Ultrafast Processes in Chemistry
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Lecture # 03
Spectro Photometer

Al, so far, we have learned about absorption and emission spectroscopy in the sense that we know that absorbance is.

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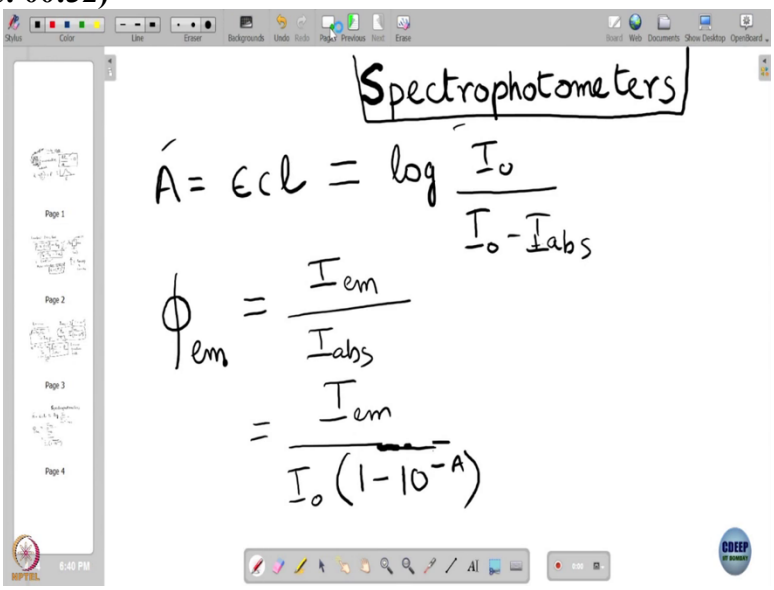

Epsilon CL and absorbance actually defined as log off I_0 by I_t where I 0 is the intensity of the incident light I t is the intensity of the transmitted light and we also learned that for a non-reflecting, absorbing sample I t is simply I 0 - I abs I used the I abs is important quantity for us. Let me write it like that. They are also studied that for emission spectroscopy define something called phi em emission quantum yield, which is given by I em divided by I abs.

And little bit of mathematical manipulation for this expression, give us I em divided by I 0 into 1 - 10 to the power - absorbance as ever said if you now have an instrument by which we can record absorbance we have an instrument by which we can record emitting intensity of emitted light, then we should be able to work out the emission quantum yield also. Now, why we want to know emission quantum yield means that we come to later, but let us first see how it is recorded these are recorded by using instruments that are called spectral photometers

If you are working with absorption spectrum, it is called an absorption spectrometer if you are working with emission spectrum, then it is called an emission spectrophotometer it was just spectrophotometer sometimes can be more specialized, some of them might besides that you they allow you to look at fluorescence they are called fluorimeter, so on and so forth. But what is fluorescence will not discuss that yet we will do it later. Now, let us see what is there inside a typical spectrophotometer what do we need to do in order what do we expect.

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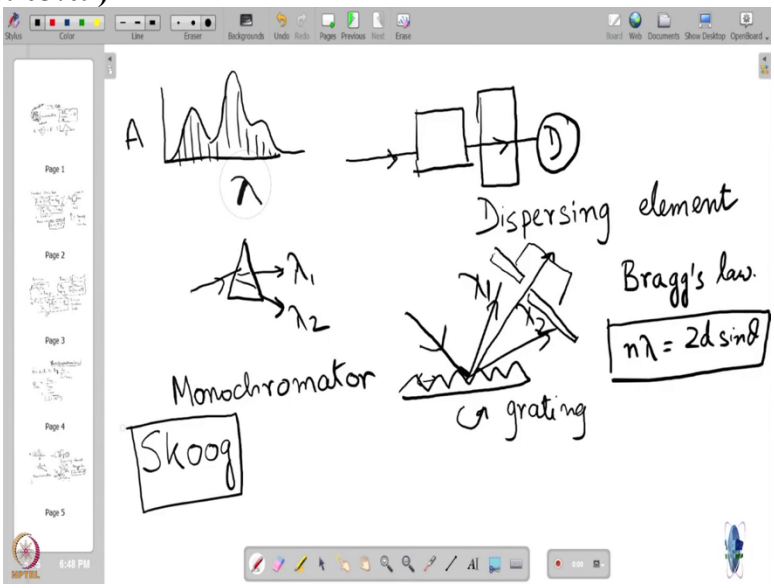

From a spectrophotometer what is the output, as I said in one of the previous module, the output is this plot where X axis is this energy of some measure of it, Y axis is intensity or some measure of it. So, if you want say an absorption spectrum, now we know that here we are going to write absorbance. If you are talking about a mission spectrum, in the Y axis, we are going to the intensity of emission. And then we expect to see a plot that looks maybe something like this to get this, I should be able to record absorbance in this case.

And in the case of emission spectrophotometer, emission intensity at different wavelengths or different energies, since most of our discussion will be on electronic spectroscopy, and it is conventional and to use either centimeter inverse or more commonly wavelength and go to a wavelength for now, but one thing that we should not forget is that wavelength is a reciprocal scale, one by lambda is actually energy.

So, direction of increasing wavelength is actually direction of decrease in energy. Let us not forget that. So, I need to be able to record the intensity of light at different wavelengths. So, how do I do that? What I drawn earlier is we have a sample and now we are talking about absorption. Some light falls on it part of the light gets through suppose I put some kind of a detector here detector in this case is something like an electronic eyes will you see what we see the detector is going to sense the entire amount of light that falls on it.

And it will not be wavelength resolved or energy resolved or anything it can tell you what is the total intensity. So, in this case what is total intensity, total intensity is the area under the curve? So, it is very easy for the director to tell you what is the area under the curve is, but if you want to know what the curve looks like, then we need to put in something more in between something that will be able to differentiate colors from one another, something that will be able to differentiate the energies of wavelength of light from one another.

How do you do it? So, we have to use the phenomena of what is called dispersion? We have to break down a polychromatic light not necessarily white light but polychromatic light into each component. So, for that, we have to use some kind of a dispersing element. Has anybody seen any dispersing element once again outside the lab? So, everybody is seen a rainbow and the reason why you see it is that you have this droplets of water in the air, which serve as a dispersing element.

And I think all of us have read of this famous experiment when Newton had collimated sunlight and waited for on a prism and sunlight broke down into colors of different into components of different colors. So, this is a way of preparing rainbow. So, what we essentially have to do is from this slide, we have to prepare a rainbow and then we have to make different parts of the rainbow fall on the detector at the same times. So, that is our job.

How do you do you can use a prism nobody uses a prism anymore. Why? Because in a prism, what happens is a light actually travels through some amount of glass or sodium fluoride or whatever it is, and they have invariably this absorption. So you lose light, you lose signal. Instead, the dispersing element of choice is a grating. What is it grating it sounds solid object in which you

have lines that are parallel to each other at regular intervals. Has anybody seen a waiting outside the lab? CD It says that the groups are circular.

That is why if you look at the shiny surface of the CD, you can see a rainbow. And the principle on which this grading works is that it is called what Bragg's law what is it n lambda = 2d sin theta. What essentially says is that different wavelengths travel in different directions. So pointed light falling on this lambda 1 will go in this direction. Lambda 2 will go in this direction. What is the d, d is the spacing between the grooves.

So, you have created a rainbow. Now what happens? One option is take my detector here and here and here, that is not so easy. So what is usually done is, first of all, you put in a slit what is the slit, a slit is like 2 solid plates with a very narrow opening between them. So if I usually try so the way I have drawn it here is that this is these are solid plates, so no light will go through them, but there is a gap between so, whatever light is here will go through and you can understand that this light that goes through will have some particular wavelength of course.

It will be some lambda and + - delta lambda, so now if I do something, I put a slit, I have a grating and I put the grating on a revolving something so then grating is this position, some wavelength lambda n goes through if I congregating like this, there is some other wavelength will go through. So, this way I can select which color goes through the state and I do not have to move my detector the detector can sit nicely here. So, this is a dispersing element and a slit, the combination is called a monochromator.

We do not wish to go into more detail of this in this series of lectures. Once again wherever is interested, please go through our all lecture series on spectroscopy there we have spoken in a little more detail about this and if you want to know more, I would suggest that you read the book by Skoog. It is about chemical instrumentation in the Skoog, get some somebody but I forgotten the second name Skoog is usually enough to find the book. So you need a monochromatic, so let us clean up this a little bit.

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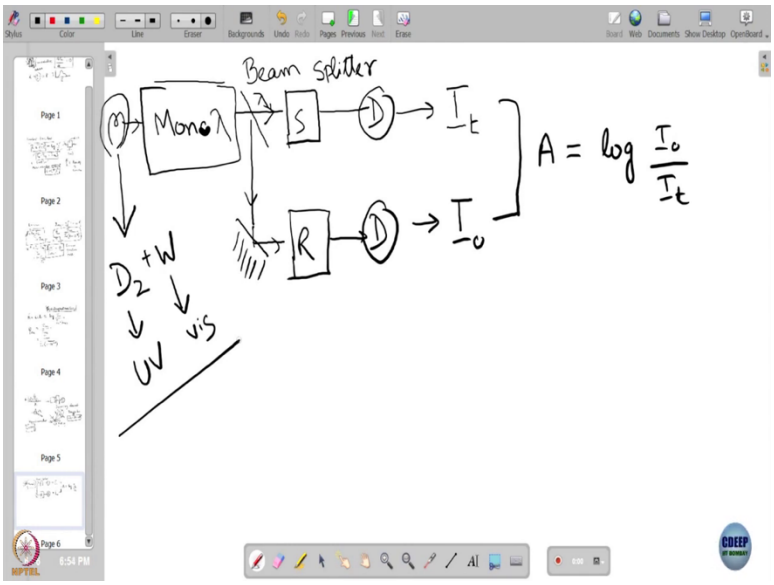

So what did we say we have light, we have sample and we will put the monochromator here, I want monochromatic, I want light of particular we are going to go through some lambda 1. So here and put in a monochromator. Since I am making a mess of it, I just write one more lambda n and of course, the lamp is somewhere here the lamp is the source of light. And remember, we are talking about absorption spectrophotometer here.

And here we put a detector if this is a sample, then this detector, you see an I 0 what I 0 or I t or what intensity of the light that is this detector is it transmitted light or incident light reflected light or what? Transmitted light, so this detector gives you I t. But I need I 0 as well So the most common there are 2 ways of doing it first is do the measurement twice, have a sample and do not have a sample. So, spectrometers that work in that way, are called single beam spectrometer.

But split beam spectrophotometer is much more common, or sometimes what is called a do I have spectrometer. What you do is you put in a beam splitters. You can think of this beam splitter as a partially reflecting mirror, typically and absorption spectrophotometers. You want to use a mirror with 50% reflectivity 50% the light goes through 50% is reflected and here nothing is absorbed. So here what will happen is like I 0 will be I t in this direction. + I r I reflected, but that I t will actually be I 0 for this. So it goes here, and then you have a completely reflecting mirror.

From there, you put your reference what is the reference, suppose, you are doing the experimental solution phase, there is some solvent, it is usual that you put in that same solvent in the different side. So, light goes through, there is another detector here. And that gives me an idea of I 0 and then all instruments are run by computer and computer is good at doing math. So this gives you the computer gives you A = log off I 0 by I t.

Now, if we go back to the previous diagram see you have a grating and you a slit what happens if you open the slit more light gets through so intense it is higher but what do you compromise on in that case resolution definitely. So, in a typical absorption spectrophotometer, you do not really care about the intensity that is going through plus in any case you will take a ratio. So, you want to measure you want to record small slit width.

So, the delta lambda talking about the width of wavelength, the range of everything that gets through that is typically bandwidth the most usual value for an absorption spectrophotometer of bandwidth is 2 nanometers, but sometimes you might need more accuracy. So, some spectrum meters have variable bandwidth can go from point five nanometer to higher, that is one thing. The second thing is what is a lamp here again I will not go into detail because the lectures already exists in a diff in that spectroscopy course.

But let me just say that for electronic spectroscopy, UV visible range you use a combination of lamps deuterium lamp and tungsten lamp deuterium gives you ultraviolet tungsten gives you visible in some spectrophotometers they also use xenon lamp, but it is not very popular because first of all, xenon lamp is more costly more intense and in absorbance kind of experiment you do not want an intense lamp because what you are recording is a difference.

If it is too intense reference will not be too much. So, deuterium and tungsten combination is the most popular the choice for absorption spectrophotometer. Now, let us move over and top bottom emission spectrophotometer in emission spectrophotometer remember, that we brought 2 spectrum together.

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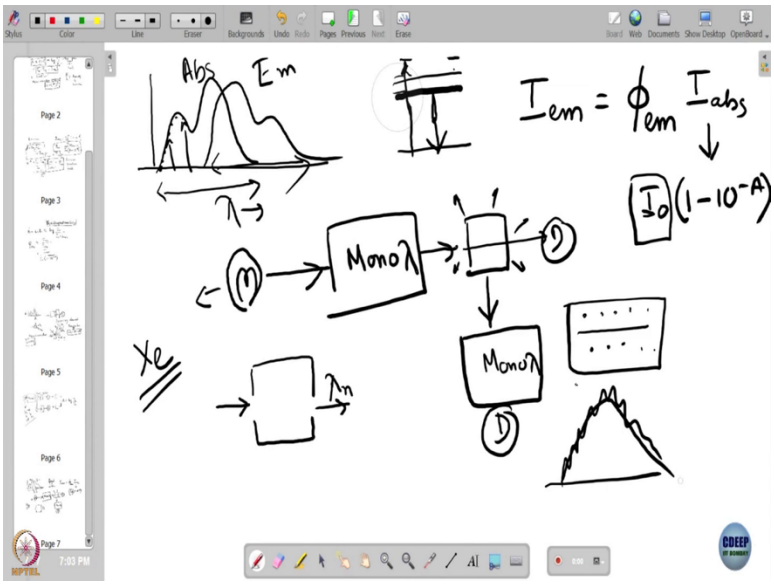

Let us say X axis is lambda that this is the absorption spectrum and let us say this is the emission spectrum. Emission typically occurs at lower energy than absorption for reason is not very difficult to understand. Now, the thing is in order to get emission remember, for a diagram that is we are exciting somewhere and then emission takes place and especially for electronic levels, it is not this simple you have associated vibrational levels and all that emission always takes place on the lowest vibrational level.

So, the question is why do I excite I might want to excite here I might want to excite here and for different samples different molecules, I might need different excitation wavelength. So, in an emission spectrophotometer, instead of 1 monochromator we have two. first of all, you have this light source and the light source for you visible range is typically Xenon lamp. And you go to the lab with actually show you what it looks like.

But, you know, xenon lamp gives you white light. In fact, you are actually seen as you know, lamp on the road, maybe Sometimes you see these cars with very very bright headlight. So they are expensive cars that are fitted with you know xenon lamp headlights. So it is very bright. The LED lights in car are all tungsten lamps not so bright. So, usually use 0 left for 2 reasons. First of all, the output spectrum of Xenon goes from ultraviolet to IR huge width.

So, you can get whatever wavelength you want. Secondly, it is a source of intense light. Now, unlike absorption spectroscopy, when you do emission, you want an intense source of light. Why? Remember, I em = phi in emission quantum yield multiplied by, I abs and I abs what is I abs I 0 into 1 - 10 to the power - absorbance. So, how much is the absorbance depends on the sample, but the other control you have is I 0.

If you use a more intense source in emission, it is actually beneficial because I 0 is more and consequently intensity of emission light is also more. That is why Xenon is a source of choice for emissions spectrophotometer in UV visible range, but then it gives you a white light. So you have to break it down into its components. You have to use a monochromatic here. What is the monochromator, monochromator is a combination of a dispersive element and slits.

Next, you have the sample and the sample emits. If you are talking about Spontaneous emission then emission is in all directions like what you see in this light. So, you can in principle collect it in any direction, but it is most useful to collect at 90 degrees unless there is some problem in doing that for some reason, typically want to get 90 degrees why because in addition to the emission, you also have transmitted light.

So, if you put your detector here, then there is a very strong chance that your spectrum will be contaminated by transmitted light of course, will use a monochromator but monochromator also have their own limitations. So, that problem is usually avoided by recording at 90 degrees so 90 degrees you have another monochromator and then you put a detector in when you come to the lab we will show you 1 detectors.

The kind of discussion may be in reusable range the detector of choice is photomultiplier tube, you can have more expensive detectors you can have multiplex detectors, you can have diode arrays, but this is the most usual thing will actually show you an example of multipliers detector as well. Now, in absorption as well as emission how is the measurement done we said that we have some kind of light falling on the monochromator and the output is some particular wavelength lambda n but want lambda n to go from here to here, or from here to here.

We want to span a range. How do you do that? We said that by changing the grating, turning the grating. So, here now you think of this spectrum, the spectrum in this arrrangement does not come all at the same time it is built point by point. So, you turn the grating at a particular angle while the grating is moving, no measurement is done, then it stops, then you make a measurement now, for how long does the grating have to stop for how long do you have to make measurement at every point that depends on what kind of intensity you are dealing with.

If the intensity is large, then perhaps it is enough. If you spend say one 10th of a second per point, but if the intensity is low, then it is essential that you spend more time because, for the time that is the detector gather signal computer averaging goes on so, suppose you record the signal for some 10 seconds, this is the signal that you get, you decode the signal for the next 10 was one 10th of a second we will signal you get.

So they will always be a fluctuation and the point that you get here is actually the average of all these points. So, now, if you spend one second instead of 1 10, second for collecting this ensemble of points and averaging then as we know in statistics, larger the sample size the better it is. So if you have a greater integration time or better residence time at every point, then you actually get a better spectrum.

If you spend lesser time you get a more what is called noisy spectrum. So Then that we use the judgement, there is a no Golden Rule. If you look at your spectrum, maybe run it using a small integration time, see whether you get a good spectrum or a bad spectrum and then increase your acquisition time accordingly or decreases the spectrum is too good. You do not need spectrum. But it is important that when you record a spectrum, it should be noise free.

Nobody likes to see a spectrum that looks like this. Stubbles maybe fashionable, but spectrum is stubble is not cool. You want your spectrum to be absolutely clean shaven. And for that, you have to decide what is the minimum amount of acquisition time you need, there is no Golden Rule. You have to think on your feet and decide on the spot, how much time every measurement is required, there is another kind of measurement that one can do. And I am saying this only because we will show you an example of this.

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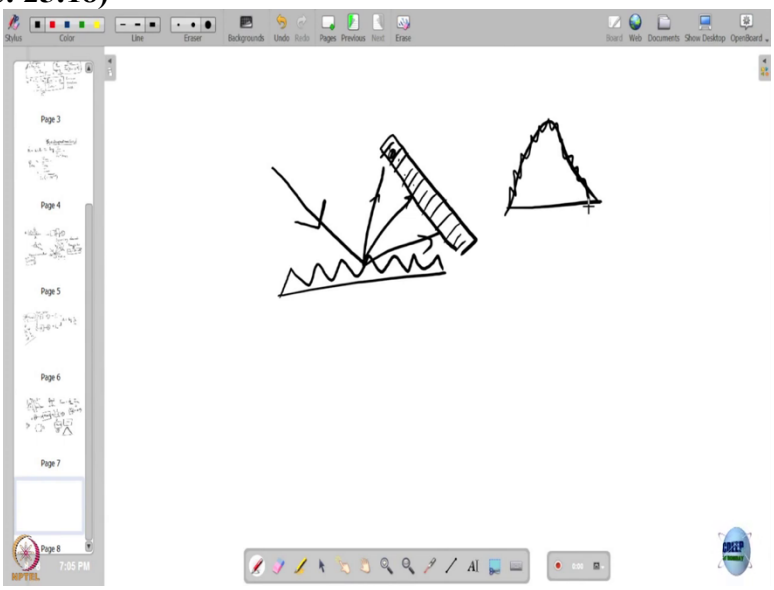

Let us say you have this grating polychromatic light has fallen on it. And it has been broken up into different components. The discussion we have so far we said we put a slit and at a time only one way things will go up and we will have one detector, but now it is possible to have not one but hundreds of detectors. So each point here is a detector. And you are actually familiar with this also.

Your cell phone camera is basically made up of a detector like this. It is just it is more complicated. You have drawn a one dimensional array of detectors, the cell phone camera has a 2 dimensional array. So if you have something like this, then you can actually get the spectrum in one shot, then you do not have to do it point by point. But even then, do not forget that what has happened is that the entire spectrum has come at one time.

Because this every detector has actually recorded something. They are also acquisition time is important. They are also even though everything is recorded at the same time, the spectrum will be noisy, if your acquisition time is not enough. In fact, in the example that we are going to show you, we do get a noisy spectrum because we do not need an accurate measurement there. So it does not matter whether you do whether you use a point detector or an error detector.

It is important to decide what kind of acquisition time what kind of integration time you require to get a good spectrum. We stop on this note, there is something else that we want to talk about in terms of excitation spectrum. But that can wait we can talk about it when we actually come to a

problem. But let is stop here today. Next day, we are going to actually show you the instruments in the lab, and then maybe we will even get an opportunity to talk about existing value.