Ultrafast Processes in Chemistry

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Lecture- 02
Steady State Spectra

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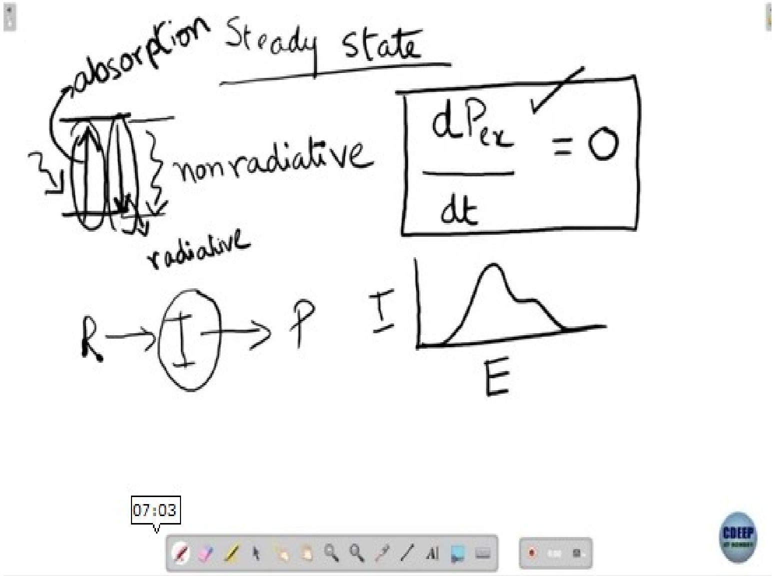

So we start with steady state spectroscopy. What is the meaning of steady state spectroscopy those who have used this would know that it essentially is that we are recording spectra. But, why this recording spectrum for steady state? To do that again we go back to something we learned in class 11. What is the meaning of steady state? What is the difference between equilibrium steady state? Open system. Steady state means see an apparent change, but the system is open, equilibrium happens in a closed system.

So, for the sake of simplicity let us consider a molecule with 2 energy levels, lower one and a higher one to shine it with light that causes some upward transition. This is called absorption. And then this molecule comes back to the downstate as well either by a radiative pathway or by a non radiative, well the names are self explanatory, but tell me what is the meaning of radiative pathway, what is the meaning of non radiative pathway, there is a pathway means light is emitted non radiative pathway means light is not emitted.

So, molecule comes down from excited state to down state light is not emitted where does the energy go? It gets redistributed in the various modes of motion of the surroundings, this is a solution then it gets redistributed in various kinds of motion in the solvent or in whatever medium it might be. So, now, if you keep the light on, then what happens? You can think like this you turn the switch on there is no excitement no molecule in the excited state, excited state population is 0.

If you have kept the lights on for some time upward transition absorption is taking place, but downward transition has also started in this scenario what is the population of the excited state? I mean, I do not know what the population of the excited state is, what does the population of the excited state remain the same or does it change? In the initial period, population of the excited state is 0. So, the light is switched on the population increases for some time and then what happens is it starts getting depopulated as well.

So, eventually what happens is this rate of excitation and rate of the re-excitation they become equal. So in that state in that situation dP ex, ex is the population of the excited state, dt is equal to 0. This when this condition is satisfied, then we say that a steady state has been achieved. Have you encountered the term steady state sometime again in class 11 or maybe first year college, chemical kinetics we use a steady state approximation for what?

If you have a reaction like the reactant goes to intermediate, intermediate forms product then we say that after an initial indefinite periods population of the intermediate does not change. So, you get this kind of an equation there that is called steady state approximation and not allow myself to (())(05:12) and talk more about steady state approximation, there is a favorite topic but so, that is what happens when you shine molecule with light as well.

If you keep the light on then after a very short time and very short time means pico second or something steady state is achieved. Now, if you record an absorption spectrum or an emission spectrum, provided the sample does not degrade, the spectrum will not change. So, the question is, what is the meaning of a spectrum I just use the term spectrum. What is the spectrum? Range of wavelengths and in English language a spectrum means varied collection.

Like a spectrum of events or something like that, but in spectroscopy the spectrum is a plot where y axis is intensity or some measure of intensity. And x axis is energy or some measure of energy, it can be energy, it can be wave number, it can be frequency, it can be wavelength, something like that. So, if I there is some kind of a spectrum absorption or emission under steady state, provided your sample is stable, the spectrum does not change.

And of course, you can do 2 things. You can focus on this and try to record absorption spectrum or you can focus on this type of record emission spectrum. So, before we go on to the actual measurement, what we would like to learn is how do you what is it that you measure? And how does say intensity depend on various factors. So, we start with something that many of us might actually know.

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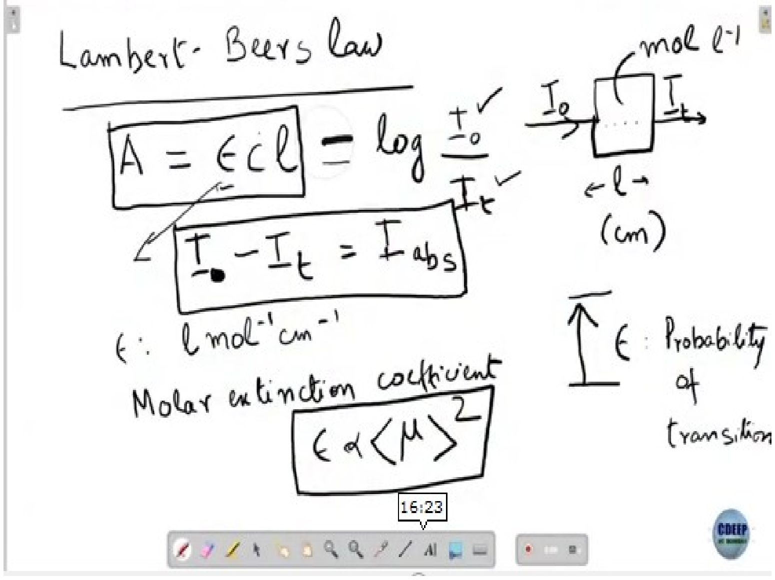

Lambert- Beers law

$$\boxed{A = \epsilon c l} = \log \frac{I_0}{I_t}$$

$$\boxed{I_0 - I_t = I_{abs}}$$

ϵ : $l\ mol^{-1} cm^{-1}$

Molar extinction coefficient

$$\boxed{\epsilon \propto \langle \mu \rangle^2}$$

ϵ : Probability of transition

We start with Lambert-Beers law. What is Lambert-Beers law? A = epsilon cl, I just write absorbance, this equals absorbance not absorption and then write its expression log of what is it? I 0 / I t. So, let us say this area is your sample light with intensity I 0 falls on it and the intensity of light that goes out or is transmitted is I t. So, I t is usually less than I 0. So what is I 0 – I t? Where is that intensity gone? It must have been absorbed or it might have been reflected. So, for now we talk about samples that absorbed and do not reflect.

So, then for those, I 0 - I t will be equal to I abs. So, this is something that we are going to need in a minute. See, if I want to measure absorbance I need to know I 0, as well as I t. So, must have a way of measuring both. And in one of the next one will actually will go to the lab and we are going to see how an absorbance spectrum we actually recorded. One of us going to record it and then we will see it with our own eyes. But let us not forget that we need to know I 0 as well I t we are going to draw the schematic very soon.

So, this is the important thing for absorbance spectroscopy. Before we leave this tell me, What is the unit of c here? Mole per liter molar. What is the unit of L length? This is a light length of the sample through which the light goes that is in centimeter and c is in mole per liter. What is the unit of absorbance, there is no unit please remember absorbance does not have a unit sometimes the literature we see absorbance written in arbitrary units it is wrong, the unit is not there. So, it is arbitrariness question does not arise.

You can have normalized absorbance sometimes you want to make all the spectra the same size that is a different issue and you like normalized absorbance. So, then what is the unit of epsilon? liter per mole centimeter. And what is epsilon called? Well, I used to call it molar extinction coefficient. But then, about 5 years ago, I have a student who told me that the extinction coefficient is apparently outdated. And we must call it molar absorption coefficient. I actually like the term extinction.

Because it tells you how the light slowly gets extincted as it passes through the sample, but then it is outdated. It is outdated, what can you do, but I think everybody understands the meaning of the extinction coefficient. So, now, let me ask another thing. Again, going back to something that we learned at the beginning of thermodynamics, we all know what extrinsic and intrinsic quantities are right. So, in this expression for observance, can you tell me which quantities are extrinsic which quantities are intrinsic, absorbance itself is extrinsic no doubt about that.

Well is extrinsic concentration you can change. Well, for a given solution concentration is intrinsic. But for the substance, if I think of the substance no matter what the concentration is no matter what the length of sample is, epsilon is an intrinsic quantity, so what is epsilon? What does it tell us about? What does epsilon tell us about? We are talking about 2 states. And absorption is an upward transition between the 2 states. And what we are saying is that it does not depend on the number of molecule.

If epsilon uses an idea about the probability of transition in fact, it is proportional to the square of what is called transition moment integral. Transition moment integral is the probability of transition, the measure for probability of transition that we calculate using time dependent perturbation theory epsilon is something that we get experimentally the related. We are not going to deal upon this further, whoever is interested to know more about this, you can go through our lectures in the NPTEL course on molecular spectroscopy.

So, so much for absorption, the take home message from the point of view of spectroscopy, what are the take home messages first of all absorbance has no unit epsilon does have a unit and if you have to record absorbance you must know I 0 as well as I t and that is what determines what kind of instrument you have to use to measure absorbance. And before leaving this topic one more question what are the things that epsilon depend upon, epsilon is probability of transition. So, of course, it depends on which 2 states it is.

So, if you take it is a thinking of a did everybody knows that d-d transition is photons of data. So, if you are talking about transition between 2d orbital's of course, if epsilon is going to be small, if we are talking about N pi star transition, if you are talking about pi pi star transition in which will epsilon be larger. pi pi star right N pi star transition is actually forbidden. Once again for more discussion of this, please refer to our molecular spectroscopy lectures that are available on NPTEL and YouTube.

So, that is first thing, which rays involved experimentally well actually, this is what it leads to, does it depend on concentration? Epsilon? Usually no will actually no. But does it depend on wavelength? Yes, otherwise, your spectrum would not be a spectrum it would have been flat. Of course, it depends on wavelength and wavelength a dependency is sort of comes from what we stated already that it depends on which levels are involved in the transition.

Transition moment integral does it depend on temperatures, not unless one of these states get populated by change in temperature otherwise, it is not an activated process. Generally only activity processes depend on temperature. But here it may be that we are talking about transition from one state to another one and one of the states is not formed at a particular temperature, then it might but that is not something that usually happens. So, that is for it is. Now, let us remember this and let us also remember this is I 0 - I t is equal to I abs for an non reflecting sample.

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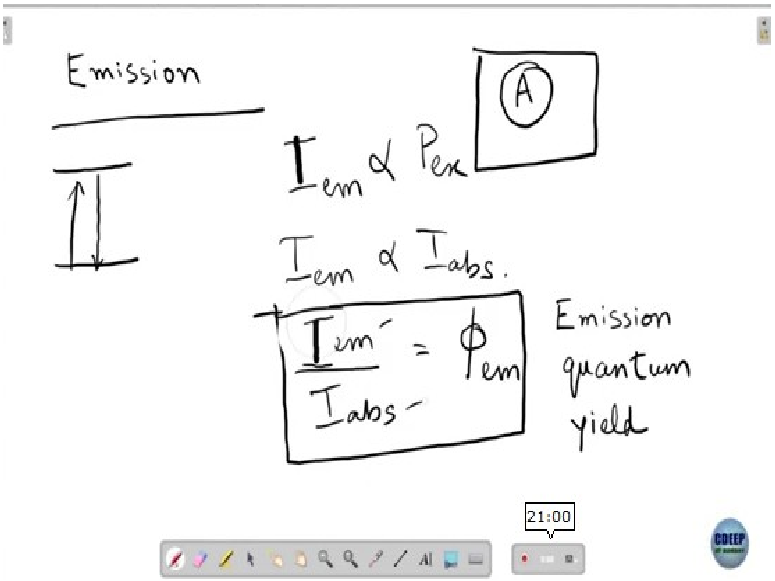

Let us do a quick discussion on emission. We will talk about electronics state, let us say that once again, we go back to those levels and there is whatever I am not saying they are electronic levels at some level. So we have populated the excited state and comes down these are the same picture once again. So you have some intensity of emission. And we only discussed intensity of the light that is absorbed. That is I 0 – I t. So, let us see what kind of intensity I will get depends on 2 things.

First is once again, what is the probability of downward transition between these 2 levels? So, if you go back to Einstein state, which you are going to do a few classes later, here we are talking about spontaneous emission. So, that would depend on something called Einstein's A coefficient what else suppose intensity absorption is very high will that affect the intensity of emission, intensity of absorption, what is the definition of intensity, number of photons per unit area per second per unit time.

So, if that is high for absorption that means what? What the photons do? They promote molecules to the highest state. So, if I bombard the molecule with more number of photons per unit at a per second the necessarily the excited state will be formed a greater extent and if the excited state is formed to a greater extent, it is not very difficult to understand that I em should be proportional to the population of the excited state and population of the excited state depends on I abs.

So, I em also depends on I abs so I would write like this, I em / I abs is is a constant since you are doing a generalized discussion here, will call it phi em and for Knowledge just write emission quantum yield. Anybody want to say anything about this quantity emission quantum yield? Is it related to something that we have discussed already? Yes. So, what is that what are we said about intrinsic property? For emission what is the quantity that we mentioned a few minutes ago, which determines the intrinsic probability of transition.

Einstein A coefficient is not it? So, this quantum yield you can say is actually this Einstein A coefficient so, now suppose I experimentally want to determine quantum is what will I do? Is it enough? If I required the emission spectrum or do I need the absorption spectrum as well? Remember it is not so easy to get absolute values of an intensity from these experiments you only get relative values and even if you get absolute values is it enough to require the emission spectrum?

If I want the quantum field or do I need to measure absorption spectrum as well what is required because quantum yield is I em / I abs I need to know I abs as well and remember something we said I abs what is it? I 0 - I t. So that is what will come in here I 0 – I t. Now, what is what would be the relationship between I abs and your absorbance?

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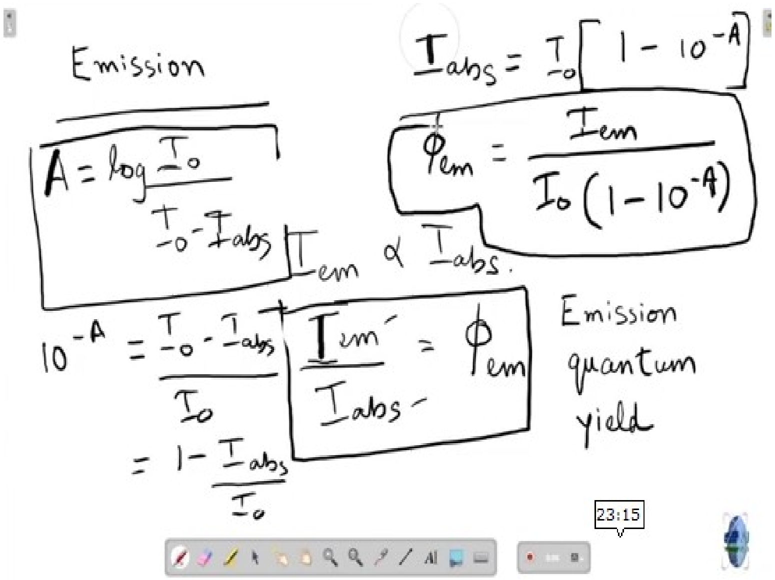

Will there be some relationship A is equal to log off I 0 by instead of I t now write I 0 – I abs. So it is not very difficult to see I hope that a rearrangement of this can let me actually get rid of well, so I have already got rid of I t. What happens if I rearrange this log right? So I will write 10 to the power - A on the left hand side. What is the right hand side be? I 0 – I abs divided by I 0. So, that turns out to be 1- I abs - I 0. I can perhaps get rid of all this now. So now I abs for make that the subject of formula what do I get?

1- 10 to the power -A multiplied by I 0. So in this expression i can write phi em is equal to I em divided by I 0 1 – 10 to the power – A. Well, there is one factor that we have not written here it becomes important in solution sometimes and that factor is your refractive index. But generally, the error induced by it not so much, but it is important to note this 10 to the power – A, this is what pi em is. So, we have all the working family. We know what we need to record.

We know that if you want to measure absorbance then it is important that I know not only I t but also the transmitted intensity of the transmitted light, but also I 0 the intensity of the incident lights, I should have some way of measuring both. And we now know what emission quantum yield is? And we learned that in order to determination quantum yield, it is not enough to do an emission experiment only, you must perform an absorption experiment as well. In fact, you must perform the absorption experiment first.

So, the right sequence of doing things is record absorption spectrum first and then record the emission spectrum. Many times we see that students want to work on emission spectroscopy, just record an emission spectrum. It is not enough if you are going to talk about emission quantum yield. So, always it is a good practice to record an absorption spectrum first, then record the emission spectrum, then you record something called an excitation spectrum that will come to that in the next module.

So the next module let us discuss rudimentary structure of the instruments that are required to record absorption and emission spectra. They are called absorption and emission respectively spectrophotometer that is what we will do in the next module. And then we are going to go to the lab and we will have a look at an actual absorption spectrophotometer and actually emission spectrophotometer.