Indian Institute of Technology
Kanpur

NP-TEL
National Programme
on
Technology Enhance Learning

Course Title
Advanced Characterization Techniques

Lecture-13

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So in the last class I started discussing about advanced spectroscopic technique and I elaborated you on the different basic principles which are used for this techniques to remind you that we normally use this techniques for spectra analysis of different in organic and organic compounds so whenever an isolated molecule suppose is subjected to any kind of rations and it is excited form a state suppose.

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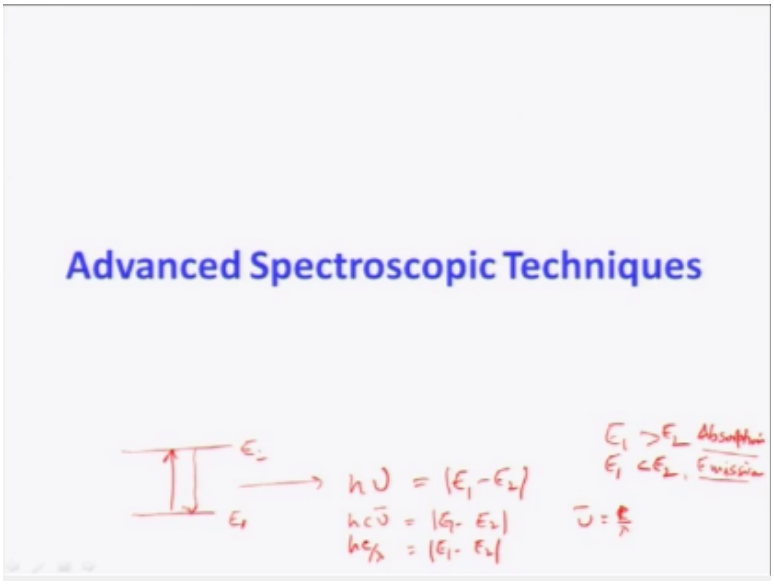

If I write it probably you want to you to it undergoes transition where application of any kind of radiation does not matter what is the wave length of the radiation and in such a case the molecule or the species rather will come back from high energy state E2 to E1 by emitting certain radiation and if we know what is this frequency of radiation we can relate this as this one like this that means the emitted energy of the radiation hν = the modules of E1 – E2 right.

So therefore I can always write this one as hcν bar = mod E1 – E2 so where μ bar is nothing but the inverses of frequency that is c/λ sorry 1/λ and that means it can be written as hc/ λ= mod E1 – E2 so therefore depending on the type of interactions the radiation will have on the molecule on the precise we can either have absorptions or we can otherwise what is known as emission so either we can have a absorption spectroscopy or emission spectroscopy.

Now depending on the kind of energy levels if E1 suppose is greater than E2 then we can have we will have absorption that means if the molecule is going to the higher energy state to the lower energy state by absorbing certain amount of energy then it is absorption on the other hand that means this is absorption another hand of the molecule is going to hid this state to form the lower energy state by absorbing the radiation.

And it comes back that is if you E1 is less than E2 we call it emission so we can measure the spectroscopic measurement we can do either in absorption state or in emission states that is the way normally the spectroscopic techniques are done now the kind of radiation which will be emitted from the absorbed by the species will be depending on the what is the input radiation where applying.

So therefore depending on input radiations different kind of situations can be as possible I have shown the slide in the last class I am showing you again.

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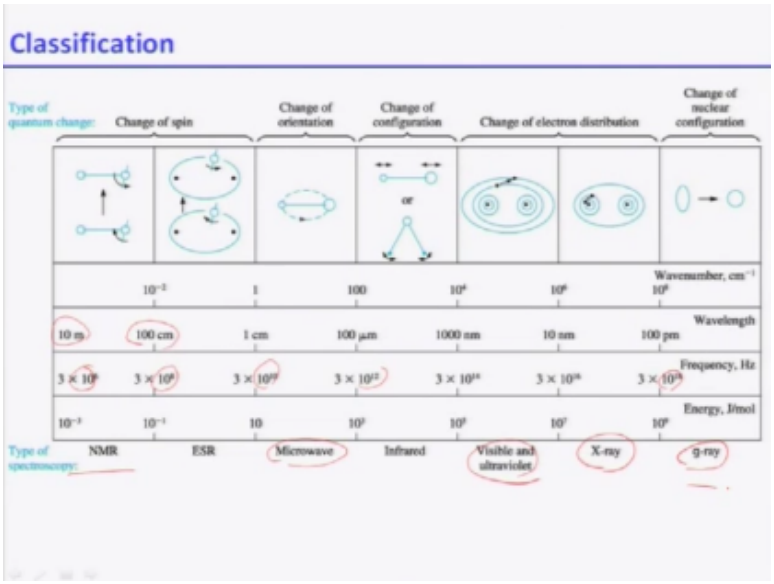

If we have suppose very high frequency like 10^6 10^8 or rather we can have radio frequency like wave length starting from 10m to 100cm we will have normally change of the electronics change of nucleus spine okay can be changed nothing will happen to this molecular the atomic species present on the other hand if the energy levels are little increased form as a frequency level form 10^{10} to 10^{12} Hz that is obviously corresponding to the energy increase.

That is if we go to microwave prisms and then we have change of orientation in the molecules okay or change of configuration of the molecule infrared can also lead to change configuration under molecule and in the visible ultraviolet energy you have change of electron distributions or rather you can always have sign some kind of rotations or tangential between different electronic states which can inclusion of the rotations.

Finally in the ultra monitory x ray regions tragedian can occur which can ionize or dissolvent a certain molecules that is what is shown here in the x ray and if you apply very height energy that is γ ray okay that frequency into where 18 very high frequency then you can have change of nuclear configuration itself like you have the nuclear pieces can undergo tangents so by using host of radiation starting from radio waves to the γ rays one can get a large number of spectroscopic studies done.

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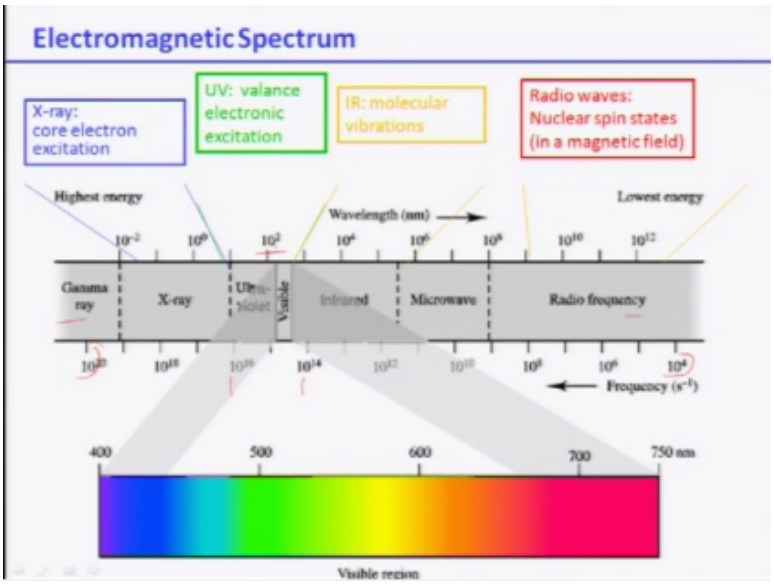

If the students lecture what I am going to do is we are going to analyze or look at it the most simplest one or most you know widely used and the oldest technique in the spectroscopy is called UV visible that is if we use the radiations which where lens are in the range of visible or near was called visible but in the out of valid range so I have show the whole spectrum starting from γ ray to the radio frequency 10^{-} 10^{20} rather 10^{18} to 10^{4} so I can Hz and UV visible comes every small 10 you can see this frequency under per 1600/ 14 that means the wave lens would be a couple of 100s nano meters.

It will be something like 182, 160 or 70 nano meters inner range and visible we know it consisting of large number of wave lens like red to already white is called red to violet red, orange, yellow, green, blue, indigo and violet 7 colors are possible that took a very simplistic prospective of this ultraviolet and UV visible spectroscopy I just start my very basic thing you know the obvious difference between many compounds is color.

Right to give an example color fill is was called green on the other hand very complex once like say 24 dry nitro phenyl hydrogen and derivatives of any alkenes, ketenes are okay basically bright yellow kind of on the other hand yellow so this is this are the general difference of the color of different compounds now obviously the you have already leant in your different course that quite different materials are different chemicals show different kinds of color.

Well that is basically that is somewhere on I perceives or I basically sees an object and then se determine the color sky is blue sun yellow like that so why it so because the light reflect on the

surface of page solid basically passing through a liquid is comes vector eyes and we see the particular wave lens of light can form a particular substance and that wavelength obviously corresponding to different colors like red, or may be yellow or may be your violet.

In the whole visible sectors meter this is what we know so that means your I is basically a spectrometer acting as a spectrometer to be frank our I can actually distinguishes different colors kind from different objects so this probably the simplest spectrometer one can always say that I can be of many things it is basically a camera is basically a filled camera or we can I can always steel that from probably spectroscopy point of view this is a spectrometer simply spectrometer.

So and then there are many compounds which a color less correct there is no color so that means where light falls on them no light basically comes to our eyes in the wave length range in the visible so that we can do not see any color so most important aspect will be those objects which are which looks color less there emitting lights or emitting radiations whose wave lengths does not fall in the normal visible spectrum this spectrum range.

Red to violet so they may be coming in the near α red α ultraviolet regions that is why we do not see them are do not see their colors we at red then colorless now weather light wide light consisting of all kinds of this wave lengths starting from red different colors started red to the violet is passing through are basically getting reflected by any colors outstands and we know that it basically characteristic positions of the mixed wavelengths okay all this mixed wavelengths one to 200, 300 to may be 600 nanometers is absorbed remaining positions other light reaming light will assume that complementary color obviously whatever we will be observe will not be seen and whatever those wavelengths will not come tour eyes, so whatever we will not be observed by that colors substance we will come back to the eyes, so we say the complementary colors so that means we can say that if something is observed in the two port and put that in 30nm into the land or real log like if something observes light in the wavelength 500 to 520nm it will be looking red higher lengths red.

That we know why that is why the rates signals and this of the for lights and therefore there are many so on, okay so early human beings actually seen this different colors and that is the just of the story actually goes and use this for decorative purposes you know many of these are organic minerals in fact we know the many stones which are used for dually purposes are colorful

because of the color there are many organic substance like dyes there also color, so that the question is no dissolve well known.

To all kinds of students so even the schools students also they know question is that how can I use this concepts as I said this I using lights to determine molecular or electronic transmissions in the real that is called scientific purpose and so that can be done you know by using common feature of these colors compounds whichever displays whatever I have told you basically system which is extensively conjugated by electrons you know probably the electronic structure there are σ bonds ϕ bonds and other bonds.

So these are the ϕ electrons which observed radiations in the visible range and that is what we see the different colors so this is all very typical or many spectroscopic techniques and this are that we will discuss and I will discuss different parts of that, now as I showed you that.

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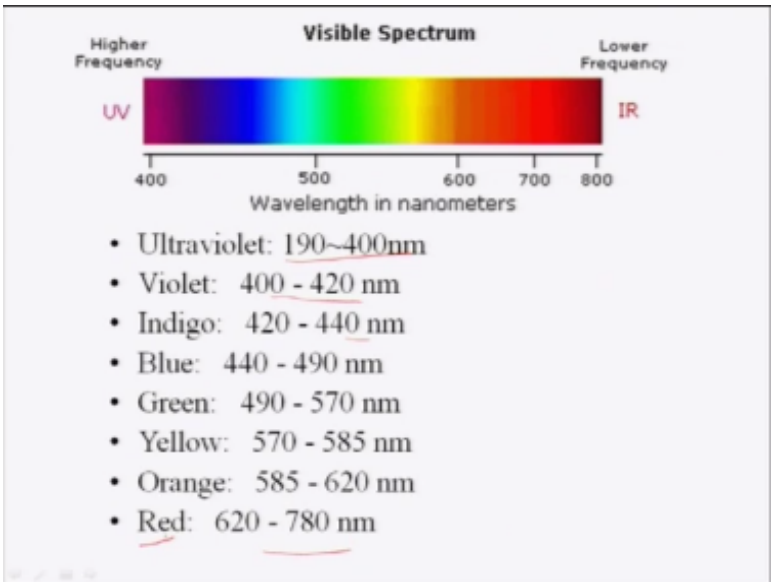

I will show you the visible spectrum in detail manner ultraviolet falls in the 190 to 400nm violet is 400 to 420mm indigo is 420 to 440 and red very high wavelengths 620 to 770nm so that means red will have very what is the smallest frequency from ultraviolet to red.

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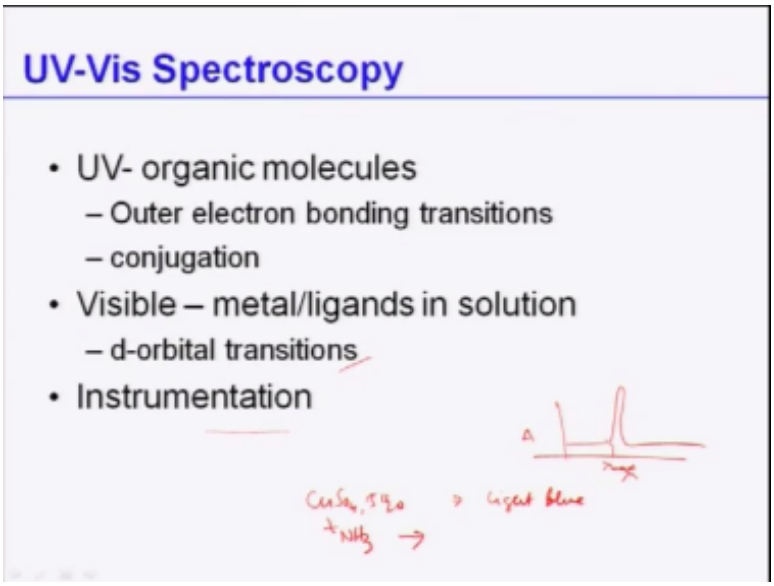

So what are the different things we will use spectroscopic can do while the principles spectroscopy as I said and now said can be use for determining the different molecular transitions or electronic transitions are there in the organic molecules like outer electron binding transitions conjugations which we will discuss in detail are visible ones can be used for metal/ligands in the solutions like d – orbital transitions okay, and at the end of this lecture if I will discuss our instrumentation is also so to give a better idea UV spectroscopy is routinely.

In many of the de chemistry labs if we just walk in the chemistry labs people uses now-a-days in fact the metal sands also those who people studying it different kinds of nano particles in the solutions we use extensively visible spectroscopy, and we can actually do both qualitative study and the quantitative study like transitions metals stands we know that they show different kind of colors because of the de alloy electron transitions and they will similarly they are many others, so solutions transitions.

Solutions of transition metals stands are colored okay and that mean they observe visible lights because electrons with these metal atoms can be excited for one electronic state to one in the electronic state that is what sure, so that because we know that the color is because of the electronic transitions form electron transitions form electronic transition from the lower by energy to the higher energy, so that means we can actually determine what is the exact electronics state and these can be basically.

Affected by different and then you know that different this colorful media has different PCs like different ligands okay two example copper sulphates Us is for and 5 H20 this compound basically is very light blue we know that we all of use copper sulphate in the school days for doing experiments, if we add ammonia to it NH3 it becomes in a color is more light or rather the blueness of the copper sulphate increases and that means there is a change in the wavelengths where the observes in maximum.

Happens so we can actually if you plot the absorption by wavelengths a versus wavelengths so at a very high absorption wavelength λmax will see high absorption and these λmax will tell us the electron transitions, similarly organic compounds like DNA RNA those are very high conjugations sub so light in the UV region on the visible regions, solvent of digital of this determinations are of an water or water solution we know that it all can also used, so that means the absorption in the ultraviolet.

And near the ultraviolet in the visible spectroscopy regions visible wavelength region can be used to study this kind of features, and to tell the excite ultraviolet of the absorption process let us look that.

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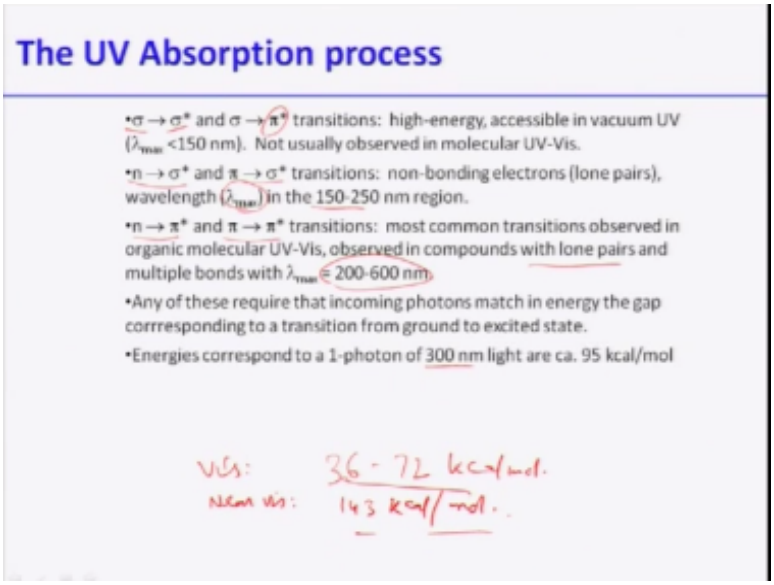

So we know that5 as I told you that different kinds of ball σ1 ϕ bonds so we can have σ from bonding are metal to the into bonding are metal are σ to anti bonding π* arbitral transitions there are high energy all we accessible in vacuum ultraviolet that is when the wavelengths are less than 1 50nm not usually observes in the ultraviolet visible spectroscopy, at the end to σ is tell discuss about Nσ or π in the detail movements time or π to σ transitions they actually bonding to non transitions.

Always staffs stands corresponding should non bonding transitions that is along pair electrons normally wavelengths while these absorption is maximum falls into 250nm to 50nm region or you can have like n to π* or π to π transitions was common absorbs in organic molecule this transitions and they absorb with loan payer and molecule bonds normally in a little higher wavelengths 200 to 60nm any of this equals in coming photons to be matched in the energy the gap correspond to transitions.

From the ground state to the excited states like combine to the π* energy is correspond to a one photon of 300nm slides are basically 200 and 50, now visible region or spectrum obviously

corresponds to the energy level form that is 6 to 72kc/m right now the near volume which will be high so there energy will be near this is visible then near visible to a little high so this will be approximately 143kc/m and in that case we know this energy is or the energy is to dissolve submission and up to promote.

Are excited molecule transitions this is very high from this and up to kind of transitions and absorb and so therefore we normally can use this as a transitions.

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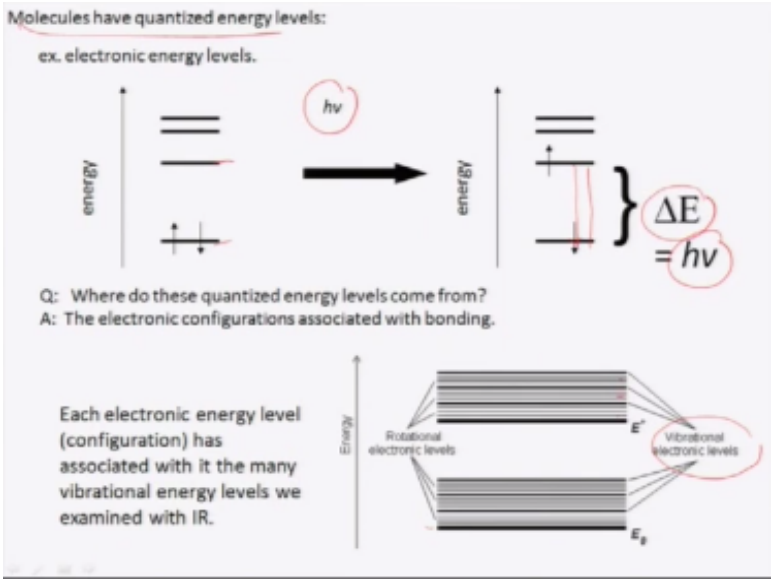

Can use this as a transitions so to give you some better idea let us know that molecules have quantize energy levels from quantum mechanism we have already started you know then your energy and their different energy levels okay and if I applied certain energies is like are visible spectroscopy visible range then you can see the transitions happen from this level to this level okay so whenever this excited state will go back to the ground state that will be emission and emission will correspond to the wavelengths.

And sometimes you know each electronic levels can be thought of as to be many energy levels so like this, this higher energy levels in with each you can see that different vibration energy levels matches okay and they are studies in IR infrared spectroscopy which we will discuss after sometime and you can rotation energy level or electronic state can be get rotated also, so therefore one can determine this transitions.

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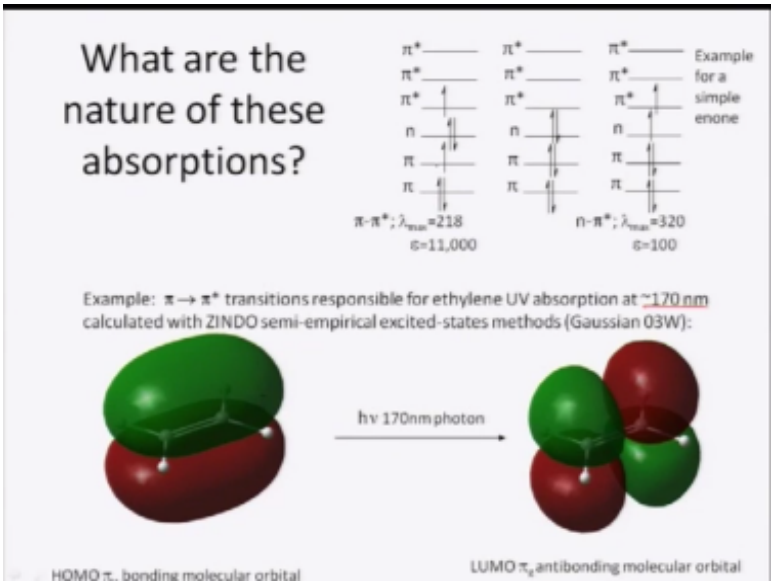

So what are the methods of this absorption just now I told you like one example is σ2 there is π2 π transitions ethylene so at about 170 and it can be calculated actually using the software and like this, this is the homo πu HOMO means if you know high occupied molecular orbital and you can have a LUMO lowest occupied molecular orbital and you can see it is going from one molecular orbital to into molecular orbital the dis π to π* if I apply 170nm photon.

And this transitions cab be easily detected this is absorbs, so one can actually show that in different charts and like you can see there π πn then there is a anti bonding orbital so you can have different transitions from π to this π or π to n then n x π* or you can have this type also like reversible transitions or you can have n x π* others are reversible. So how can different transitions possible this happens are laminar max of 218 this happens in a 11, 000 so 320.

And the so this is in what happens in ethylene molecule ethylene this we know that this is CC H 2 H2 that is CH situate for so there is a double bond here and this is what shown there.

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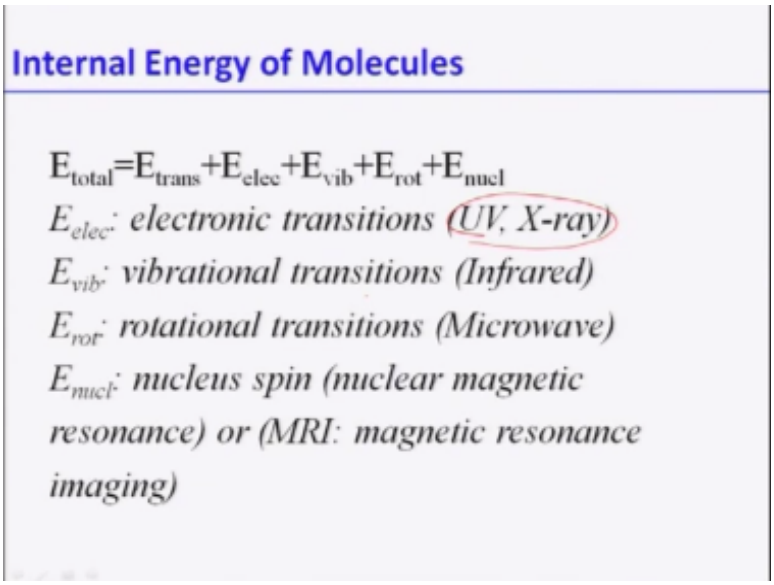

Well so if I consider the total internal energy of the molecule to be simplistic let me consist of E trans at electron transitions are E electrons that is sorry E transitions is the transitions then the electron transition elective then vibration transitions rotation transitions and nucleus transitions. So normally electron transitions are determine by UV and X- ray, the vibration also had infrared and they are just thus I have just told also.

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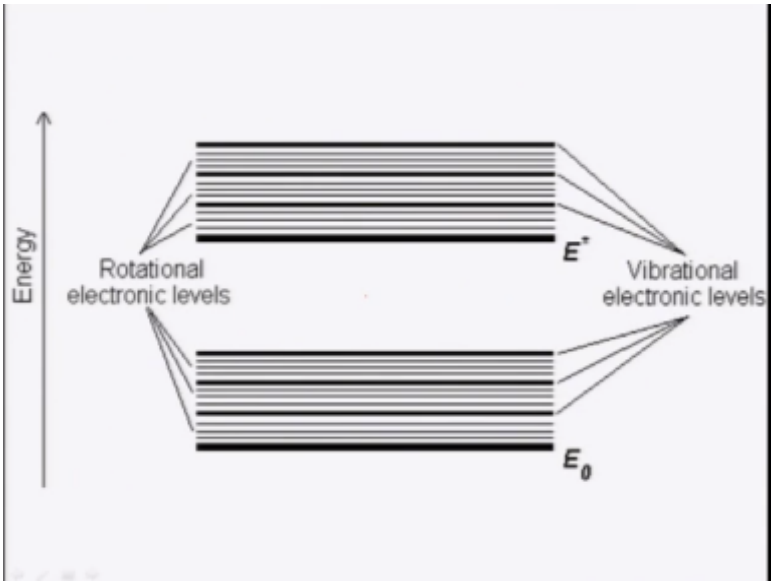

And this is a different assailable that I have shown you.

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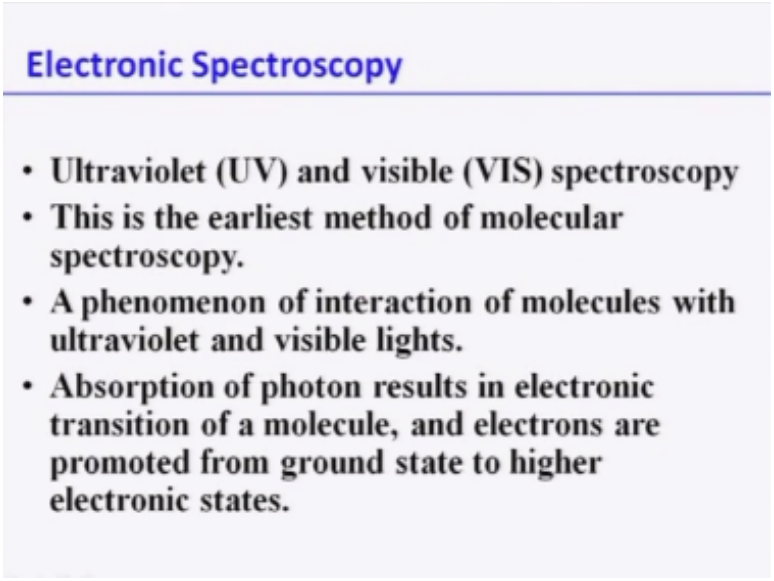

So in UV and VIS spectroscopy this is the interactional molecules and absorption of photon results in electronic transitions I have also told.

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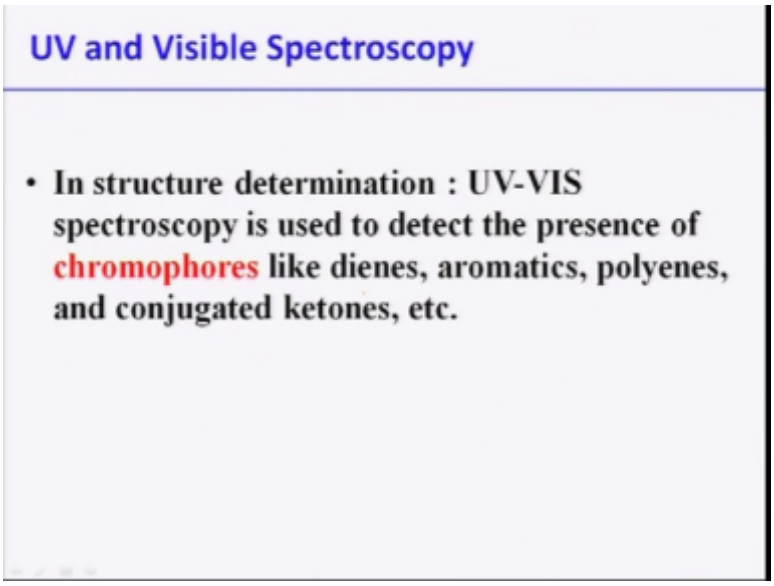

What is most important thing is that this once are used to detect the presence of chromospheres like dienes, aromatics, polyenes, and conjugated ketones etc, we will also discuss what is this okay.

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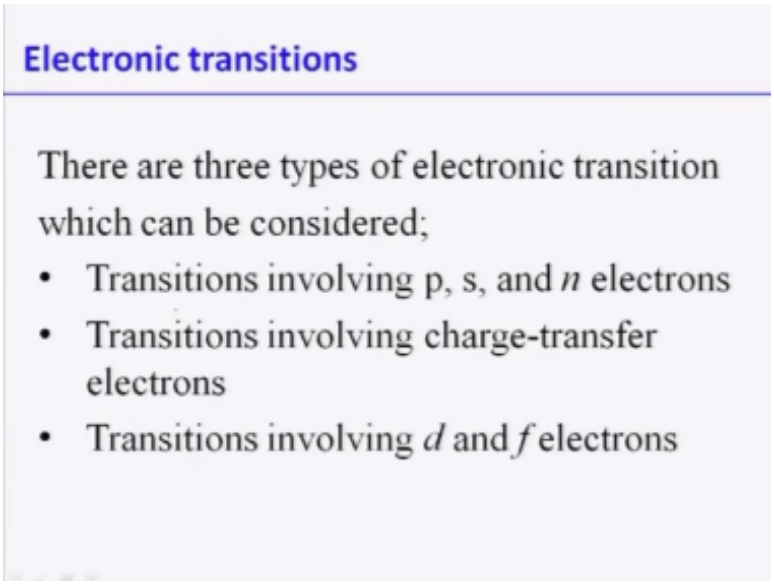

So there are as I said I will discuss about these different electrons etc θ which can happen actually one is p, s and n electrons and transitions involve basically charge transfer, and transitions involving d and f electrons also possible in metal lanes.

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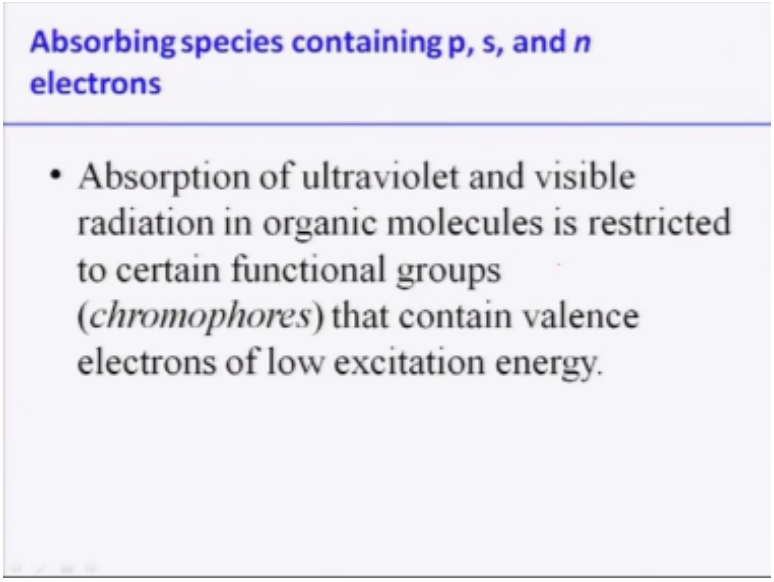

Like transition metals absorptions of this lights like ultra water visible radiation organic molecules is restricted to certain functional groups like chromospheres, that contain valence electrons of low electronic excitation energy that means if we want to have a transitions in the visible spectroscopy for p, s and n electrons the excitations energy should be as low as possible. Otherwise because UV and visible not very high energy so it will not happen.

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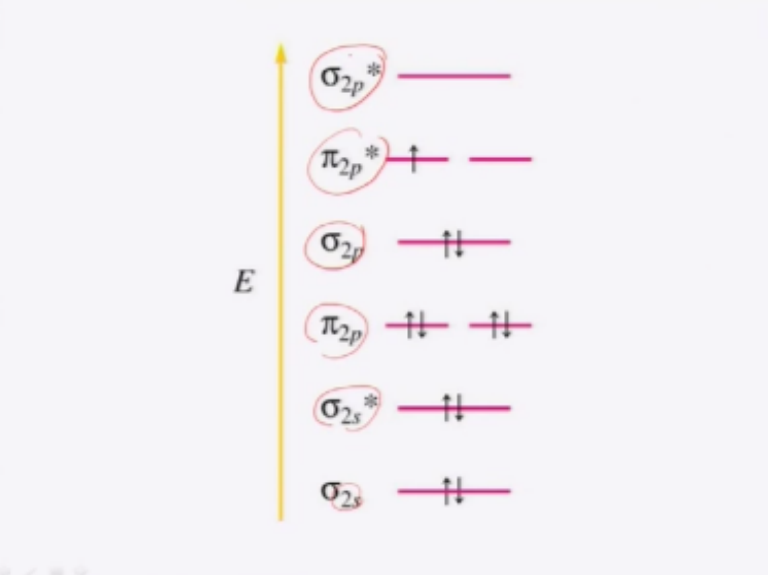

This is again shown here this is like σ2 s σ from 1 x anti bonding π to p to π 2p* bonding tan t one is σ 2p to σ 2p* bonding to anti bonding orbital.

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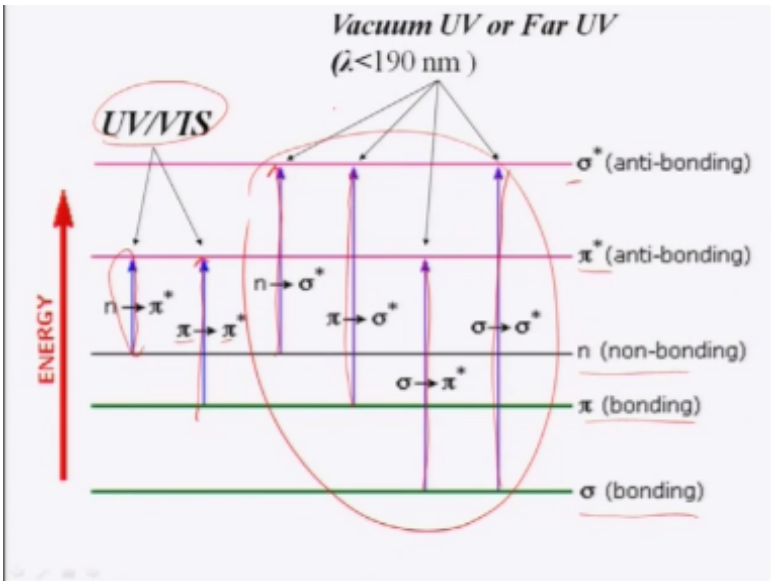

And if I want to show in a detail this what I shown here this is the σ bonding orbital or n non bonding orbital then π* anti bonding σ trans anti bonding, energy level increases this way. So transitions are like this from n to π* is this one which is shown here left one or σ π to π* is this one shown here this can detect by UV visible okay. Now you can also have transition like a x σ* like non bonding to anti bonding or you can have π bonding orbital to σ anti bonding orbital or you can have σ to π* you can have a σ to σ *.

So and you know that these transitions required different as levels, so depending on these energy is available we can basically use different wave lengths of light or UV to have the transition possible. So that is what I said in a martial in a UV visible spectroscopy U actually got to know the exact transitions happening from different electron are growths. And these are the different electronic arbiters possible.

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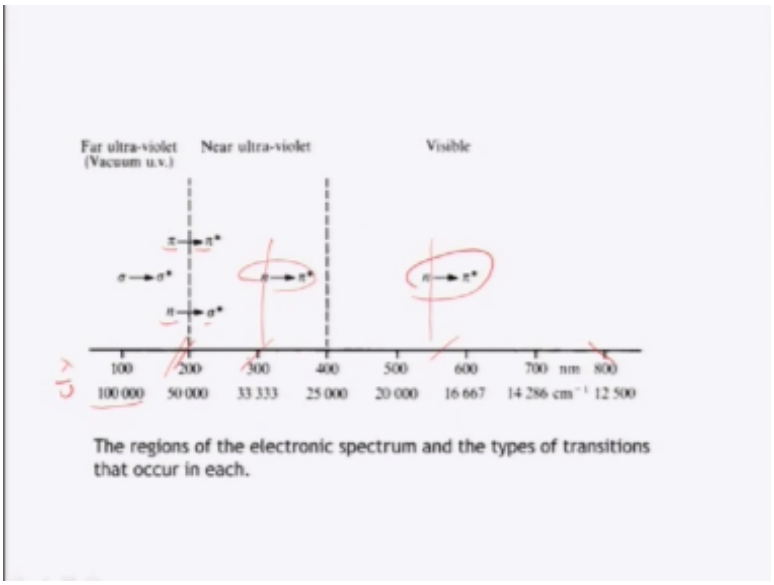

The regions of the electronic spectrum and the types of transitions that occur in each.

And again this is shown in detail manner okay so that you can even look at it and this is I think this is the new bar and this is λ, so 100 200 300 400 nm up to 800 and this is visible from 200 to 800 and then 200 200 near ultra violet 200 200 is 5 ultra violet or vacuum UV which are normally you not used in usual spectroscopy.

So we will talk about from 200 to about 800 or 700 nm and you can have this kind of transitions and 200 wave lengths you have these are actually so π to π* n to σ * possible and in 300 level is n x π* and very higher visible then you can have n2 π*. So therefore if you use these wave lengths we can determine these transitions very easily.

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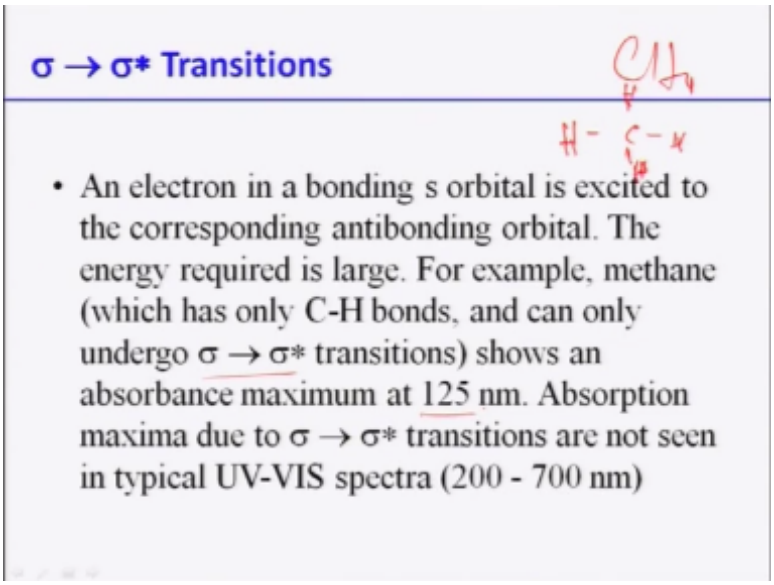

Now let me tell you each of this transitions, σ to σ transition and electron in a bonding s orbital bonding s orbital s is one of this ASPD orbital they are in a atom, so electrons and electron in a bonding orbital s is excited to corresponding anti bonding orbital. The energy required is obviously very high because s is the lowest energy level so you have to take it from the s and the state to the anti bonding state is very high.

So that when you methane like you have CH 4 in a methane saturated compound all you see is bonds are there so I can actually write down there are four CH bonds in methane molecule, and this bonds are actually all saturated you know that and can only the undergo this σ to σ* transitions that means electron can be excited from s of bonding orbital and to the anti bonding orbital and maximum absorption for this is at about 125nm.

So this transitions are not seen because 125 is you know in far UV and not seen in the visible spectroscopy to the edge they have to be use we have use for UV or vacuum UV>

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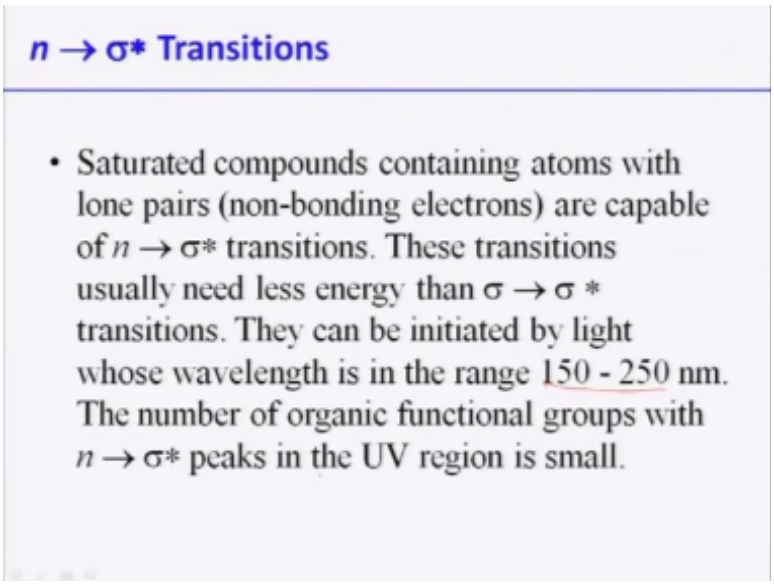

And if we have a end σ* transition that is non bonding to anti bonding σ* such that compounds like contain atoms like lone pair non bonding electrons they are able to this transitions this transition usually need less energy than the σ to σ* obviously because you are going from one in to anti bonding σ of our transitions saturated. They cannot be initiated by light whose wave length is in the range of 150- 250nm number of organic functional groups with n * peaks in the UV region is very small. Because the range is 150- 250 that range is has to come very small.

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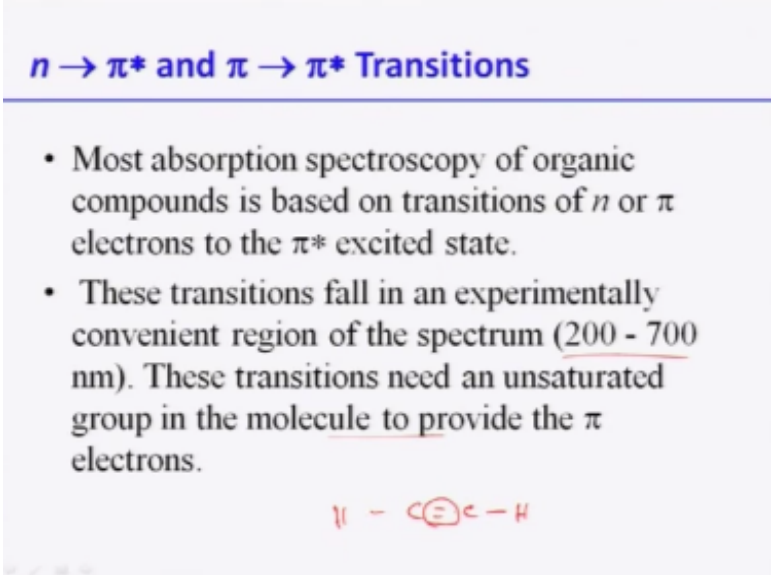

Now if you want to look at n to π* or π to π* transition there the most one most is easily detectable in UV visible most aspect to be organic compound is basically based on the transition from a and π electrons to the π * excited state. Transitions fall in the experimentally convenient region of the spectrum like 200 – 700 that is visible to UV this transitions are need an unsaturated group in the molecule provided the π that is the ethylene.

Ethylene has unsaturated this bond double bond and it has also π electrons which can undergo transition from 1 into anti bonding. So these are the things which are called chromospheres,

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Chromophore	Excitation	λ_{max}, nm	Solvent
C=C	$\pi \rightarrow \pi^*$	171	hexane
C=O	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	290 180	hexane hexane
N=O	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	275 200	ethanol ethanol
C-X X=Br, I	$n \rightarrow \sigma^*$ $n \rightarrow \sigma^*$	205 255	hexane hexane

CC double bonds CO double bonds NO double bond or you can have CX x can be bromine adding, and CC the all one types you will normally have π to π* transitions and like ion XN is all went if this is the maximum wave length possible absorption can happen you can have n - π* σ or n to π* transitions π to π * and these two wavelengths for kitons for maters grope you can have a different wavelength such and these absorption maxima and for this kind of CX bonds you can have n – σ* or this is non bonding to anti bonding σ* or transition that is a these wavelengths possible. In all cases except niters bonds we use what is called XN in this situated and is all went.

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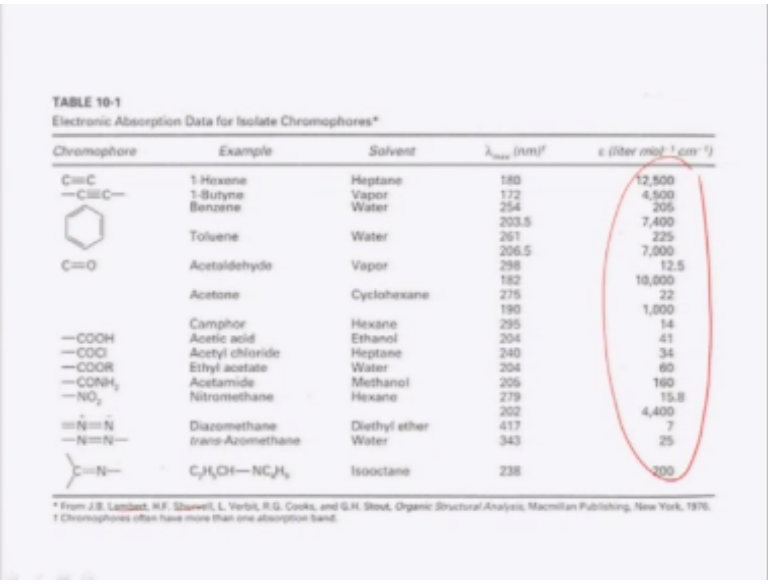

TABLE 10-1
Electronic Absorption Data for Isolate Chromophores*

Chromophore	Example	Solvent	λ_{max} (nm)†	ϵ (liter mol^{-1} cm^{-1})
C=C	1-Hexene	Heptane	180	12,500
—C≡C—	1-Butyne	Vapor	172	4,500
	Benzene	Water	254	205
			203.5	7,400
	Toluene	Water	261	225
			206.5	7,000
C=O	Acetaldehyde	Vapor	298	12.5
			182	10,000
	Acetone	Cyclohexane	275	22
			190	1,000
	Camphor	Hexane	295	14
—COOH	Acetic acid	Ethanol	204	41
—COCl	Acetyl chloride	Heptane	240	34
—COOR	Ethyl acetate	Water	204	60
—$CONH_2$	Acetamide	Methanol	205	160
—NO_2	Nitromethane	Hexane	279	15.8
			202	4,400
=N=N	Diazomethane	Diethyl ether	417	7
—N=N—	*trans*-Azomethane	Water	343	25
C=N—	C_2H_5OH—NC_2H_5	Isooctane	238	200

* From J.B. Lambert, H.F. Shurvell, L. Verbit, R.G. Cooks, and G.H. Stout, *Organic Structural Analysis*, Macmillan Publishing, New York, 1976.
† Chromophores often have more than one absorption band.

And this is the table which is obtain from this book Lambert and Verbit Cooks Stout Shugell organic structure analysis from annular publications and what is showing you this different chromospheres and the present in different compounds solve and to use absorption maxima and one can actually molar absurdities values can be calculated from the Lambert we are slop we are slop rather which again I will discuss.

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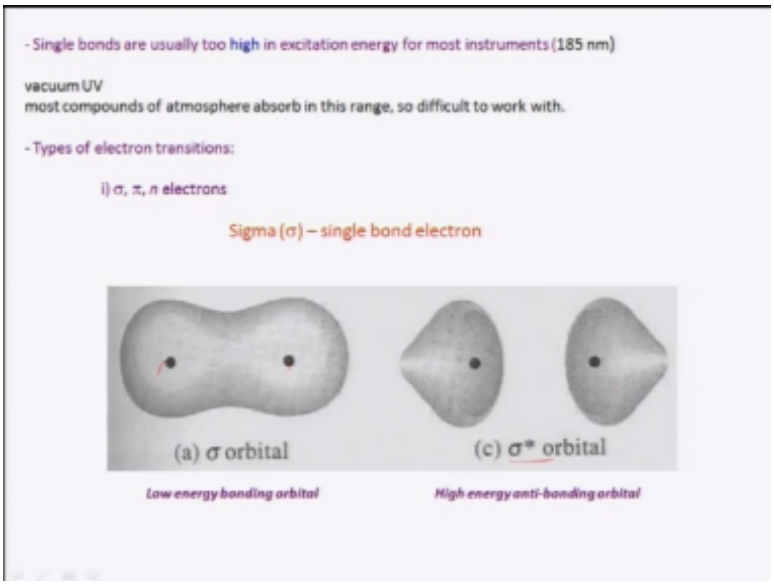

And to for those of you by not have to understood exactly what is a σ bond σ bond is basically suppose you have two nucleus and this is of the electron distribution happens in a σ bond okay, single bonds usually too high and you know it because very high satiations we want this to go to the σ* transition σ to σ* transition that is σ bonding to anti bonding transitions this is a very high we have seen also.

So we need vacuum UV and then you can have this is the anti bonding, so you break this bond between them and from this kind of transitions. So this is low to high from bonding to anti bonding σ.

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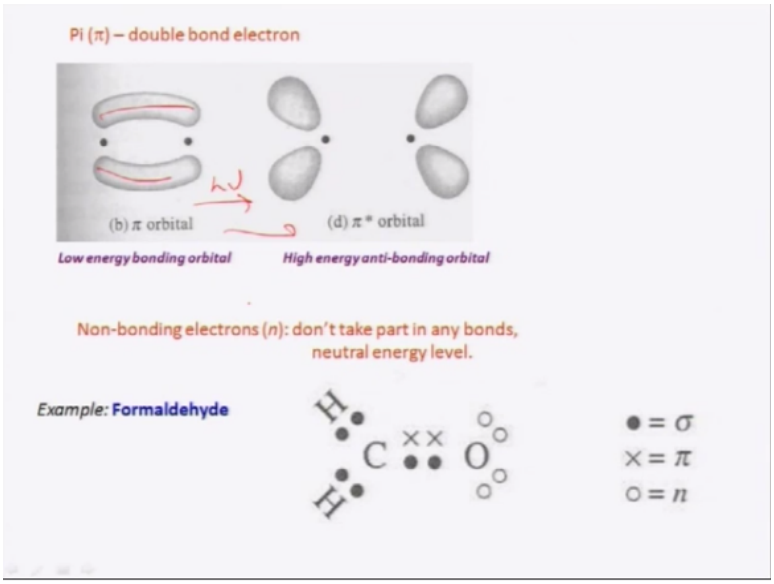

π is the orbital is like this you can have electrons distribution in this kind of geometry and if you want to excited by using of certain energy it will go to the anti bonding state of π* where there are difference states different say this is easily accessible by visible spectroscopy and non bonding electrons do not take path any bonds actually they are neutral energy levels.

.To give an example like a formaldehyde very classical compounds either a carbon there are two oxygen or there is a double bond here and carbon. So this is like this I can write down, so there are two electrons here, there are 4 electrons here 2 are bonding on two others and the oxygen as 4 electrons.

So we can clearly write this black dots filled once a basically σ cross are basically π and these are actually none bonding type. So you can have in this molecule itself if I apply energy there are different kind of possible. I hope I have given you enough idea, so in a ethylene if I want to write it down properly ethylene.

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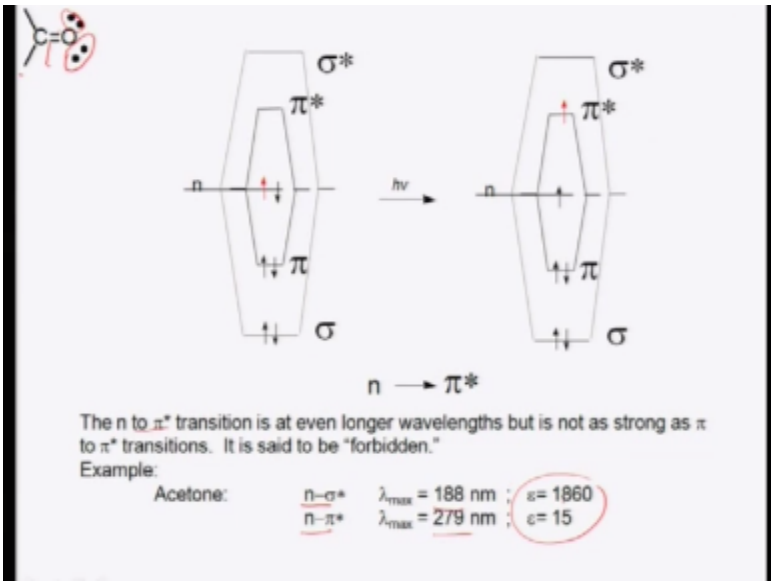

You can see that this is the π and this is σ and different energy levels I am putting and these are the σ π * and σ anti bonding and if I apply energy levels all has probably has happen because it is of double bond within the 2 carbon atoms. So this chemosphere is cc double bond. So you can undergo from π to σ π * I am giving this much of energy and this happens and this lens. So these are known classically so one can use it very easily, similarly in a ketene these are non bonding electrons.

And there is the double bond and there are π and other electrons, so you can have different kind of transition like π to π x * or π to π * σ to σ * by putting an energy level. And when into π * transition is actually longer lens but not as strong as π to π *. So therefore x π * is normally forbidden. In acetone this aim to σ transition happens at 188 nanometers and π * happens 279 nanometers with given by this value.

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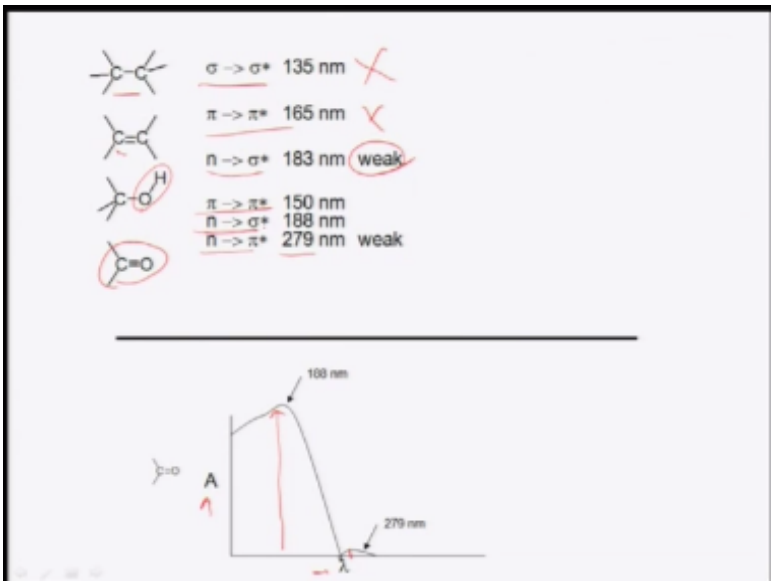

And I can actually go and tell different terms of this is saturated carbon bonds where we can see that is the only possible thing is σ to σ * is very high energy not possible in visible spectroscopy CC single bond π to π * is also not possible. And the end to σ * in this case very weak, so may be possible 183 and then you can have group that is the alcohol, you can have σ 2 π to π * x σ * into π * transition.

So same thing is possible in this to give a ketone situation you can see that there are s πkes in the wavelengths at 188 when you put an absorption wavelength and 279 so these two are telling you two kind of transaction are possible one is at 279 is basically correspondent to n to π * and 180 it correspondent to n to σ transition.

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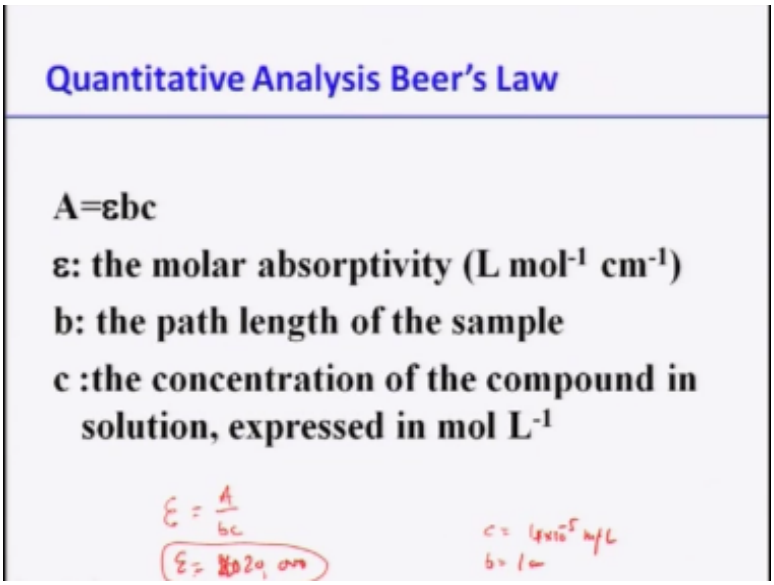

Now this are all quantitative discussion now what we can do is that, we can basically use Beers law to quantify different kinds, as you know that when light passes through a molecule subject to the light or particular wavelength is passing through a solution when a molecules are there, they can go under transition passing through a solution when the molecules are there they can undergo transition.

And obviously some lights are getting absorbed some light is used to promote this kind of transition, records the wavelengths at which the absorption happens eyes is also optical spectra meter it also do the same stuff and then the spectrum which is presented as a wavelength and it gives you peaks. So absorption usually range is form there is small value like 0 to 99% possible and it can be precisely determined by the specter meter.

So because the absorption of the sample is basically proportional to the number of the absorbing molecule present in this solutions, the molar concentration is basically determines the absolute sample and then that one needs to correct this absorption by different kinds of parameters like optional parameters and to exactly obtain the amount of the light and the amount of the radiation absorbed by the molecules present in the solutions.

They collective absorptions is obviously called as molar absorptivity and they can be used to determine basically this is molar absorptivity using this formula which is given here a/bc where a is the absorption and the b is the path length through which the light is passing through and the c

is known as the concentrations. So this can be done so suppose I will give you an example if I take a iso plane is a rubber all of you know this natural.

It is obtained from the tree and it is used for many kinds of purposes, actually in dilute solution if you have c = -5 moles per liter and if the path length p is basically 1cm and then we can use this formula and get σ to be about 20000 amount. So by knowing this ε we can actually quantify the different kinds of absorption behavior by the molecules.

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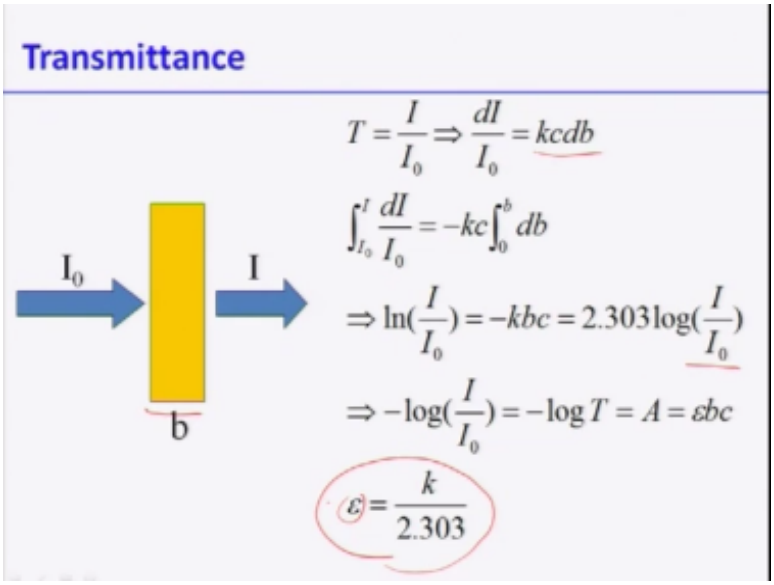

And this can be even formulated by this way suppose I is the initial radiation initial intensity of the radiation and this is the path length and I is the final which is coming out I/I0 d I/d0 is basically Kc db you can say this k is the constant and then one can get this kind of formula and the ε which is the molecular absorptivity can be written by k / 2.303 which is from log.

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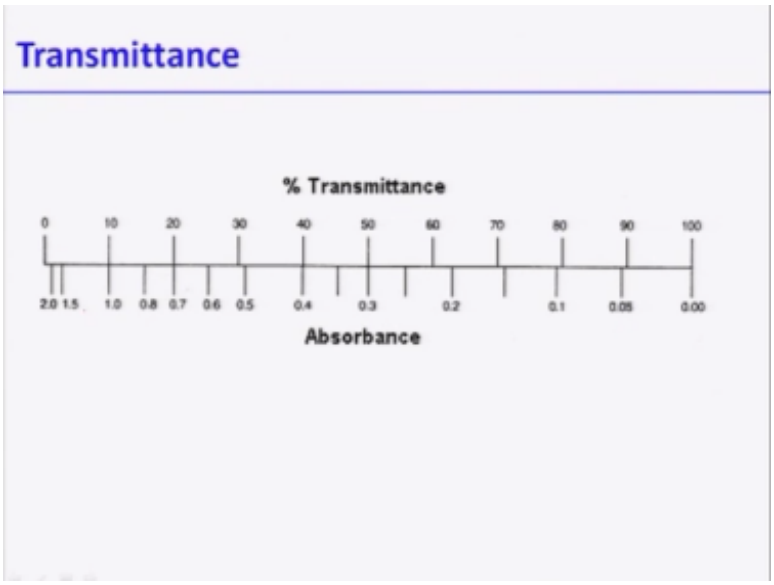

And transmission as I said can vary from 0 to 100 opposite is the ε can vary from 0 to2 % in this way, so one can actually get an idea.

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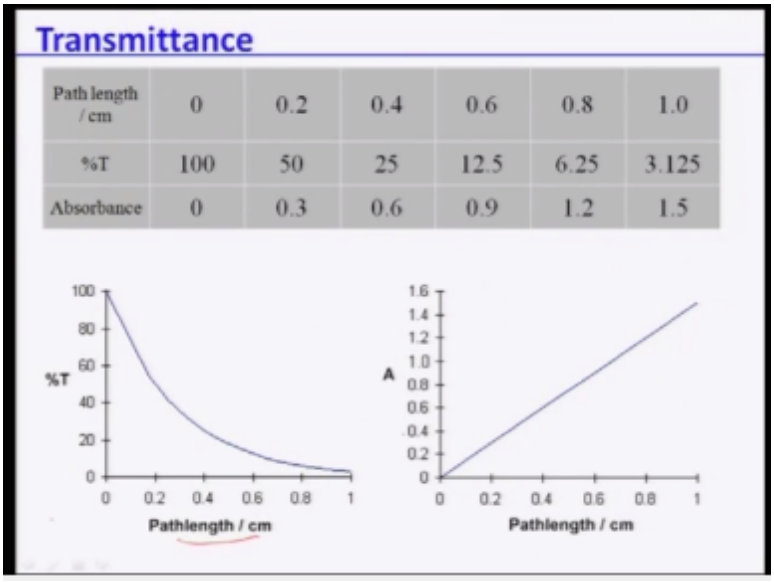

Now depending on the path lengths obviously 0 to 100% transmittance if you have 0.2 so one can get % absorption versus path length this kind of behavior and,

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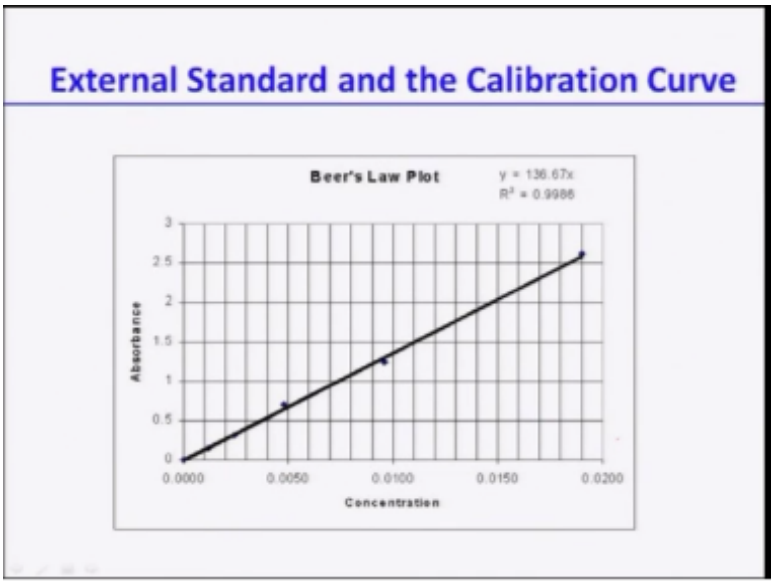

Then one can actually use this external standard and calibrate this curve so this is the absorption and this is the concentration you can see it the follow of the linear raw law where r is very high so the fitting which is almost 99%.

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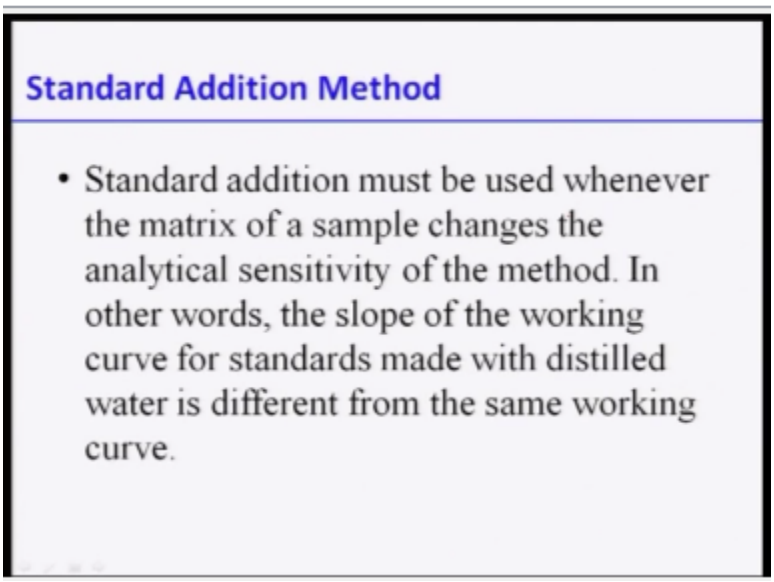

So standard addition method must be used whenever you have a matrix because you have lot of other factors which determines the absorptivity and the slope of this working curve the standard made it distilled water is different from the same curve.

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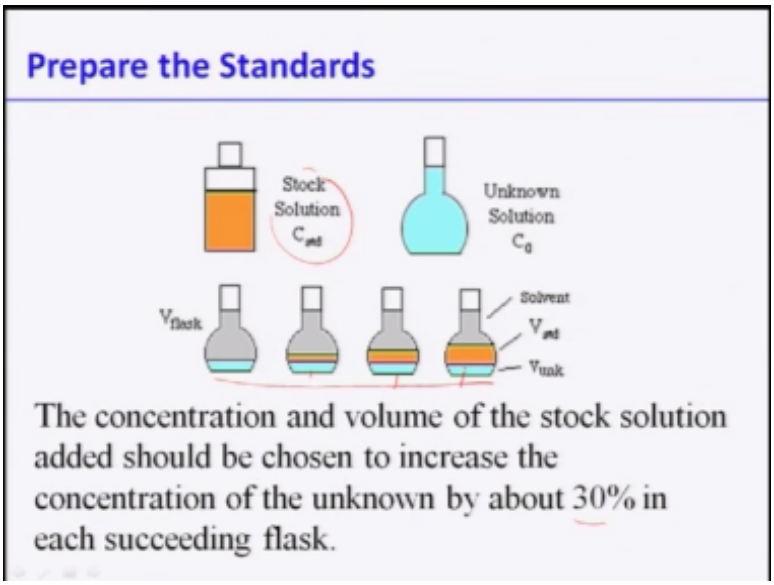

How do you prepare the standards can be prepared in different ways like this is stock solution and then you can dilute it and get the different concentrations and that is why you can prepare the standards. The concentration and volume of the stock solutions added should be chosen to increase the concentration of the unknown by about 30% in each flask. That is this is the known and this is the unknown so you add unknown quantity concentrations and then add up to maximum 30%.

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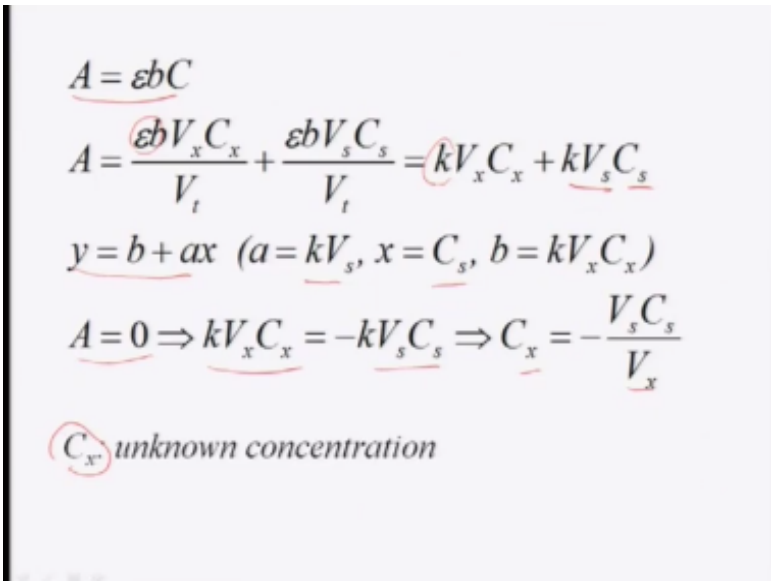

And this is the response one can see that if you plot Csa and this is the deadline it passes from these two points, so using this one can actually find out this is the unknown concentration Cx as you know A is given σ bc c is the concentration and the b is the oath length. So we can write σ bcx / bt and this is the known and this is the unknown and this is k σ ε b/ Vt and V t is the total volume.

Cs is known and basically x is the Cx and therefore when a goes to 0 Kvx is – Kv Cs so that is why we have to do. Before I go to the real instrumentation how the experiments are done let me show you some spectrum.

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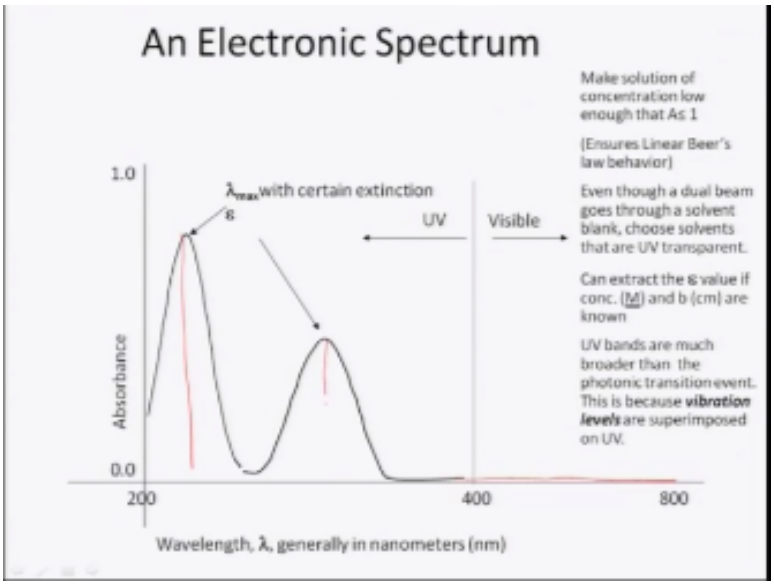

So this is 1 spectrum electronic spectrum basically shown here you see there is nothing in the visible range these are nothing absorbed in the visible range so 0, what as happen is that there are two peaks in the uv range for this compounds and they are coming at different values of the λ and the one can actually determine this ε that is molar absorptivity by using this two different compounds. First one can find from the speaks right at the exact so what is probably done is that normally if you want to apply we need to use very small concentration and as I said UV bands are broader when the photo therefore this is bi rational research normally super imposed that is now people say.

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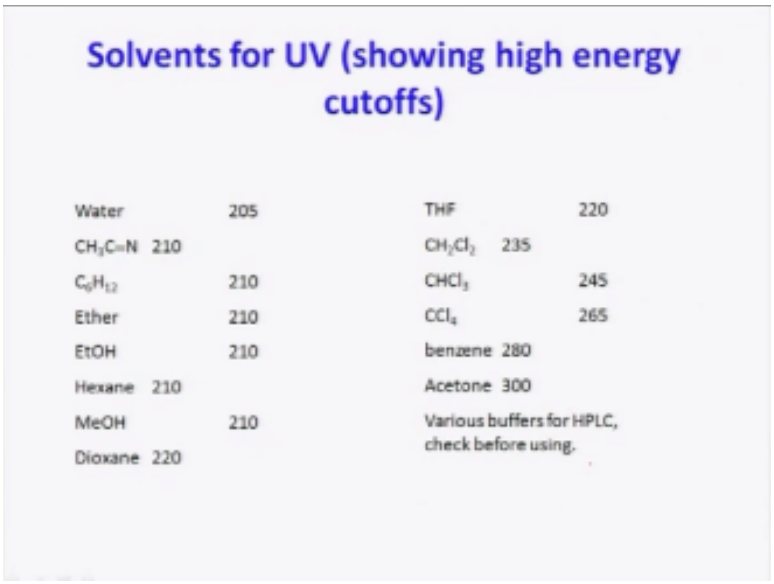

While what solvents normally used for UV like water or you can use this very high epsilon you can use CH3CN okay which has two C6H12 is hexane to 1 and 10 ether 1 and 10 very small we have literally call and 10 hexane also 210 methyl alcohol 210 dioxin 220then you have CH2CL2 235 CHCL3 245 CCL 265 benzene 280 acetone 300 this are the different energy cut offs okay.

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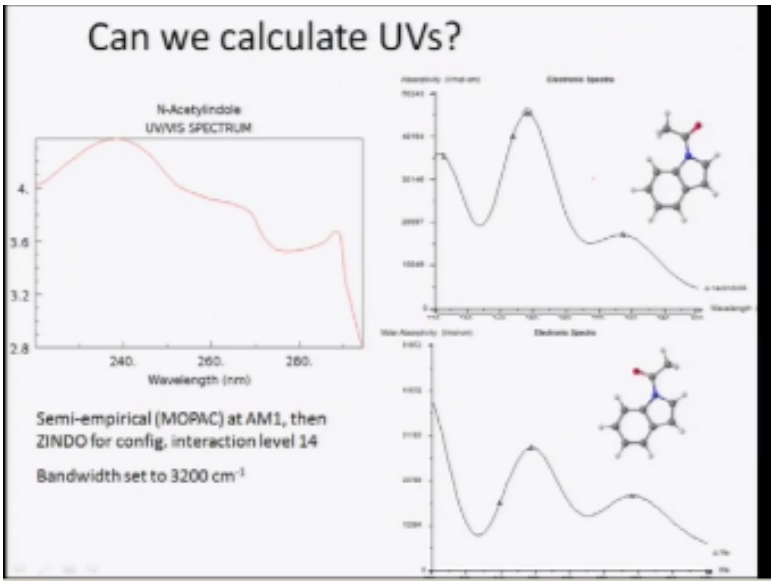

So now but you can calculate this spectroscopy actually so one can actually calculate by looking at the local structure so this is suppose the local structure of certain compound and then one can calculate the absorption happen even absorption happening at disturb wavelength one is this is 21 and 321 41,44,45 and these are about 275 similarly this is another one this is same molecule okay this is sort of changes the rotation this is the tangent we are talking about it form this to this and this to this here so one can determine this spectroscopy things.

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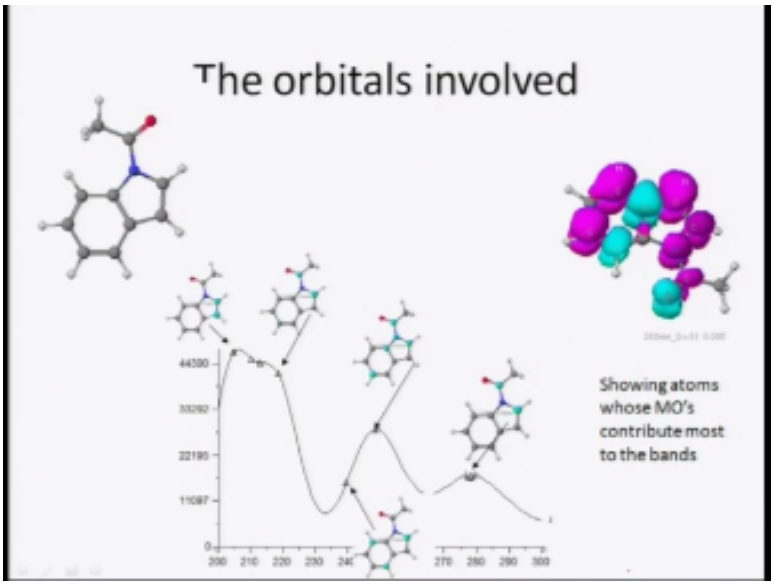

If I have arbitrarily involved like here you have a arbitrations which is shown here atoms of the molecule orbital contributed most to the bands like one this one can be construct to this tensions this one construct to be this tensions this are all and then you can have this corresponds to base one or you can have this things cos 1 x molecules go into σ2π so one can determine that.

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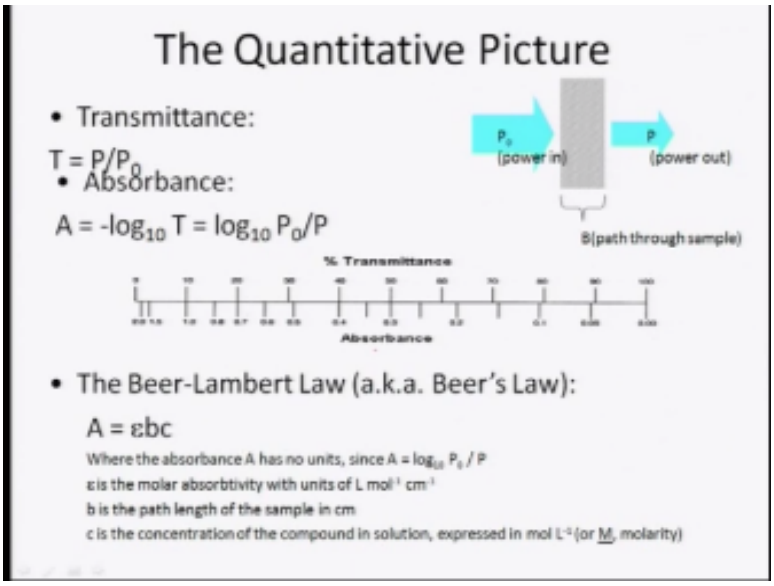

And quantification also I just told you so I do not want to discuss.

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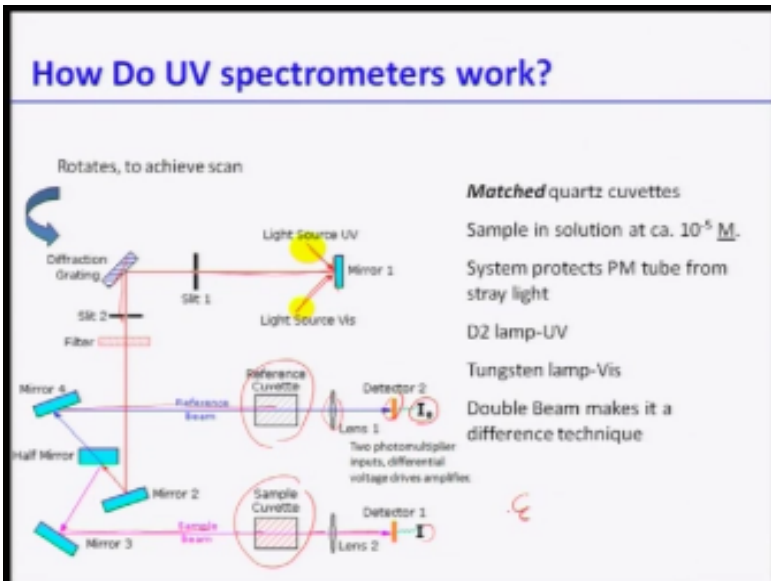

I go to this spectrometer principles are they instruments of that well as you can see that this is the schematic picture what I can tell you that you have basically a reference another sample is a sample tools which is used okay now you have a light source like this you can have a light source from UV and light source from visible and then falls on a mirror it passes through the slide and then falls from the refraction getting passes through another slide it can filter also because you want to use probably.

The exact wavelengths to require and then it can basically go one of these can basically go to the difference beam can go to the reference sample and it will be then focus by the lens one to detector in this it will be recorded other part you can go to the sample and then falls on the lens and then you focus by the detector and get intensity I and then once you knew the absolute value condensed then you can use the lamberts law beer lamberts law to get the value of the molar.

For the particle of the sample well normally we use quartz as a corvettes samples obviously are to be very small concentration like in -5 molar and it can to be protected also these tubes has to protect it from stay lights which I discuss in the first class so the stray lights are bad and normally D2 lamp is uses for UV and tungsten lamp is basically used for visible and double beam actually is made makes a difference techniques.

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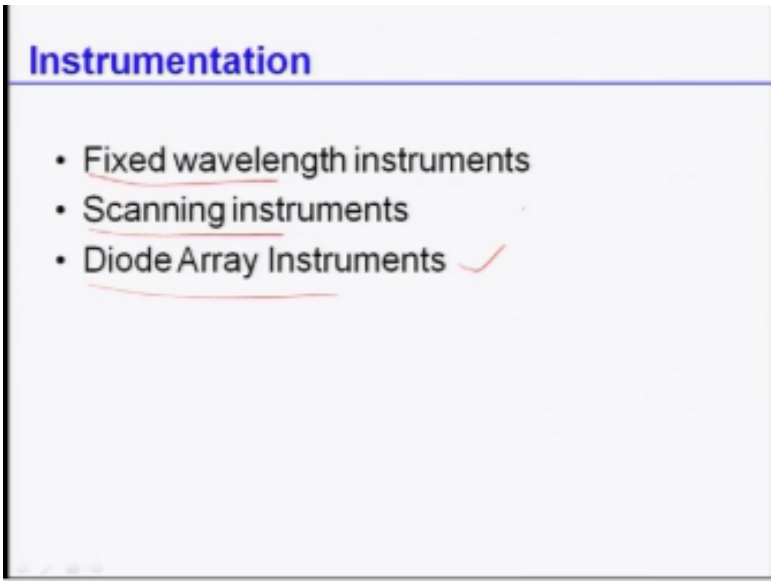

Now the different kinds of instruments can be used one fixed instruments scanning instruments or diode instrument to moved just in one is diode array.

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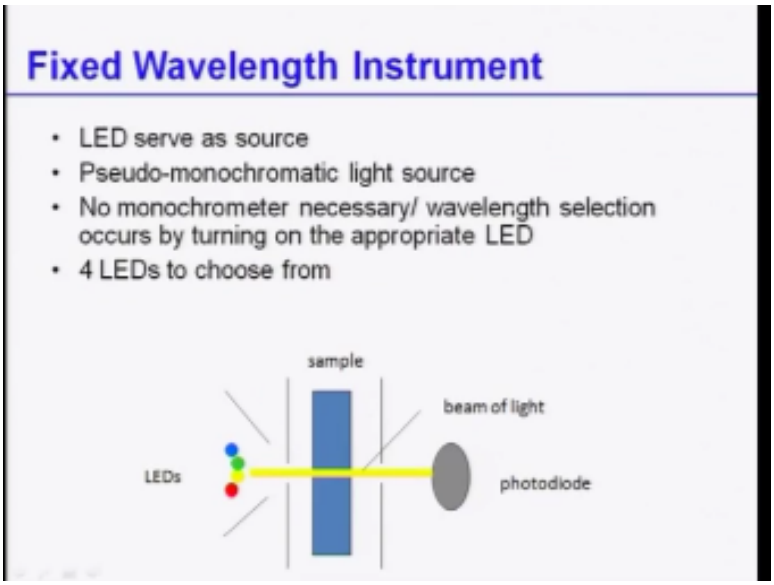

So in a fixed wavelength instrument you have LED light emitting diode as a source LED green LED blue LED all kinds of visible LED are possible so this LED size you can see red yellow green and blue so this LED are actually emit particular light of wavelengths of light and then fall from a sample and no monochromatic needed because LED is actually emits very in a precise monochromatic light and then it falls on a sample and then what ever getting out detected by a photodiode this is how the fixed instrument work normal there four led is to be used to the four wellness can be chosen by this.

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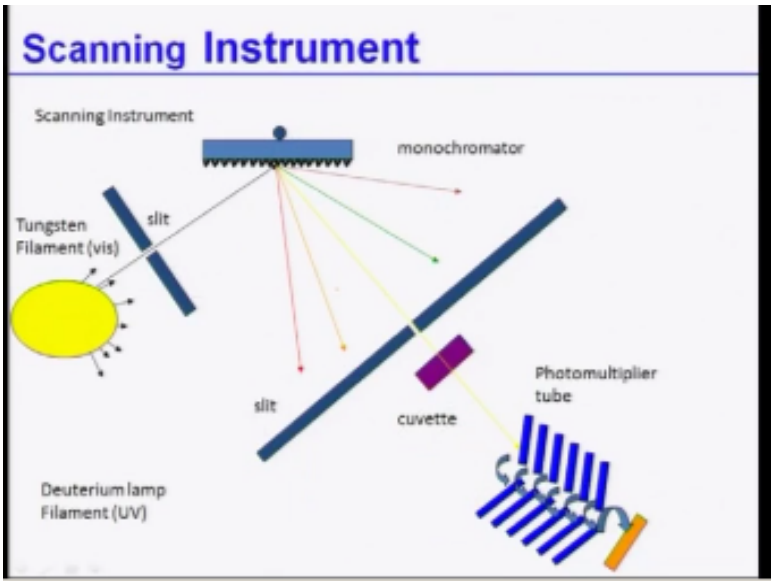

Now in scanning instrument we do not do that what I do is that we have to tungsten filaments are visible and even day to lamp that is deuterium lamp for UV this is d20 okay this is tungsten as showed so both of them actually comes and process through the slit and then you have a monochromatic here how the mono-chromator works is basically as crystals.

The selenium backs law I will tell you how it works so the crystal and then form h you can orient this scan this move this one so that it can fall and when you scan this one all this is detail so only particular lamps will pass through this slits and it will form the sample corvette and the photomultiplier tube which will determine the whatever radiation come out very simple so how this monochromatic really works.

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Okay there are different lamps can be used you can use general lamps also.

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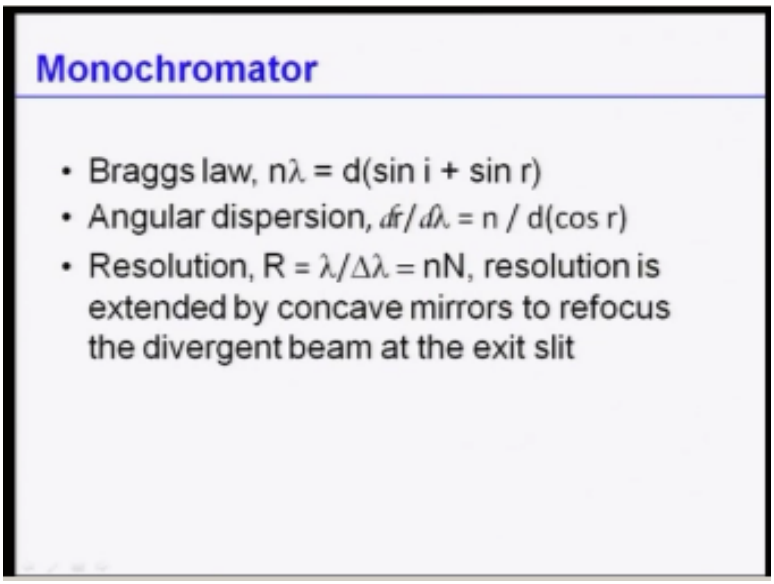

And monochromatic basically applies this Braggs law okay and this is the Braggs law nλ=dsini+sinr it can be written let us say angular dispersion given by 2i/ts n/d/cos r is this basically reflection and I is the incidence beam so lλ=2dsinθ, sin θ is basically the extend the angle but here you can split into like this sin i+d sinr.

So that is nothing if r and I are different then one as to write like this obviously given by λ/δλ is extended can be actually extended by concave mirrors in this one of the matters this is what is done here you have this crystals which is sitting there are actually reflecting the lights at different directions so if you scan it out all you fixed pass through these scan.

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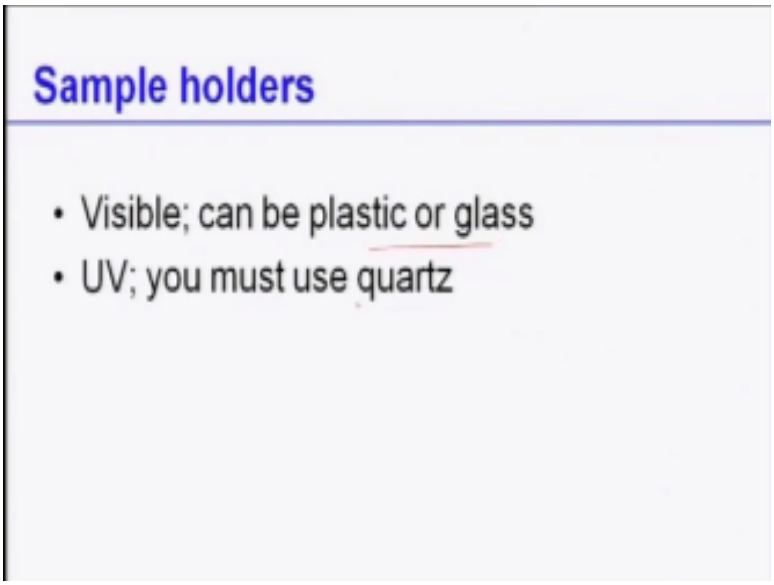

And hold as sample this is also very important for instrumental purpose you have a visible you use plastic or glass for UV you must use quartz.

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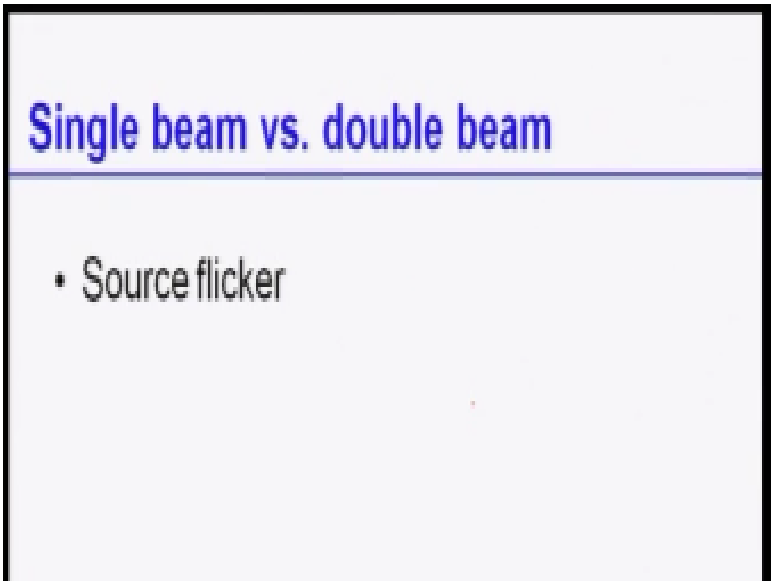

These are all examples you can have single beam double beam normally single beams are used double beam are normally used for single beam can be used but we have a source pick up.

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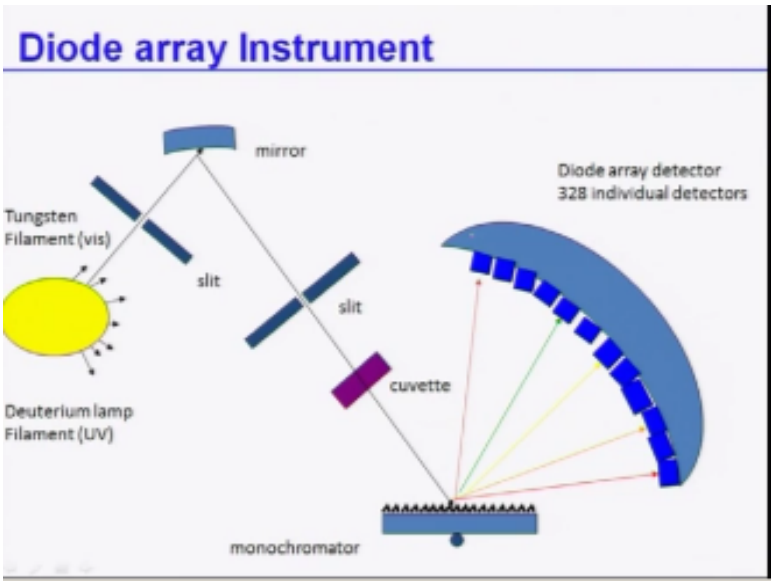

Last one is diode array instrument in which you have both the lamp structure and the for the deuterium lamps for the UV and tungsten for visible and then go to the slit and falls an mirror and the mirror focus it on to the sample and then this is also mono-chromator this is opposite to what you have seen in case of the techniques scanning techniques and then these by mono-chromator actually moves and then different wavelengths of lights falls on 328 detectors which each of one detector each one is a direct and direct measure the amount of the radiation which is coming out well.

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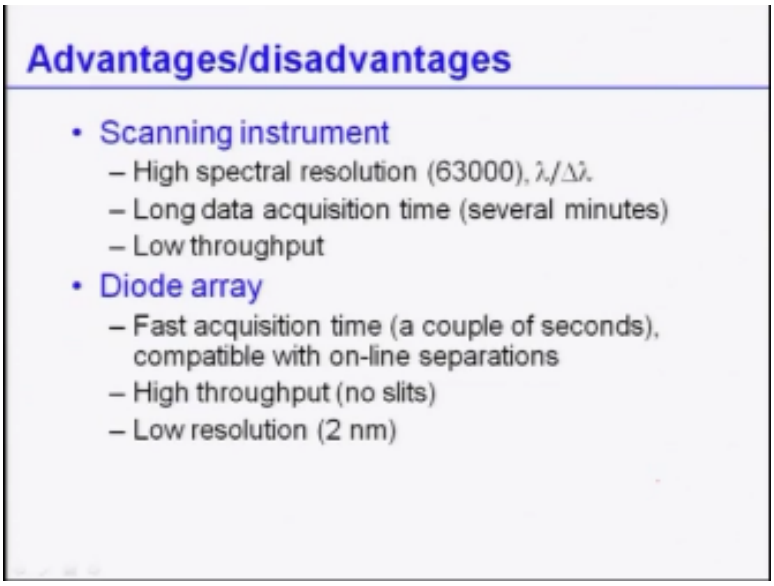

So there are advantages and disadvantages for the both scanning and diode array scanning as slow spectrum resolutions high spectrum resolution is λ/λ is very high but it has a long data recursion time which has be several minutes thus the sometime problem for different solutions and it has a low through output through put so diode array has a very fast recursion time because it is diode array is basically determined the intensity of this radiation which determine in different wavelength after it passes through the sample.

And normally in couple of seconds in several minutes and this is comfortable with online that is computer compatibility is there very high through puts does no clips and one problem is very low resolutions so if you want to go for high resolution you have to use scanning instruments you want to go for high fast and the what is called high through put instruments you have to go for direct normally people has both in the labs.

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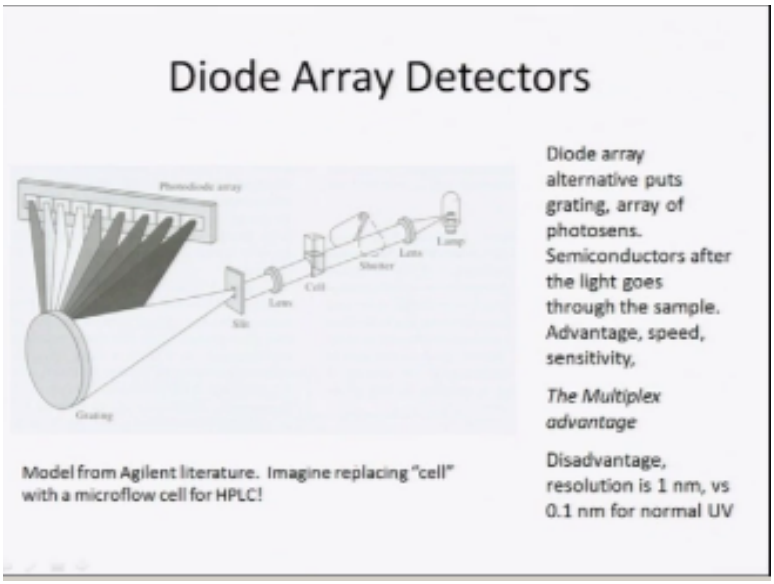

Normally and this is extended way of diode array and I am showing you this are the 328 diodes which are slit at the sample radiation comes under the sample it is detective diode well so that's all in the next class we will I will show you some more spectrum from the UV visible results in my lab and some of the details things which I gathered from literature and then we move on to the next techniques.

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