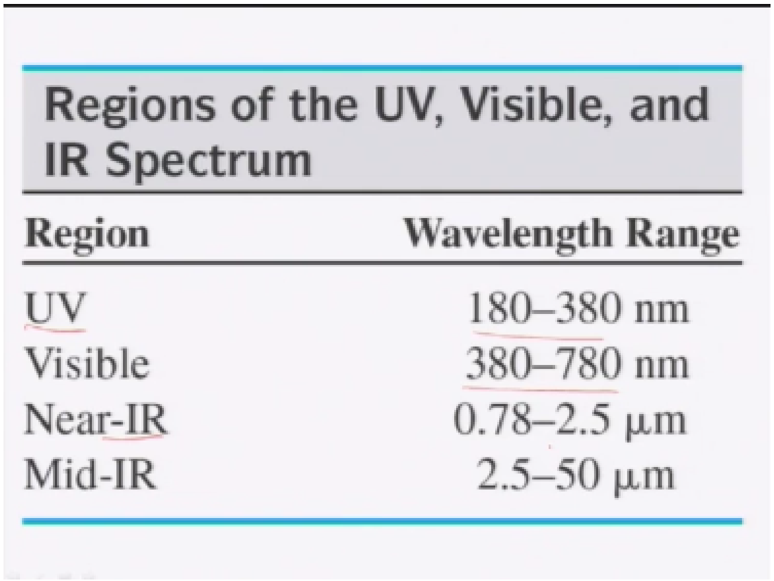

**Regions of the UV, Visible, and IR Spectrum**

| Region | Wavelength Range |
|---|---|
| UV | 180–380 nm |
| Visible | 380–780 nm |
| Near-IR | 0.78–2.5 μm |
| Mid-IR | 2.5–50 μm |

Now as I told only discussed the what is called the different spect electromagnetic spectrum region I am going to tell you the one exact values now normally we ultra valid comes in the range of 180 to 380nm visible come created to 380 to 780nm normally you study visible will comes from 400 to about 880nm but it can be externally little bit more nearer are infrared comes about 0.782 to 2.5m very large wavelengths mean infrared comes in 2.5 to 50 and rest is these called microwaves which are very high of lengths may be of the or our centimeters.

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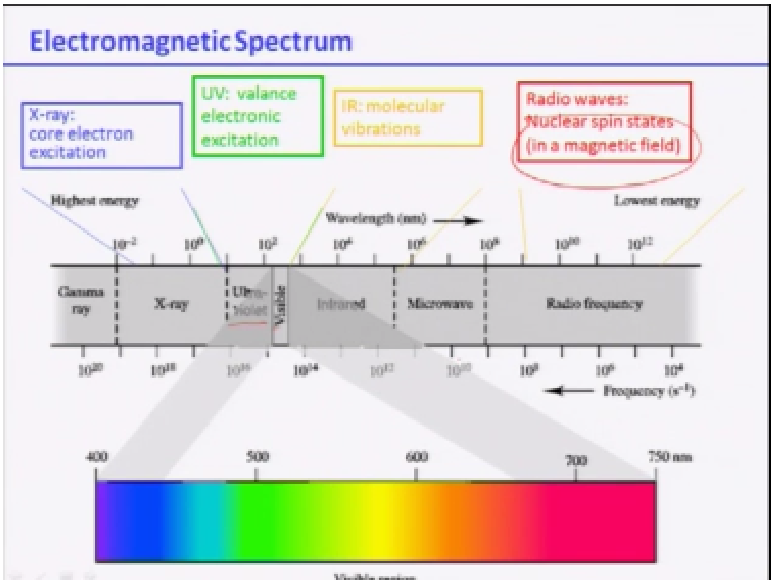

Electromagnetic Spectrum

X-ray: core electron excitation

UV: valance electronic excitation

IR: molecular vibrations

Radio waves: Nuclear spin states (in a magnetic field)

With that is what I have shown you in the slide you can see microwave can I have actually 10$^{8}$ almost nm that means about 10.1m well now if you got to the molecule.

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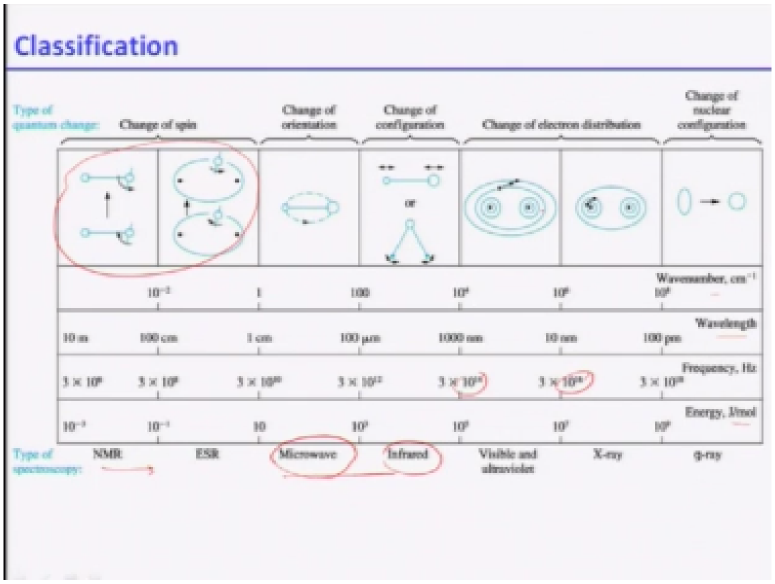

Classification

Well now if you go to the molecule of the structure wise why the radiation is falls a material lesson kind of changes happens and this changes will be depending on the type of radiation de materials of submitted to that means the wavelength or the frequency of the radiations which is used to prove the material, so if I am going to show you like this things in a two ways one there is a type of spectroscopic techniques study for mean MR to microwave in for a ultra is x-ray and γ ray.

And these are all the different what is called parameters this is the what is called the frequency you can tell $10^{6}$ $10^{8}$ $10^{10}$ after $10^{8}$ 18 and energy is – 3 to 10 9 energy there is j/m and wave length you know the λ was can be calculated, now if you have if you are basically focusing on very small energy that is 10c 10 –1j/s corresponding to very low frequency or rather very high of lenses 10m to 200cm which is used for the microwaves as a when larger than microwaves even so what you see is nothing but changes has been.

That is what normally happens quantum mechanically speed basically change is when you apply that so that means you can study nuclear $90^{0}$ when as the Spain of the both the particles are actually electron changes depending type of material so we can understand that now if we use microwaves then all are even infrared which comes in the frequency $10^{14}$ in this range hatch so you can have the change the orientation of the molecule so is what is shown here then you can have the this kind of molecules suppose.

We get a small atom connected by a bond they can create differently oriented or you can have a geometrical change of the configuration so this is what thermally happens when use this in this range then any kind of radiation was frequency varies in this range, now if you go to higher frequency level it higher $10^{14}$ to $10^{16}$ then you can have basically changes made in terms of electronic distribution in the material thus what is shown here you can see the electronic distribution can get modified and that can be studied and if you go to very energy like γ rays $10^{18}$.

Which corresponded to 100pm of valence energy is 10 9 joule per mode it could not even change in the configuration in nuclear configuration that is what we will know I we compact λ certain materials nuclear configuration gets change you can keep white shiver in the material by remember to the material.

These are all very well document to the literature so after knowing this aspects let us now look at what actually spectroscopic technique does really, because as I should told you at the beginning and for the last few slides that we use certain electron magnetic radiation and allow it for the material and then see it is the change is happening in the material in terms of upon the radiation becomes out.

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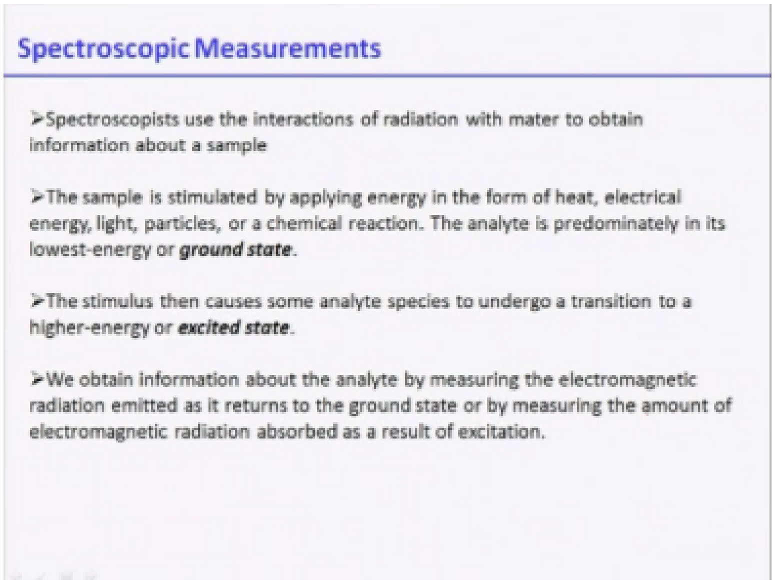

## Spectroscopic Measurements

➢Spectroscopists use the interactions of radiation with mater to obtain information about a sample

➢The sample is stimulated by applying energy in the form of heat, electrical energy, light, particles, or a chemical reaction. The analyte is predominately in its lowest-energy or ***ground state***.

➢The stimulus then causes some analyte species to undergo a transition to a higher-energy or ***excited state***.

➢We obtain information about the analyte by measuring the electromagnetic radiation emitted as it returns to the ground state or by measuring the amount of electromagnetic radiation absorbed as a result of excitation.

So spectroscopy is actually use like this interactions, so in this case sample is stimulated rather by applying a energy in form of either heat or you can apply electrical energy or even light actually or you can have a chemical reaction. So basically any kind of sample is stimulated by this energy sources and it is you know at the beginning the we assume that analytical solutions of the material is in the ground state.

So therefore always suggested therefore as I stimulated to with energy always certain kind of energy source it will cause this material to undergo a transition that is it is expected that there energy will make the material to go from ground state to higher at the state or exited states. So if this is what actually perceive to be happening in a material then we can obtain information of the analytic material by measuring the electromagnetic radiation that will be emitted for rate turn to the ground state.

Because if we exist any materials by energy to high energy level then obviously after certain time the material will come back to the ground state or the low energy state and extra energy will be emitted. So we can actually then measured the radiation emitted as a material comes back under measuring the amount of the electromagnetic radiations and also type of the radiations coming out absorb we can do we can get lot of information about the material. So that is in a very simple way any spectroscope do does in the real in a laboratory.

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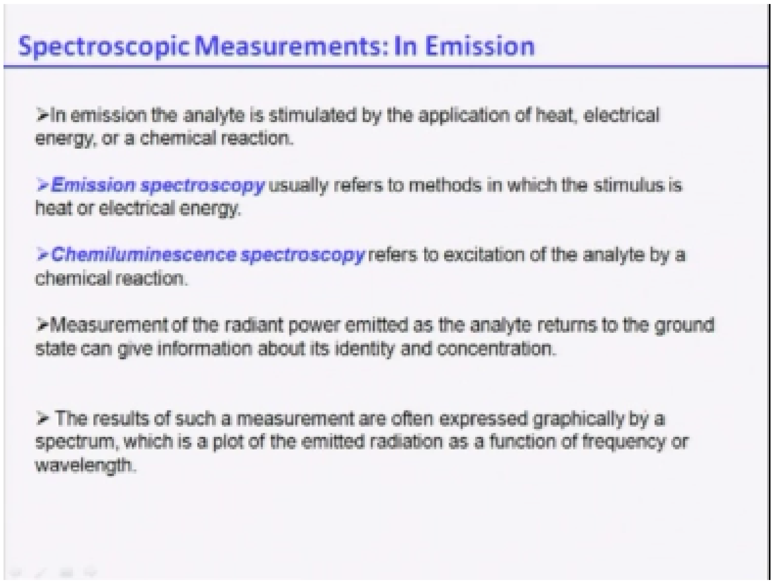

## Spectroscopic Measurements: In Emission

- In emission the analyte is stimulated by the application of heat, electrical energy, or a chemical reaction.
- ***Emission spectroscopy*** usually refers to methods in which the stimulus is heat or electrical energy.
- ***Chemiluminescence spectroscopy*** refers to excitation of the analyte by a chemical reaction.
- Measurement of the radiant power emitted as the analyte returns to the ground state can give information about its identity and concentration.
- The results of such a measurement are often expressed graphically by a spectrum, which is a plot of the emitted radiation as a function of frequency or wavelength.

Now depends obviously then depending on that we can have different kinds of techniques you know in emission analytic basically sample is stimulated by heat or electrical energy or chemical reactions and this is called emission spectroscopy. So normally the stimulus is heater in electricity in this emission spectroscopy then you can are a chemiluminescences spectroscope that means in this case the sample is existed by chemical reaction not by heater electric it is by chemical reaction that is why it is called chemiluminescences spectroscopy.

So measurement of the radiation power emitted from the materials come back to the ground state can be used both the cases to measure identified the concentrations, results of this measurements are basically re3presented by a graph of spectrum which will see in few minutes time in some of the plots and this cases this is the y axis is can be any parameter as whatever radiation coming out and x axis will be either γ or 1 / γ. So γ wave length or one λ is wave part.

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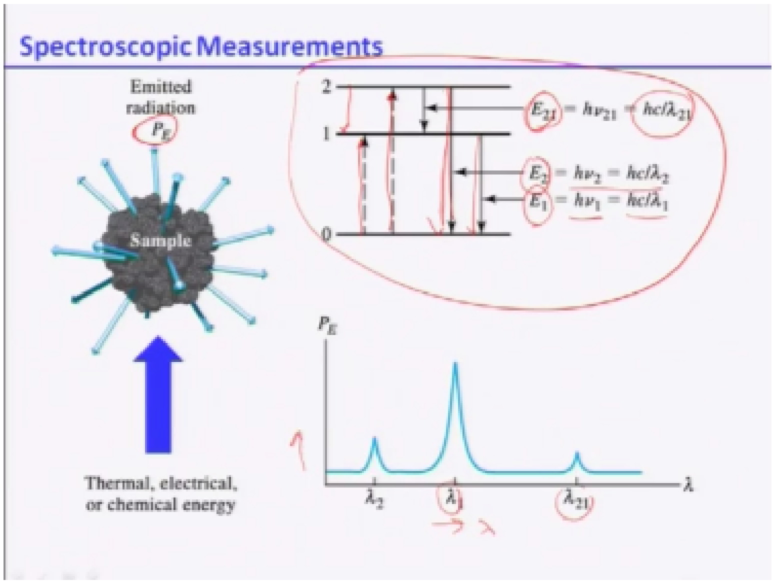

Spectroscopic Measurements

Let us do the some of the see the some of the things suppose we have a sample like this and we have a energy source thermal chemical or electrical and your existed the material, once you exited the material obviously sample will absorb the energy certain part of energy and it will go to high energy state as I said and then it will come back to the ground state of different time another process it will emit the radiation that is what is known as Pe here okay.

So what are eliminations whatever you can say that is Pe now if I go back to this place this one the energy states here so suppose 0 corresponds to ground state and now I have an excite material like sight of the material so that it can go to the higher energy state like one and two which are the exited states and as after certain times one it comes back to the ground state it can have different parts.

So this is the excitation to go to suppose state one this excitation go to suppose state two. Now very fast thing can happen is basically it can come back from state one to the ground state and the which corresponds to the energy emission of the U1 or can be related to H new one or it can be twice C / λ 1okay. Our second thing can happen basically that from the energy state two if it is exited at we given so much of energy that you go to energy state two and it is comes back to the ground state.

And then this much of energy will be released heat to one and which corresponds to Hc / λ 21 sorry so in this case it will be emitted not e2 1 e2 we correspond to Hc well λ 2, you can have a inner transaction that is from two state to one state exited two to existed state one in that case energy will be released like E21 with the wave length given by 21. So as you can see here the energy U1 is obviously higher then E2 okay the amount of energy is sorry E2 is higher than the U1 and then E2 1.

You can see the length of the emitted determine that also that this expected understand about, so if I plot Pe passes λ which is done in this case that is what the plot the spectrum you call and you can see we gets spike corresponding to λ 2 that means this term this is corresponding to tangential from 2 to 0 then another p correspond to λ 1 this correspond to tangential from 1 to 0 or we can have a very small peak corresponding to tangential from 2 to 1.

So these are all mark like λ 2 λ1 λ 21 so that means these are the characteristics wave lengths which will decide the type of material we are provide, so this wave length so once you know then we can actually probe we can say that what kind of materiality's what kind of states of material has all this kinds of features can be done but these are all very simplistic way of plotting the data or doing the measurements. Now we can actually have something like absorption instead of emission.

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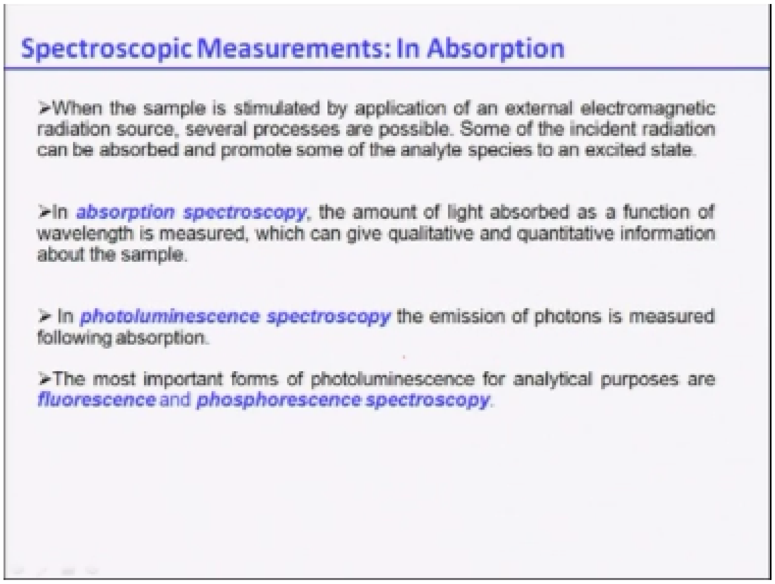

## Spectroscopic Measurements: In Absorption

- When the sample is stimulated by application of an external electromagnetic radiation source, several processes are possible. Some of the incident radiation can be absorbed and promote some of the analyte species to an excited state.
- In ***absorption spectroscopy***, the amount of light absorbed as a function of wavelength is measured, which can give qualitative and quantitative information about the sample.
- In ***photoluminescence spectroscopy*** the emission of photons is measured following absorption.
- The most important forms of photoluminescence for analytical purposes are ***fluorescence*** and ***phosphorescence spectroscopy***.

So when a sample is stimulated by application of the external electromagnetic source several process are obviously possible and you know some of the incident radiation can be absorbed and then this absorb radiation can promote this species to go to the excited state. And in absorption spectroscopy which is just I have shown in to the last slide the amount of light absorb is basically function of wave lengths and it can be measure.

And then obviously we can use both this wave lengths as  qualitative measurements to the di material and the area in this curves will give us the amount energy released at the particular wavelength and that can be used quantity paralysis. In the photoluminescence spectroscopy emission of photon is measured following the absorption. The most important forms of the photoluminescence spectroscopy is fluorescence or phosphorescence spectroscopy, which we will discuss in alter.

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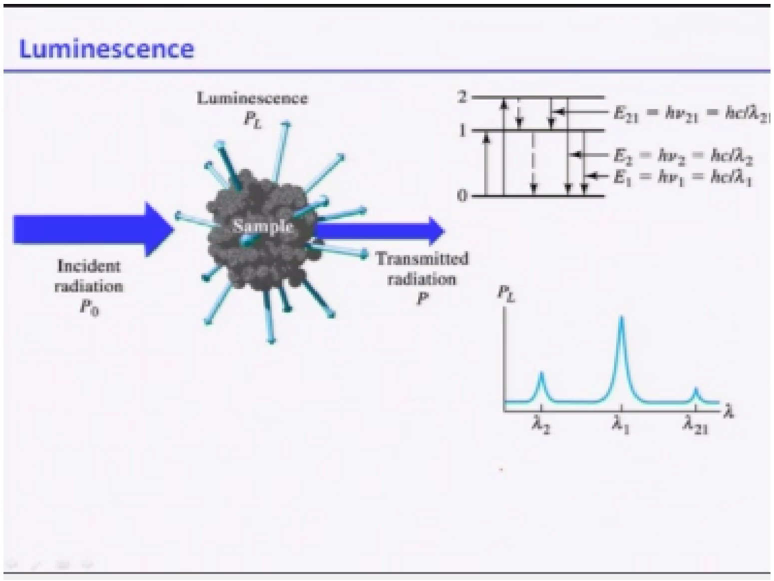

Luminescence

Well what the absorptions look like the last one is the emission absorption is like this, so you intensity it falls on a sample and then transmitted radiations and we can assume that initial sample was ground state. Once the radiation is absorbed in the material it goes either to state 1 or state 2, so this is the transition from 0 to 1, the transition from 0 to 2 or then we can basically measure A this is the absorption as a function of wavelength λ.

And you are goi8ng to get two peaks again to λ to λ1 is correspondence to excitation from 0 to 1, λ to form, 0 to2 so this is absorption. Once it gets absorbed we can actually measure the absorbed energy as the function of wavelength and find out the whole catalyst of the whole process.

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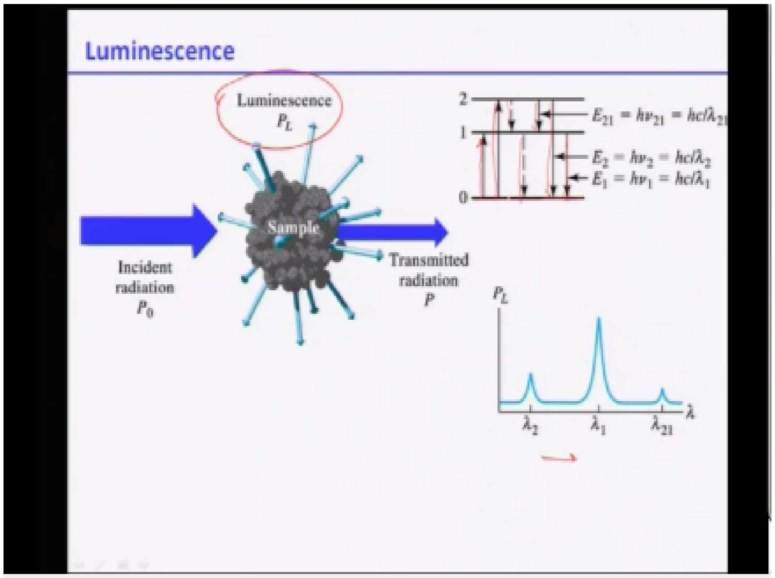

Luminescence

Well another one is luminescence as I said so you have supposed incident radiation P0 falling on a sample okay and then sample the radiation will be transmitted and some part will come as the luminescence. Well luminescence means some kind of inside transition and which we just discussed and then you can just measure this luminescence as a function of λ. So I have discussed emission I have discussed absorption now I am discussing luminescence.

So in luminescence again we can consider a sample at the beginning and once you energize it can go absorb energy and go to state 1 okay. And then you can have different kind of transition obviously first one transition can happen is basically form 1 to 0 or the 2nd one is 2 2 0 or even you can another way you can have is form 2 2 1. This dotted as basically talking about transition suppose to form 2 2 1 followed by 1 to 0.

So and this all this come as a specific wavelengths and we can actually get this wavelength very easily the area on the pics tells you how much is the energy comes out as luminescence.

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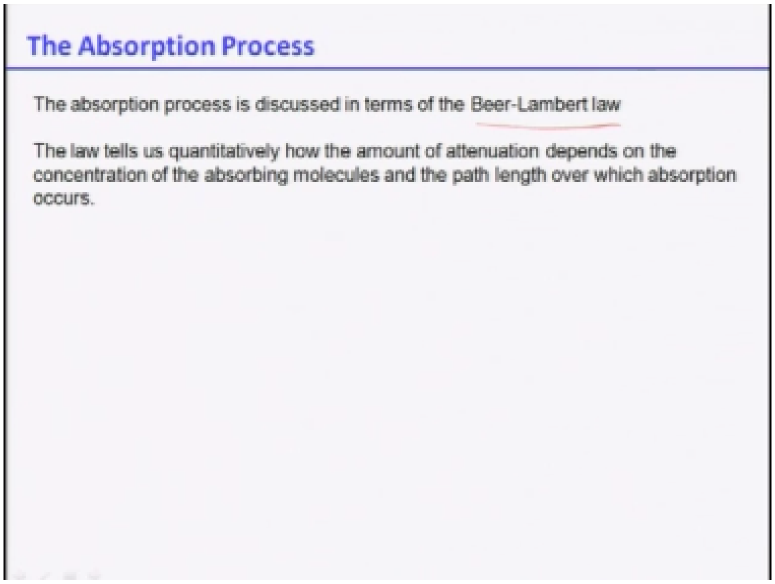

## The Absorption Process

The absorption process is discussed in terms of the Beer-Lambert law

The law tells us quantitatively how the amount of attenuation depends on the concentration of the absorbing molecules and the path length over which absorption occurs.

So we will discuss more about absorption process it is very important part of the spectroscopic emission, absorption and luminescence. Discuss in terms of Beer Lambert law many times people call Beer law in terms λ. This law if you look at it tells us exactly how the attenuation of this energy depends on the concentration of the absorbing molecule and the path length of the absorption occurs.

Obviously you know in a solution in a material if it is not 100% and this attenuation energy how much will be absorb how will be emitted. It will depend on what is called as the absorbing molecule also the path length.

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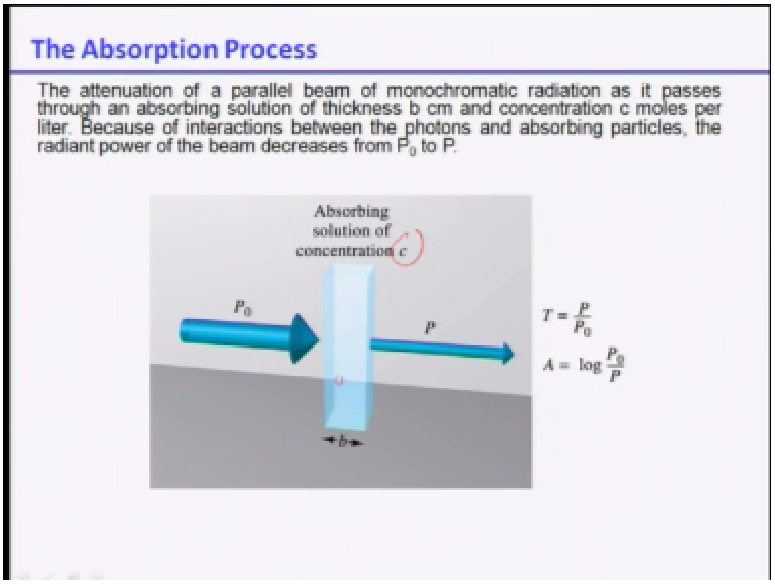

The Absorption Process

The attenuation of a parallel beam of monochromatic radiation as it passes through an absorbing solution of thickness b cm and concentration c moles per liter. Because of interactions between the photons and absorbing particles, the radiant power of the beam decreases from $P_0$ to P.

$$T = \frac{P}{P_0}$$

$$A = \log \frac{P_0}{P}$$

So how we can show this schematically this can be shown like this suppose if you have a parallel beam λ it forms on the fall on solutions and it passes through and the thickness of absorbing solution is B and the concentration is C, B is cm because of the interaction of this energy with this solutions okay that means interaction of photons on the radiation with the molecules or the materials in absorbing particles.

So we can define the transmission actually T like this ratio P/P0 and absorbs basically the log of P/P0 at P.

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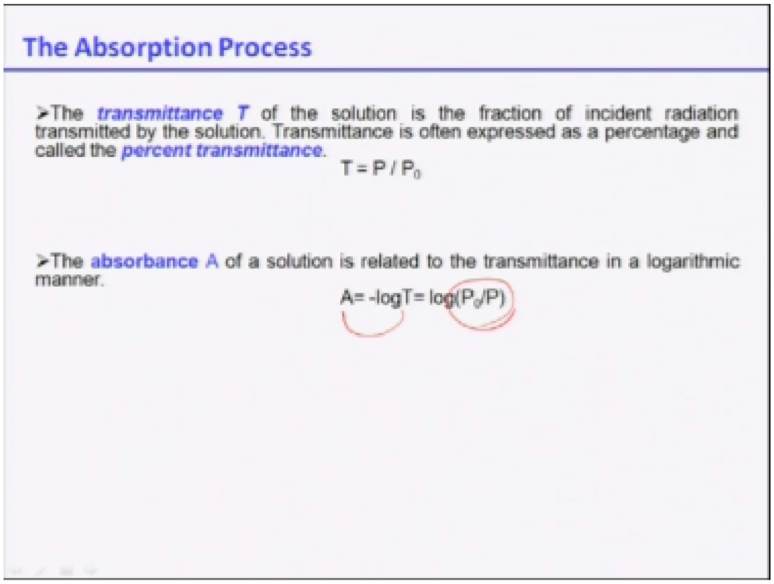

## The Absorption Process

- The *transmittance T* of the solution is the fraction of incident radiation transmitted by the solution. Transmittance is often expressed as a percentage and called the *percent transmittance*.

$$T = P / P_0$$

- The **absorbance A** of a solution is related to the transmittance in a logarithmic manner.

$$A = -\log T = \log(P_0/P)$$

Now so again I am doing that the transmission is basically fraction of incident radiation transmitted by the solution and it is % transmitted that is p/p0 x 100 and the absorption is basically into the transmittance in logarithmic manner or that is log T that is log P0/P rememember this is P0/P that is the difference.

So – log T is absorption so that is the relationship between T and A so this is how they are related.

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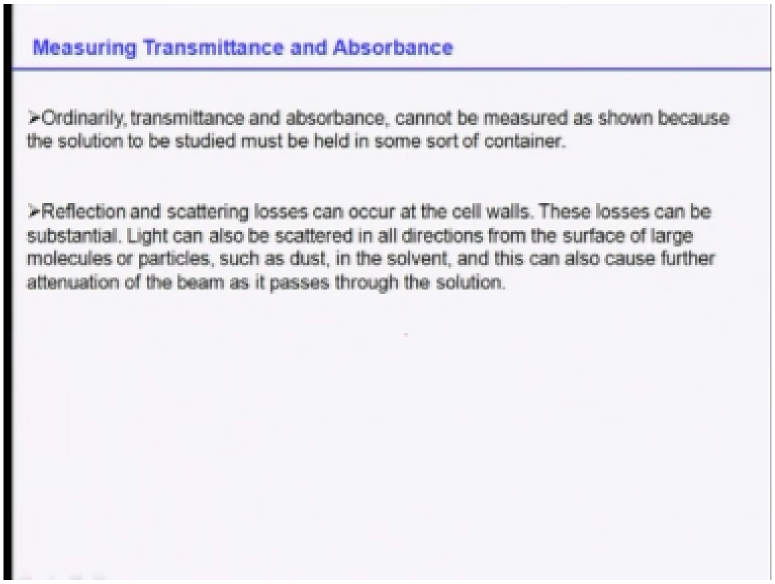

### Measuring Transmittance and Absorbance

- Ordinarily, transmittance and absorbance, cannot be measured as shown because the solution to be studied must be held in some sort of container.
- Reflection and scattering losses can occur at the cell walls. These losses can be substantial. Light can also be scattered in all directions from the surface of large molecules or particles, such as dust, in the solvent, and this can also cause further attenuation of the beam as it passes through the solution.

Now ordinary transmitted and absorbance cannot be measured the way I have told you okay that means what I say the current measures are shown in a container we cannot simply take the solution and floated in the air or measure. We need to cure the resolution in a certain container that means whenever you keep a container you will have the picture like and reflections or scattering losses.

One has to take care of those losses you know light for example can be scattered in all the directions surface of the large molecules even particles which is dust or even solvent. And this can cause further attenuation of the beam as it passes the solutions. So one actually needs to take care of those, how to take care of those?

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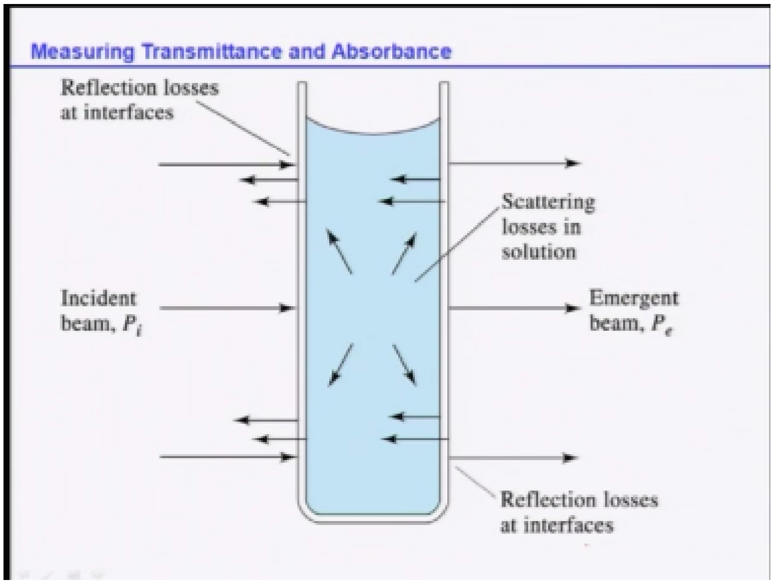
Measuring Transmittance and Absorbance

Let me first show you the different process, suppose you have the interfaces with Pi and you can have reflection losses, you have scattering losses, you can have reflection losses at the even interface are you have a foreign particle inside or a big map inside you can have these process techniques taking place again.

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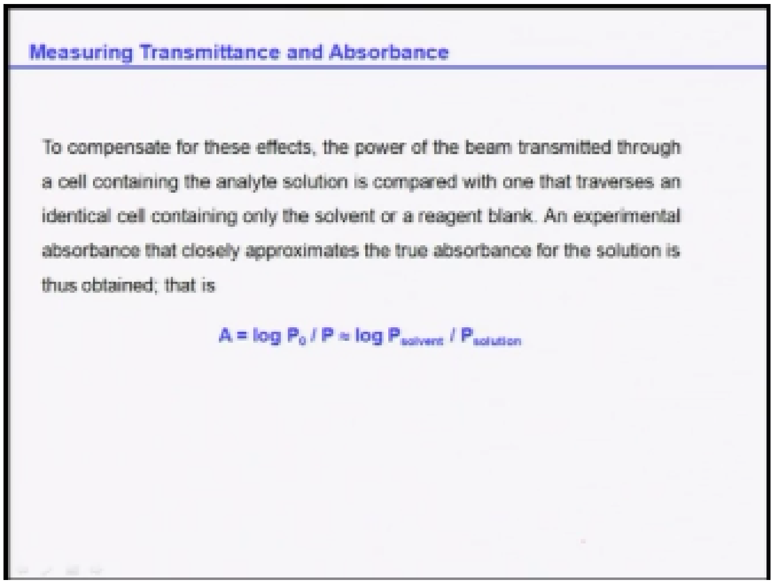

## Measuring Transmittance and Absorbance

To compensate for these effects, the power of the beam transmitted through a cell containing the analyte solution is compared with one that traverses an identical cell containing only the solvent or a reagent blank. An experimental absorbance that closely approximates the true absorbance for the solution is thus obtained; that is

$$A = \log P_0 / P \approx \log P_{solvent} / P_{solution}$$

So to compensate this affects how to take care of these power that transmitted beam power of the beam transmitted to the cell are they containing the is compare with one that traverses an identical cell containing only the solvent or a reagent blank so basically you are using a standard so the experimental absorption that closely approximate the two absorption of the solution can be obtained so that means you can write absorption equal to log pc/p approximate equal to p solvent by p solution if I have this kind of content which cut an arc which contains all the solvent of the reagent.

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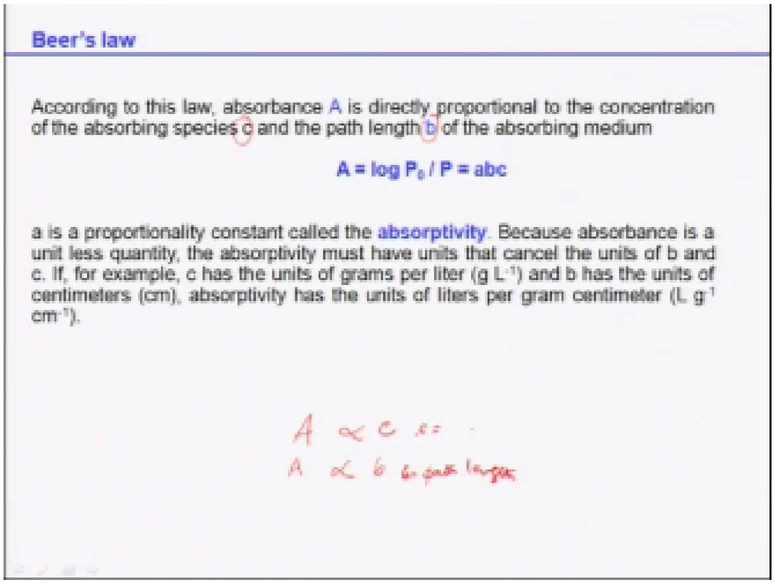

**Beer's law**

According to this law, absorbance A is directly proportional to the concentration of the absorbing species c and the path length b of the absorbing medium

$$A = \log P_0 / P = abc$$

a is a proportionality constant called the **absorptivity**. Because absorbance is a unit less quantity, the absorptivity must have units that cancel the units of b and c. If, for example, c has the units of grams per liter ($g\ L^{-1}$) and b has the units of centimeters (cm), absorptivity has the units of liters per gram centimeter ($L\ g^{-1}\ cm^{-1}$).

$A \propto c$ c=

$A \propto b$ b= path length

So that is how one can take this is very simple to describe I do not need to go into detail of that now by after knowing all this step let us know why this beam slow action now law according the absorption a is directly proportional to the concentration of the absorbing pcs see and path length p of the absorbing media so that means a is directly proportional to c is the concentration of this absorbing pcs and a is directly proportional to t b is nothing but a path length okay so that is what I can write down.

And c is basically the concentration of absorbing diseases because absorption is unit less quantity a you know a as no unit as no units so therefore the call c and b should have units which cancel out c has a unit of compare liter b as unit as unit of centimeter so therefore absorptive should have unit of liter per gram per centimeter otherwise A will never be this is why it is called bears law or bears lamps law whatever you can say in the literature.

This is very simple straight forward absorption proportional to c absorption proportional to p path length so therefore absorption equal to axbxc where a is the constant collapse of t b is the path length in centimeter and c is the concentration gram per liter so any express the concentration in mole per liter.

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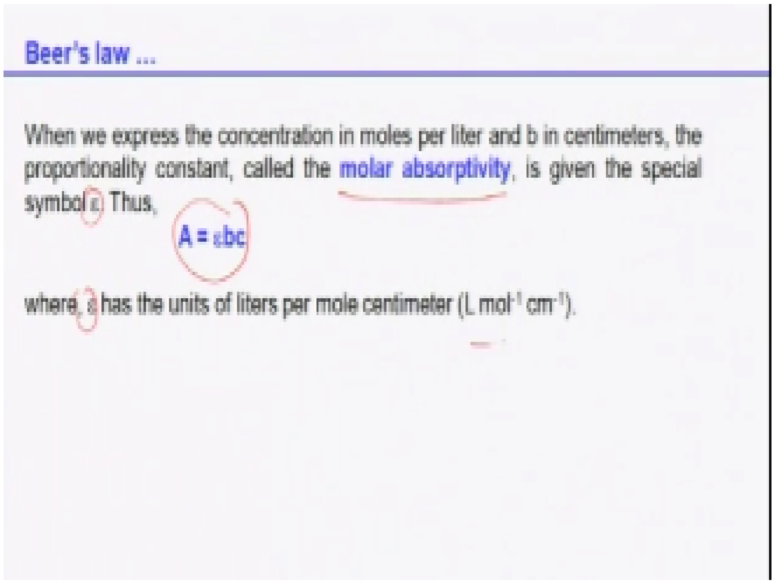
**Beer's law ...**

When we express the concentration in moles per liter and b in centimeters, the proportionality constant, called the **molar absorptivity**, is given the special symbol $\varepsilon$. Thus,

$$A = \varepsilon bc$$

where, $\varepsilon$ has the units of liters per mole centimeter (L $mol^{-1}$ $cm^{-1}$).

B in centimeter the proportionality constant is sometimes called molar absorptive and then it can be reason given a symbol like absorbent and a= this formula and obviously having units in liter per mole percentage.

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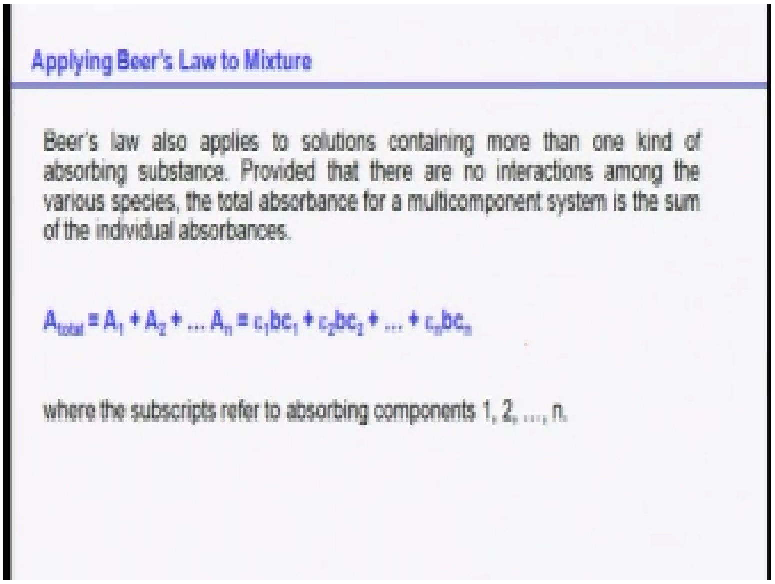

### Applying Beer's Law to Mixture

Beer's law also applies to solutions containing more than one kind of absorbing substance. Provided that there are no interactions among the various species, the total absorbance for a multicomponent system is the sum of the individual absorbances.

$$A_{total} = A_1 + A_2 + \ldots A_n = \varepsilon_1 bc_1 + \varepsilon_2 bc_2 + \ldots + \varepsilon_n bc_n$$

where the subscripts refer to absorbing components 1, 2, ..., n.

So one can actually apply this is the mixture so beer law can be applies to any solution containing more than one kind of absorbing species or substances obviously we need to consider the fact that there is no interaction between these species so total layer absorption is nothing but the summation of the individual absorbs so that means I can write a total =∑i=n to 1 ai that is what I can say and this is very step one now.

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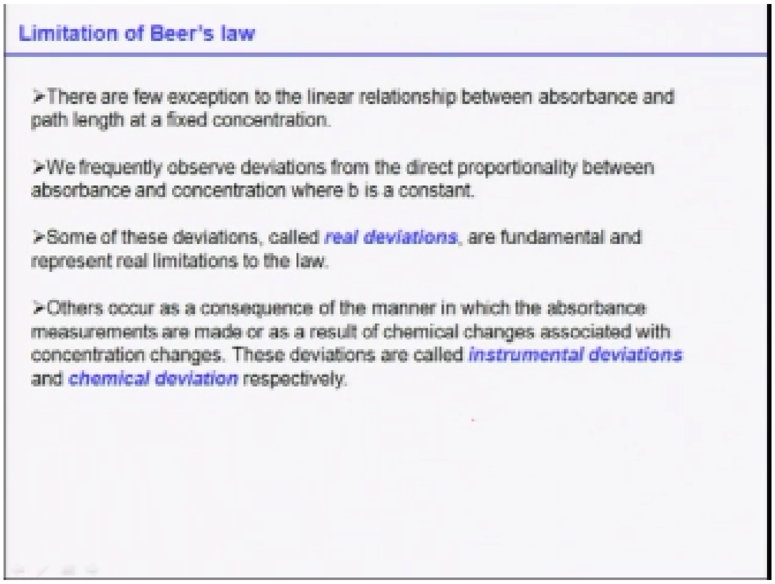

## Limitation of Beer's law

- There are few exception to the linear relationship between absorbance and path length at a fixed concentration.
- We frequently observe deviations from the direct proportionality between absorbance and concentration where b is a constant.
- Some of these deviations, called ***real deviations***, are fundamental and represent real limitations to the law.
- Others occur as a consequence of the manner in which the absorbance measurements are made or as a result of chemical changes associated with concentration changes. These deviations are called ***instrumental deviations*** and ***chemical deviation*** respectively.

So that means one can actually study that absorption process by using beers law and there are advantages of using this, this is very simple and straight forward law but one also known what are the limitations that so that you can take care of there are few exception to this linear relationships between the absorption and the path length that are fixed concept as I said a =axbxc therefore c1,a1 a=b this is the linear law.

We can frequently absorb the deviations are seen in absorb just like deviation in all of we known also linear law but there are deviations here also and these deviations can be real deviations which are fundamentals and we need to talk about this limitations very clearly because we can also have limitations as coming consequences of the absorption measurements like chemical change asset to the concision changes they can be instrumental deviations or chemical deviations so we will discuss one by one first.

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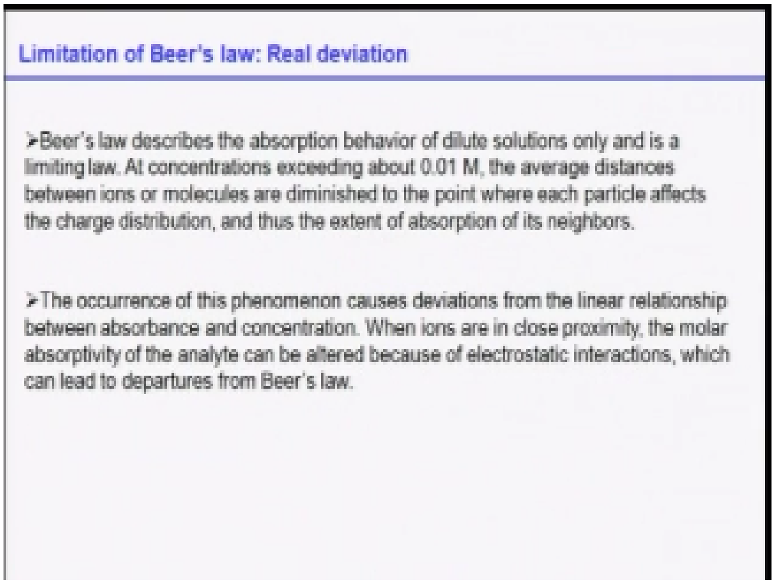

## Limitation of Beer's law: Real deviation

- ➢Beer's law describes the absorption behavior of dilute solutions only and is a limiting law. At concentrations exceeding about 0.01 M, the average distances between ions or molecules are diminished to the point where each particle affects the charge distribution, and thus the extent of absorption of its neighbors.
- ➢The occurrence of this phenomenon causes deviations from the linear relationship between absorbance and concentration. When ions are in close proximity, the molar absorptivity of the analyte can be altered because of electrostatic interactions, which can lead to departures from Beer's law.

Almost one is the real deviations as I said beers law describe the absorption behavior of the dilute solutions only for your kind information and it is very limiting law like law as concentration exceeding about 0.01 molar every distance says between the ions and the molecules are diminished to the point where is the particles effect the charge distribution and thus the extend of the absorption of its neighbor.

So that means if you have pc solution is consists of more than points 0.1 molar beers law cannot be applied to that so that means beers law can be applied only for solutions on pcs in the solution is constant is base small tokens of this phenomenon causes deviations whenever you have more than 0.1 you can cause deviations  between the objections and the concentration and when even ion setting close proximities the molar absolved of the solution of the can be altered because of the electrostatic interactions  this can also lead to departures this is not widely absorbed this is very permanent things.

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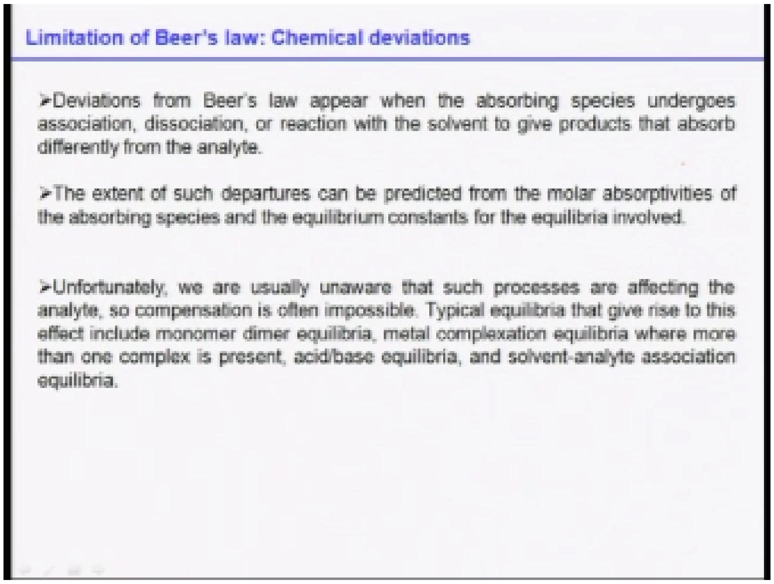

Limitation of Beer's law: Chemical deviations

- Deviations from Beer's law appear when the absorbing species undergoes association, dissociation, or reaction with the solvent to give products that absorb differently from the analyte.
- The extent of such departures can be predicted from the molar absorptivities of the absorbing species and the equilibrium constants for the equilibria involved.
- Unfortunately, we are usually unaware that such processes are affecting the analyte, so compensation is often impossible. Typical equilibria that give rise to this effect include monomer dimer equilibria, metal complexation equilibria where more than one complex is present, acid/base equilibria, and solvent-analyte association equilibria.

Chemical deviations as I said so the deviations can obviously can also appear when observing pcs under goes distortions or associations or even reactions in the solvent that means if there is any reaction of the chemical pcs either it is decision or reactions does not matter it will give you different values of absorption then there is no kind of reactions and when departure and such a kind of departure can be predicted obviously can be molar absorptivities is the absorbing species and.

The and if we know that and absorbing we should also known aquarium constant unfortunately we are usually unaware of such processes at the beginning okay we do not know that and so compensation is now impossible difficult equilibrium that gives us this kind of things that actually monomer or dimmer with polymaths medal complexation and then more than complex is present acid base equibria and solvent analyze so these are the things you should remember can give rise to reactions.

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